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Original Research Article

Analysis of Essential and Toxic Elements in Jujube Fruits Collected from Different Locations in China

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Abstract

Purpose: *To develop a simple and precise method for the determination of the levels of both essential and toxic elements in jujube collected from different locations in China.*
Methods: *Dried jujube fruits collected were digested by optimized microwave procedure. Inductively coupled plasma atomic emission spectrometry was employed to evaluate essential elements, viz, calcium, magnesium, manganese, iron and copper (Ca, Mg, Mn, Fe and Cu) and toxic elements, namely, aluminum, lead and cadmium (Al, Pb and Cd) in four jujube fruits.*
Results: *The results show that the jujube fruits were rich in essential elements and had low contents of toxic elements. The levels of the elements varied significantly amongst the four jujube fruits ($p < 0.05$). Method validation indicates that the proposed method was accurate and precision. The detection limits were 0.0005 - 0.0100 µg/mL while recovery ranged from 91.6 - 105.0%, with relative standard deviation (RSD) < 5%.*
Conclusion: *Five essential elements and two toxic elements (except cadmium) varied widely in their contents in the four jujube fruits. Knowledge of the contents of these elements would provide consumers with information on the quality of jujube fruits.*

Keywords: *Jujube fruits, Essential and toxic elements, Microware digestion, Inductively coupled plasma atomic emission spectrometry*

INTRODUCTION

Jujube fruit is a multipurpose tropical fruit tree grown primarily for its delicious fruit, and has been used for human consumption and medicinal purposes for more than 4000 years [1]. Jujube fruit is one of the superior herbal medicines, it nourishes the blood, improves quality of sleep and regulates digestive system [2]. Today, the fruit of jujube is considered as food supplement, it contains a variety of nutrients, including carbohydrates, minerals, vitamins, sugars, and amino acids [3]. Being a herbal medicine or health food supplement, the pharmacological results indicate that the fruit exhibits antioxidant activities [4], immunological activities [5], potential sedative effects [6] treatment of jaundice in neonates [7], and anti-inflammatory effects [8].

In the long process of plant growth, due to the impact of water, soil transformation and the atmosphere, the plants absorb all kinds of elements in the environment. Jujube fruit, in addition to its content of a large number of elements beneficial to human body, also contains harmful heavy metal elements.

This article intends to provide information about some contents of essential and toxic elements in some jujube fruit types from different locations in China.

EXPERIMENTAL

Materials

Inductively coupled plasma atomic emission spectrometry standard stock solutions of Ca, Mg, Mn, Fe, Cu, Al, Pb and Cd at a concentration of 1000 μg/mL in dilute nitric acid were obtained from Merck (Darmstadt, Germany), and working solutions were prepared by diluting the stock solutions with 2% (v/v) HNO_3 immediately before use. Purified water obtained from an SG ultra clear UV plus system (18.2 MΩ/cm, Wasseraufbereitung und Regenerierstation GmbH, Germany) was used for standard dilutions and other necessary preparations. All chemicals and reagents employed were of analytical grade.

Instrumentation

A Perkin Elmer model Optima 2100DV ICP-AES (Norwalk, CT, USA) was used for determination of selected elements in jujube fruits. The operation conditions were as follows: RF Power: 1.3kw; Auxiliary gas flow rate (Ar): 0.2 L/min; Cooling gas flow (Ar): 15.0 L/min; Carrier gas flow (Ar): 0.65 L/min. These conditions were established after optimization of the instrumental parameters.

A microwave sample preparation system of CEM Model MARS 5 (CEM Corp., Matthews, USA) was used in the study. The optimization microwave digestion conditions were as follows: Stage 1, power: 800 W; time taken to raise the temperature to 120^{o}C: 5 min; Stage 2, power: 800 W, temperature rise time: 4 min, running temperature: 140^{o}C, running time: 4 min; Stage 3, power: 800 W, temperature rise time: 4 min, running temperature: 160^{o}C, running time: 10 min.

Sample preparation

Four commercial dried jujube fruits (Xinjiang hetian jujube, Hebei jujube, Xinzheng jujube, Huixian jujube) were collected from different locations (Xinjiang hetian, Hebei, Xinzheng, Huixian jujube) in China. All samples were washed with deionized water before use for the experiments. Jujube seed were removed after natural drying. The jujube fruits were baked in oven at 50^{o}C for 8 h. All samples were smashed using high speed universal grinder.

For each sample, six replicate powder samples (0.5 g) of the same jujube fruits were accurately weighed into the different digestion vessels, 12 mL concentrated HNO_3 and 2 mL H_2O_2 were added. The samples were digested according to the microwave digestion procedures optimized. In order to reduce the acid concentration of digestion solution, the digestion solution was transferred into the different beakers and the beakers were put on a heating plate at 150^{o}C for 3 h. After cooling to room temperature, the solutions were filtered into 25 mL volumetric flask and made up to volume with 2% HNO_3. The solutions were subsequently analyzed for selected essential and toxic elements using inductively coupled plasma atomic emission spectrometry.

Method validation

For essential and toxic elements, regression equation was performed using mixed standard solutions of 0.00, 0.5, 1.00, 2.00, 4.00 and 8.00 μg/mL (Ca, Mg, Mn, Fe, Cu, Al, Pb and Cd) prepared by serial dilution of ICP-AES multi-element standard stock solution IV of 1000 μg/mL of 23 elements (Merck, Germany) with 2% HNO_3.

To evaluate the analytical characteristics of the method for each element, the detection limits were calculated. The LOD was calculated using 3 SD/b (SD is the standard deviation of the curve and b is the slope of the curve).

The precision of the method was evaluated by the relative standard deviation (RSD) in six replicate determinations on a randomly chosen Xinjiang hetian jujube sample, The equation of the relative standard deviation was calculated using $S/\bar{x}$ (S is the standard deviation and $\bar{x}$ is equal to the mean).

Recovery was carried out on Xinjiang hetian jujube to demonstrate good recovery. The accuracy of the method was determined by spiking with the mixed standard solution at different concentration levels for each element in Xinjiang hetian jujube. Triplicate experiments were performed. The ratios of measured and added amounts were calculated to obtain recovery.

Statistical analysis

The data were analysed using SPSS software (version 13.0, SPSS) and mean results were based on at least six replicates. In order to verify differences of the same essential and toxic elements content in the different jujube fruits studied, one factor analysis of variance was applied with the level of significance set at $p < 0.05$.

RESULTS

Analytical wavelength (nm), detection limits (μg/mL) and regression data

The analytical wavelength (nm), detection limits (μg/mL), regression equation and correlation coefficient are presented in Table 1. The results indicate that linearity for all trace elements was good, with correlation coefficient ≥ 0.9998. Detection limits ranged from 0.0005 to 0.0100 μg/mL.

Precision of the method

In order to verify the accuracy and precision of the method, Xinjiang hetian jujube sample was randomly chosen to evaluate the precision of method (n = 6) and the results were given in Table 2. The results indicate good precision under the analytical conditions used since the relative standard deviations were < 5% and the method was precision.

Recovery of developed method

A recovery work was carried out to demonstrate the validity of the method. Xinjiang hetian jujube was selected to detect the recovery through quantity added. Xinjiang hetian jujube samples were prepared and determined using the recommended procedure. From Table 3 the results were considered satisfactory because recovery ranged from 91.6 to 105.0%.

Table 3: Recovery of developed method (μg/mL)

Element	Base value	Quantity added	Quantity found	Recovery (%)
Ca	838.2±21.2	200	1021.3±20.1	91.6
Mg	423.3±17.1	200	609.7±10.0	93.2
Mn	4.5±0.3	5	9.4±0.3	98.0
Fe	138.4±8.3	100	240.0±1.6	101.6
Cu	13.8±1.5	10	24.3±0.56	105.0
Al	32.0±1.3	10	42.4±1.0	104.0
Pb	3.1±0.2	5	7.7±0.3	92.0
Cd	ND	1	0.97±0.10	97.0

Contents of essential and toxic elements

The contents of essential and toxic elements in the jujube products that were determined in this study are summarized in Table 4. All jujubes had high essential element concentrations of Ca, Mg and Fe. The content of Cu was lower. The contents of essential had significance differences among four different jujube samples ($p<0.05$). Ca (1297.3 μg/g), Mg (668.1 μg/g), Mn (6.1 μg/g) and Cu (73.6 μg/g) had the highest concentration in Xinzheng jujube. Fe (138.4 μg/g) was highest concentration in Xinjiang hetian jujube. The concentration of Mn was the lowest in all the samples.

Table 1: Analytical wavelength (nm), detection limits (μg/mL), regression equation and correlation coefficient for the elements

Element	Analytical wavelength (nm)	Detection limits (μg/mL)[a]	Regression equation[b]	Correlation coefficient (r)
Ca	317.933	0.0062	Y=93930X+916.3	0.999997
Mg	279.077	0.0028	Y=11520X+731.9	0.999892
Mn	257.610	0.0005	Y=838200X+19070.8	0.999986
Fe	259.939	0.0023	Y=134700X+662.9	0.999999
Cu	324.752	0.0100	Y=234600X+10609.5	0.999945
Al	396.153	0.0041	Y=123800X+1972.9	0.999993
Pb	220.353	0.0043	Y=6073X+479.1	0.999834
Cd	228.802	0.0032	Y= 24862X+229.8	0.999998

[a]*Calculated according to 3 times the SD of the blank (n = 10);* [b]*Y = sensitivity (cps), X= concentration of compound (μg/mL)*

Table 2: Results of precision test (μg/mL)

Element	1	2	3	4	5	6	Mean value	Precision (%RSD)
Ca	861.3	838.2	846.9	819.8	836.6	849.7	838.2	1.40
Mg	411.5	440.1	422.8	407.6	432	425.1	423.3	2.89
Mn	4.6	4.5	4.5	4.5	4.5	4.4	4.5	1.41
Fe	149.2	130.2	138.9	141.6	132.9	137.8	138.4	4.85
Cu	13.6	13.7	13.8	13.9	13.9	14	13.8	1.07
Al	30.2	32.9	32.7	31.6	32	30.9	32	2.50
Pb	3	3.2	3.2	3.1	3	3.1	3.1	2.89
Cd	ND	ND	ND	ND	ND	ND	ND	ND

Note: *ND = Not detected*

Table 4: Contents of essential and toxic trace elements in jujube fruits (μg/g)

Element		Xinjiang hetian jujube	Hebei jujube	Xinzheng jujube	Huixian jujube
Essential elements	Ca*	838.2±21.2	560.6±10.0	1297.3±48.9	608.8±9.7
	Mg*	423.3±17.1	330.4±4.5	668.1±30.8	324.4±20.2
	Mn*	4.5±0.3	2.5±0.1	6.1±0.3	2.2±0.1
	Fe*	138.4±8.3	112.8±9.6	72.3±3.0	49.1±3.8
	Cu*	13.8±1.5	4.8±0.2	73.6±3.2	4.1±0.1
Toxic elements	Al*	32.0±1.3	4.8±0.2	50.6±2.4	15.9±0.6
	Pb*	3.1±0.2	3.0±0.2	4.2±0.5	3.6±0.3
	Cd	ND	ND	ND	ND

*ND = Not detected; *significant difference among the four jujube products ($p < 0.05$)*

The contents of toxic had also significance differences among four different jujube samples ($p < 0.05$). Al was relatively higher than the other two toxic elements. Content of Pb was low (ranged from 3.0 to 4.2 μg/g). The concentrations of some toxic heavy metal such as Cd in jujube fruits were too low to be detected using the available analytical technique.

DISCUSSION

Calcium is an essential trace element of human body, it not only composite the body structure, but only regulate the body. It is the origin of human life and it is the most abundant inorganic elements in human body, In the human body calcium (99%) deposit in bones and teeth, and promotes their growth and development, maintain their morphology and hardness. Calcium (1%) in the blood and soft tissue cells help regulate physiological function. The Ca levels in analysed samples were high. According to the Food and Nutrition Board [9], the recommended daily intake of Ca is 1000 mg/day. Thus, the jujube is a rich source of dietary Ca.

Magnesium plays an important role in human body. It is the activator of many enzymes. Magnesium has a sedative effect and strengthens the elderly neural, inhibition function of the nervous system. Magnesium deficiency can lead to metabolic disorder of striated muscle. In our work, Mg level was the highest in Xinzheng jujube.

Manganese acts as a catalyst and cofactor in many enzymatic processes involved in the synthesis of fatty acids and cholesterol [10]. At the same time, the element plays an important role in the synthesis of mucopolysaccharide required for skeletal and cartilage structural matrix and thus is important in skeletal and connective tissue development. Apart from these, other health benefits of Mn include active involvement in absorption of calcium, proper functioning of thyroid, sex hormones and in regulating blood sugar level [11]. Mn permissible limit in medicinal plants set by FAO/WHO (1984) was 2 μg/g [12]., while its content in Xinzheng jujube was 6.1 μg/g that is about three times higher, which showed Xinzheng jujube has high tendency to accumulate Mn.

Iron is one of the main raw materials for synthesis of hemoglobin in human body. It is the body of oxidation-reduction reactions in enzymes and electron transfer of the carrier, but also an important part of catalase and cytochrome. Iron deficiency can make the content of hemoglobin and the activity of physiological decrease and cause oxygen significantly to reduce, thus affecting the supply of the nutrient and oxygen in the brain. Fe (138.4 μg/g) had the highest concentration in Xinjiang hetian jujube. But the content of Fe in Huixian jujube was the lowest.

Copper is the catalyst in carbohydrate metabolism, its main function is to assist the hematopoietic, namely the catalytic synthesis of hemoglobin. Therefore, copper deficiency will make the activity of important enzyme reduce in vivo, and can lead to bone disorder. The content of Cu was high in Xinzheng and Xinjiang hetian jujube. So, the jujube products are recommended as a source of dietary Cu, too.

The ecological importance of heavy metals has attracted a great deal of attention from governmental and regulatory bodies who are concerned in reducing the human health risk associated to the environmental pollution [13]. The toxicity of various heavy metal elements has been well-known and documented for many years. As early as the second century BC it was apparent that exposure to lead (Pb) could be detrimental [14], Cd and Pb are very harmful elements to the human body. Contaminated sediments are one of the several means through which soils are enriched with heavy metals. Al is a low toxicity metal. Food containing aluminum exceed national standards can cause a harm to human body. The levels of Al, Pb and Cd in the analyzed samples did not appear to reach pollution levels [15]. Many factors may contribute to the accumulation of metals in jujube fruits. These include organic matter contents of soil, environmental pollutions from manufacturing process, etc.

CONCLUSION

The microwave assisted extraction applied in this study is a reproducible, convenient and rapid sample preparation method for the direct determination of trace elements in jujube products by inductively coupled plasma atomic emission spectrometry. The developed method shows good precision and accuracy. The jujube fruits examined are rich in essential trace elements and low in toxic trace elements.

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