Asian Journal of Chemistry Vol. 21, No. 2 (2009), 1313-1317

Determination of Elemental Variations in Tea Leaves (*Camellia sinensis* L) in Different Harvest Time by WDXRF Spectrometry

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The percentage of elements in different harvest time in fresh green tea leaves (*Camellia sinensis*) clone Derepazari-7 grown in Rize region of Turkey were determined semi quantitatively by using wave-dispersive X-ray fluorescence spectrometry (WDXRF). A qualitative analysis of spectral peaks showed that 15 mineral and trace elements (P, K, Ca, Mg, S, Cl, Mn, Zn, Al, Fe, Si, Rb, Cu, Ni and Sr) were presented in the fresh green leaves of tea (*Camellia sinensis*) clone Derepazari-7. The amounts of P, K, Cl and Ni in fresh green leaves were the highest at 1st harvest time and decreased continuously to 3rd harvest time. In contrast, the amount of Ca, Mg, S, Al, Fe and Sr were the lowest at 1st harvest time and continuously increased from 1st harvest to 3rd harvest time.

Key Words: *Camellia sinensis*, Tea, Mineral and Trace element analysis, Wave dispersive X-ray fluoresence spectrometry.

INTRODUCTION

Tea (*Camellia sinensis*) is one of the most popular beverages in the world and it is originated in China, dates back several thousand years ago[1]. Turkey is one of the most important tea growing countries in the world. The production of tea in Turkey mainly started in the early years of the Republic along the eastern Black Sea Region. Many of the tea plantations are centered around the town of Rize and from the Georgian border to Trabzon, Arakli, Rize, Karadere and Fatsa (near Ordu), reaching in some places 30 kilometers inland and reaching the height[2] of around 1000 m.

There are two major kinds of tea, black tea and green tea and they both contain caffeine (1-5 %) with small amounts of other xanthine alkaloids also present. Tea composition varies with climate, season, tea variety and age of the leaf. Tea also contains large amounts of tannins or phenolic substances (5-27 %) consisting of catechin (flavanol) and gallic acid units, with those in green tea being higher than those in black tea[3].

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The leaves of the tea plant are used both as a social and medicinal beverage. Since 3000 B.C. traditional Chinese medicine has recommended green tea for headaches, body aches and pains, digestion, enhancement of immune defenses, detoxification, as an energizer and to prolong life. Now many of these health benefits are confirmed. The regular consumption of tea may contribute to the daily dietary requirements of several elements and tea could be an important source of manganese and the large amount of potassium in comparison with sodium that could be beneficial for hypertensive patients[4].

The minerals present in tea leaves can be determined by using atomic absorption spectrophotometer, inductively coupled plasma atomic emission spectrometry, neutron activation analysis and total reflection X-ray fluorescence[1].

The advent of commercially available energy dispersive spectrometers for X-ray fluorescence (XRF) measurements has provided an economical and powerful tool for environmental, clinical, chemical, geological and industrial analysis. XRF is a non-destructive, fast, multi-element technique for analyzing the surface layer and determining major, as well minor as some trace elements in thin and thick samples of all sizes and forms[5-21].

There were studies related to elemental composition of tea leaves[1,4,22], however the variation of elements present in fresh green tea leaves in different harvest time has not been studied so far. Hence the present study is aimed to evaluating the variation of elemental composition of fresh tea leaves in different harvest time by using WDXRF spectrometry.

EXPERIMENTAL

The following instrumental contents were used: a sieve (RETSCH); a digital scale (OHAUS TS 120); an hydraulic press (SPEX $P_{max} = 3.5 \times 10^7$ kg/m^2); a wavelength dispersive spectrometer (Rigaku ZSX-100e with Rhodium target X-ray controlled by a Software ZSX computer).

The fresh green leaf samples of tea (*Camellia sinensis*) were collected from Derepazari-7 clone in Rize region of Turkey at different harvest time (May 15, July 15, September 15) in 2005 year.

The sample was dried in porcelain crucibles at 50 ºC for 1-2 h. It was prepared as pellets for measurement. To obtain a XRF-pellet, a small metallic sample holder made of aluminum with a diameter of about 3.0 cm was used. The pellets were pressed at 3.5×10^7 kg/m^2 in a Spex hydraulic press for 30-50 s.

WDXRF Spectrometry was employed for analysis of fresh green tea samples by using the semi-qualitative method. The measurements were performed using a ZSX 100e sequential spectrometer equipped with Rh X-ray tube operated. Working conditions of the apparatus are shown in Table-1. As well known that carbon is the main element in all kind of plant tissues with *ca.* 60 %. The other 40 percentage comprises with P, K, Ca, Mg and the other elements. In this study we ignored the carbon in tea leaves because some elements present in tea leaves was minor portion.

Finally, we have been able to prepare a table apparently including minor elements with relatively higher percentage.

TABLE-1
EXPERIMENTAL CONDITIONS FOR EACH CHEMICAL ELEMENT

Element	Line	Crystal	Attenuator	Slit	Detector	V (kV)	I (mA)	Angle 2θ
P	Kα	GE	1—1	STD.	Flow	30	120	141.065
K	Kα	LIF1	1—1	STD.	Flow	40	90	136.675
Ca	Kα	LIF1	1—1	STD.	Flow	40	90	113.125
Mg	Kα	TAP	1—1	STD.	Flow	30	120	45.275
S	Kα	GE	1—1	STD.	Flow	30	120	110.820
Cl	Kα	GE	1—1	STD.	Flow	30	120	92.865
Mn	Kα	LIF1	1—1	STD.	Scintillate	50	72	62.950
Zn	Kα	LIF1	1—1	STD.	Scintillate	50	72	41.780
Al	Kα	PET	1—1	STD.	Flow	30	120	144.710
Fe	Kα	LIF1	1—1	STD.	Scintillate	50	72	57.495
Si	Kα	PET	1—1	STD.	Flow	30	120	108.995
Rb	Kα	LIF1	1—1	STD.	Scintillate	50	72	26.600
Cu	Kα	LIF1	1—1	STD.	Scintillate	50	72	45.040
Ni	Kα	LIF1	1—1	STD.	Scintillate	50	72	48.645
Sr	Kα	LiF1	1—1	STD.	Scintillate	50	72	24.987

RESULTS AND DISCUSSION

A semi quantitative analysis[8] of spectral peaks showed that fifteen mineral and trace elements (P, K, Ca, Mg, S, Cl, Mn, Zn, Al, Fe, Si, Rb, Cu, Ni and Sr) were found in the fresh green leaves of tea (*Camellia sinensis*) Derepazari clone in all 3 different harvest time (Table-2).

The major elements presented in fresh green leaf of tea were potassium, calcium, manganese, sulphur, phosphorus and magnesium, respectively (Table-2). However, there were not differences among different harvest time in terms of potassium, calcium and the other elements (Table-2). Potassium found in fresh green tea leaves which 53.86 % at 1st harvest time, 52.99 % at 2nd harvest time and 51.70 % at 3rd harvest time, respectively (Table-2). Calcium was 20.00 % at 1st harvest time, 20.38 % at 2nd harvest time and 21.49 % at 3rd harvest time, respectively (Table-2). For the majority of the elements, the obtained results are similar to those previously reported studies[1,4].

The concentration of potassium of our samples was higher than those literature mentioned above. The concentration of an element in the leaves can differ widely for samples of geochemical origin. This may be partly due to the geochemical conditions of the respective soils[23].

It is well known that minerals are very important for human metabolism and healthy. For example, iron is essential for transport of oxygen in the blood, calcium

TABLE-2
WEIGHT CONCENTRATION OF ELEMENTS IN DIFFERENT HARVEST TIME IN LEAVES OF TEA CLONE 'DEREPAZARI[7]'

Elements	1st Harvest	2nd Harvest	3th Harvest
P	4.771	3.625	3.398
K	53.861	52.991	51.707
Ca	20.005	20.382	21.489
Mg	2.634	2.819	3.306
S	4.408	4.490	4.804
Cl	1.215	1.136	0.945
Mn	9.287	10.561	8.385
Zn	0.979	0.600	1.700
Al	0.916	1.546	1.761
Fe	0.803	0.835	0.958
Si	0.641	0.469	0.790
Rb	0.170	0.169	0.233
Cu	0.128	0.102	0.126
Ni	0.106	0.097	0.086
Sr	0.078	0.094	0.246

is necessary for strong teeth and bones, copper is necessary for different metabolic processes, zinc is necessary for normal growth and development and healthy skin, magnesium is necessary for healthy nervous system and for other metabolic processes, manganese is necessary for metabolic processes and for bone growth and development (a representative graph of manganese determination is given in Fig. 1) and potassium is necessary for metabolic processes[24].

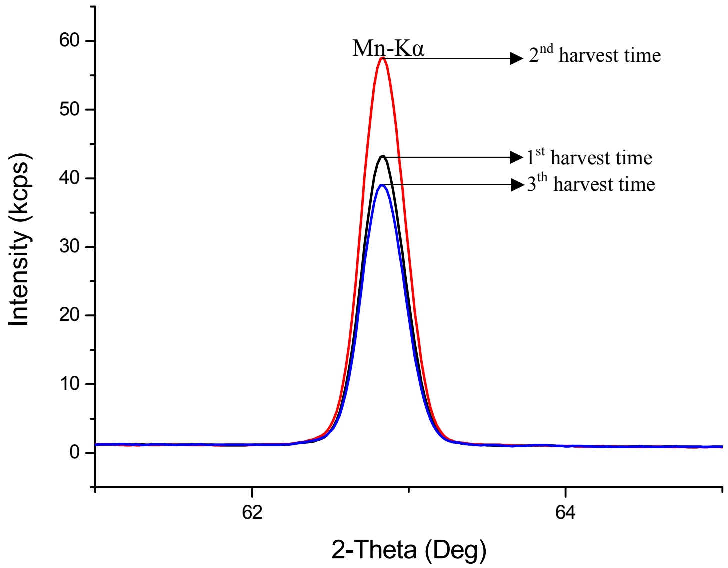

Fig. 1. Kα X-ray peaks of manganese in the 1st harvest, 2nd harvest and 3th harvest time of fresh green tea by using WDXRF Spectrometry

On the other hand, it was observed that potassium, phosphorus, chlorine and nickel contents of leaves continuously decreased from 1st harvest to 3rd harvest time. However, calcium, magnesium, sulphur, aluminum, iron and strontium content of leaves continuously increased from 1st harvest to 3rd harvest time (Table-2).

Conclusion

Considering the use of WDXRF analysis, element profile (P, K, Ca, Mg, S, Cl, Mn, Zn, Al, Fe, Si, Rb, Cu, Ni and Sr) of fresh green tea leaves could be good descriptor for different harvest times. It can also be concluded that to obtain relatively higher potassium, calcium, phosphorus ratio of fresh green leaves of tea clone Derepazari[7] grown in Rize region of Turkey, 1st harvest should be considered the better harvest time.

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(*Received*: 30 January 2008; *Accepted*: 1 October 2008) AJC-6909