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Determination of Zn, Cu, Mg, Mn, Ca, S and Na from the Leaves and Seeds of *Ziziphus spina* Chriti Tree Grown in Ahwaz City of Iran

NAHID GHARIB NASERI*, ALAMDAR ASHNAGAR†, IMAN KHAZAEI† and P. MAHDIYEH

Faculty of Petroleum Engineering, Petroleum University of Technology
Abadan Road, Kut Abdullah, Ahwaz, Iran
E-mail: ngharibnaseri@yahoo.com

The seeds of the fruits and leaves of the *Ziziphus spina* Christi tree grown in the city of Ahwaz, Iran were analyzed by atomic absorption/emission and flame emission spectrometry techniques for the determination of Zn, Cu, Mn, Mg, Ca and Na. The amounts of Zn, Cu, Mn, Mg, Ca, Na in the seeds and leaves were (8.0, 2.85), (1.8, 0.5), (1.9, 14), (270.2, 365), (98.7, 203) and (9.1, 84) mg/100 g, respectively. The S element was determined qualitatively. The results showed that this tree is nutritionally a very good source of these elements.

Key Words: ***Ziziphus spina* Christi, Zinc, Copper, Manganese, Magnesium, Calcium, Sodium, Atomic absorption, Atomic emission.**

INTRODUCTION

Ziziphus spina Christi is a shrub or tree up to 10 m height. On wet sites it is evergreen, but it loses all its leaves during the dry season. The species is long living. The plant grows in the dry and moist low lands, in wooded grasslands and edges of cultivations. The bark is grey-brown, when cut at the edge it is reddish, matured bark is grooved and cracking. The straight thorns are long and thin. Its branches are interwined and yellow-white in colour and form an impenetrable thicket. Flowers are small, yellow-green in colour. Fruits of Ziziphus species contain an extremely high Vitamin-C portion up to 1000 mg/100g. Ziziphus species are used for many medicinal purposes in folk medicines all over the world. In India and China, Ziziphus species in particular have been used to treat different diseases and ailments. Ziziphus extracts have also featured in homeopathic folk medicines in other regions such as the Middle East, Southern Africa and South America. Almost every part of a *Ziziphus plant* has been used for medicinal purposes. It is said to be astringent, depurative, laxative, stomachic, pectoral, antitumour, also used for skin diseases and even as mouthwash. The wide variety

† School of Pharmacy, Ahwaz Jundi Shapour University of Medical Sciences, Ahwaz, Iran.

of medicinal properties of *Ziziphus plants* is surprising, with uses against skin diseases, diarrhea, fever and insomnia. A general characteristic of Ziziphus extracts used for medicines is their anti-inflammatory and antibacterial properties[1, 2].

On the basis of the significant therapeutic effects of this species and also its widespread occurrence in Khuzestan province of Iran, it was decided to report the results of chemical analysis of Zn, Cu, Mg, Mn, Ca, Na and S present in the leaves and seeds of *Ziziphus spina* Chriti Tree.

EXPERIMENTAL

Preparation of the unknown solutions

First the species was identified as *Ziziphus spina* Christi and then the leaves were washed, air dried and ground by an electrical mill. The seeds of this species were crushed and the kernels were isolated, then ground by the electrical mill. 10 g of the powdered leaves and 10 g of the powdered kernels of the seeds were heated separately on a flame, then were heated in an electrical furnace at 500°C for 6 h; 1 g and 0.31 g ashes were obtained, respectively. 0.5 g of the powdered leaves and 0.3 g of the powdered kernels were dissolved separately in concentrated nitric acid and heated on a hotplate-stirrer while stirring until the ashes were dissolved completely, then filtered. The filtrates were diluted with deionized water, each to 100 mL.

Preparation of the standard solutions

For each of the elements Zn, Cu, Mg, Mn and Ca, six and for Na, five different standard solutions were prepared as follows:

1. Stock solution of Zn (1000 ppm): 1 g (15.3 mmol) of pure zinc dust was dissolved in 3 mL of dilute HCl (1 : 1 v/v), then diluted to 1000 mL with deionized water.
2. Stock solution of Cu (1000 ppm): 3.9295 (15.74 mmol) of copper sulphate ($CuSO_4 \cdot 5H_2O$) was dissolved in the minimum amount of dilute nitric acid (1 : 1 v/v), then diluted to 1000 mL with deionized water.
3. Stock solution of Mn (1000 ppm): 3.2572 g (18.2 mmol) of manganese nitrate was dissolved in deionized water, then diluted to 1000 mL with deionized water.
4. Stock solution of Mg (1000 ppm): 4.9512 g (41.13 mmol) of magnesium sulphate was dissolved in deionized water, then diluted to 1000 mL with deionized water.
5. Intermediate solutions (100 ppm): 10 mL of each of the above mentioned solutions was transferred into a separate 100 mL volumetric flask and each was diluted to 100 mL with deionized water.
6. Preparation of Sr(NO3)2 standard solution (10%): 10 g (47.25 mmol) of strontium nitrate was dissolved in deionized water and diluted to 100 mL with deionized water.
7. Preparation of intermediate standard solutions of Zn, Cu and Mn: 0.1,

0.3, 0.5, 0.7, 1.0 and 1.5 mL of the standard solution of Zn, 1, 2, 3, 4, 5 and 7 mL of the standard solution of Cu and 0.5, 1, 3, 5, 6 and 7 mL of the standard solution of Mn were diluted separately to 100 mL with deionized water.

8. Preparation of intermediate standard solutions of Mg: 0.3, 0.5, 0.7, 0.8, 0.9 and 1.0 mL of the standard solution of Mg was transferred into a separate 100 mL volumetric flask. 1 mL of the strontium nitrate solution (10%) was added to each, then diluted to 100 mL with deionized water.
9. Blank solution for the measurement of Zn, Cu, Mn and Mg: Deionized water was used as blank solution for the measurement of Zn, Cu and Mn and strontium nitrate solution (0.1%) was used as blank solution for the measurement of Mg.
10. Stock solution of Na (1000 ppm): 2.5421 g (43.5 mmol) of sodium chloride was dissolved in deionized water and diluted to 1000 mL with deionized water.
11. Intermediate solution of Na: 10 mL of the Na stock solution was diluted with deionized water to 100 mL.
12. Preparation of radiation buffer solutions: In three separate 100 mL volumetric flasks, saturated aqueous solutions of CaCl2, KCl and MgCl2 were prepared, then equal volumes from these solutions were taken (1 : 1 : 1 v/v/v) and added together into another 500 mL volumetric flask. This solution was used as the radiation buffer solution.
13. Preparation of intermediate standard solutions of Na: 1, 3, 5, 7 and 10 mL of the intermediate sodium solution (100 ppm) was transferred into a separate 100 mL volumetric flask. For the prevention of any flame spectrum interference, 5 mL of the radiation buffer solution was added to each of the 100 mL flasks, then diluted to 100 mL with deionzed water. The concentration of Na in each of these solutions was 1, 3, 5, 7 and 10 ppm, respectively.
14. Preparation of the blank solution for the measurement of Na: 5 mL of the radiation buffer solution was transferred into a 100 mL volumetric flask and diluted with deionized water to 100 mL.
15. Preparation of saturated KCl solution: In a 500 mL volumetric flask, saturated aqueous solution of KCl in deionized water was prepared.

Measurement by Atomic Absorption Spectrophotometry (AAS) method

Deionized water was used as blank except for Mg and Ca measurements for which 0.1% $Sr(NO_3)_2$ and KCl solution were used as blank, respectively. For each element the optimum experimental factors, conditions and parameters were set and adjusted (Table-1), then the analytical search lines (WL) for the elements of Zn, Cu, Mg and Mn were found and plotted. Standard solutions were fed into the flame of the instrument and the standard curve for each element was plotted. Finally, the unknown solutions prepared from the ashes of the leaves and the kernels of the seeds were fed into the flame of the instrument and their absorbances and concentrations were read directly on the instrument (Table-2).

TABLE-1
EXPERIMENTAL CONDITIONS FOR THE MEASUREMENT OF Zn , Cu , Mn , Mg AND Ca BY ATOMIC ABSORPTION/EMISSION SPECTROPHOTOMETRY

	Zn	Cu	Mn	Mg	Ca
Flame	Air/C_2H_2	Air/C_2H_2	Air/C_2H_2	Air/C_2H_2	N_2O/C_2H_2
Fuel (L/min)	2.0	1.8	1.9	1.6	7.0
Oxidant (L/min)	8	8	8	8	6.5
Burner (cm)	10	10	10	10	5
HC lamp (mA)	4	5	5	4	0
Slit (nm)	0.50	0.5	0.4	0.50	0.10
WL = Analytical search line (nm)	213.9	324.8	279.5	285.2	422.7
Mode	BGC*	BGC*	BGC*	BGC*	Emission
Signal Proc.:					
Pre-spray	3 s	3 s	3 s	3 s	3 s
Integ. time	5 s	5 s	5 s	5 s	5 s
Repeat	1	1	1	1	1
Max N	1	1	1	1	1
CV = RSD (%)	99	99	99	99	99
Conc. Calib.:					
Mode normal:					
Standard 1	0.100	1.000	0.500	0.300	0.100
Standard 2	0.300	2.000	1.000	0.500	0.500
Standard 3	0.500	3.000	3.000	0.700	1.000
Standard 4	0.700	4.000	5.000	0.800	1.500
Standard 5	1.000	5.000	6.000	0.900	2.000
Standard 6	1.500	7.000	7.000	1.000	2.500
Expansion	1	1	1	1	1
Chartspeed (nm/min)	10	10	10	10	10

*BGC = Background correlation;
CV = Coefficient variation;
RSD = Relative standard deviation = [s/X] × 100;
S = standard deviation; X = Mean.

Measurement by Atomic Emission Spectrophotometry (AES) method

For Ca element, the optimum experimental factors, conditions and parameters were set as well (Table-1). The standard solutions and KCl solution as blank were prepared. First the blank solution, then the standard solution were fed into the flame of the atomic emission instrument and the standard curve was plotted. Finally, the unknown solutions prepared from the ashes of the leaves and the kernels were fed into the flame of the instrument and their emissions and

concentrations were read directly on the instrument. The results obtained were much higher than the maximum emission of the standard solution therefore, 0.4 mL of each of the unknown solutions was transferred into a 100 mL volumetric flask separately and diluted to 100 mL with deionized water. Therefore, each of the unknown solutions was diluted 250 times. Then, the diluted solutions were fed into the flame of the instrument and their emissions and concentrations were read directly on the instrument (Table-3).

TABLE-2
THE FINAL RESULTS FOR THE MEASUREMENT OF Zn, Cu , Mn AND Mg IN THE LEAVES AND SEEDS OF *ZIZIPHUS SPINA* CHRISTI TREE GROWN IN AHWAZ CITY

Element	Zn		Cu		Mn		Mg	
	Seed	Leaf	Seed	Leaf	Seed	Leaf	Seed	Leaf
Absorbance	0.051	0.019	0.178	0.025	0.152	0.573	0.419	0.566
Concentration (ppm)	0.156	0.057	1.708	0.243	1.843	6.982	0.523	0.730
Background (BG)	0.004	0.004	0.006	0.005	0.002	0.008	0.004	0.004
Standard deviation (S) $\times 10^{-4}$	1.939		8.358		6.846		+	

TABLE-3
THE FINAL RESULTS FOR THE MEASUREMENT OF Ca AND Na IN THE LEAVES AND SEEDS OF *ZIZIPHUS SPINA* CHRISTI TREE GROWN IN AHWAZ CITY

Element	Ca		Na	
	Seed	Leaf	Seed	Leaf
Emission	0.095	0.100	—	—
Concentration	0.382	0.406	8.8	4.2
Background (BG)	—	—	—	—
Standard deviation (S) $\times 10^{-3}$	1.803		—	

Measurement by Flame Emission Spectrophotometry (FES) method

The amounts of Na in the ashes of the leaves and the kernels of the seeds were measured by flame photometry method. By feeding the blank solution and then the standard solutions into the flame, the results were read directly on the instrument. The standard curve of emission was plotte
solutions prepared from the ashes of the leaves and the kernels were fed into the flame of the instrument. The results obtained were much higher than the maximum emission of the standard solution; therefore, 10 mL of each of the unknown solutions was transferred into a 100 mL volumetric flask separately and diluted to 100 mL with deionized water. Therefore, each of the unknown solutions was diluted 10 times. These solutions were fed into the flame of the instrument and their emissions and concentrations were read directly on the instrument. The results are shown in Table-3.

Determination of sulphur

The sulphur element was qualitatively identified on the basis of chemical tests by sodium fusion test[3].

RESULTS AND DISCUSSION

Many dry farming materials are being used for human food, not just in famine years but also in years of good harvest. A large number have a direct economic value for the farmers. In the nutritional analysis screening method, *Ziziphus spina* Christi has got a high rating. But little is known about the nutritional status of many of these species. Therefore, it was considered to analyze the contents of metallic elements like Zn, Cu, Mn, Mg, Ca and Na in the leaves and seeds of *Ziziphus spina* Christi species grown in Ahwaz city in Iran. The presence of these elements in daily diets is nutritionaly important.

The fruits, seeds and leaves were picked from the trees in Ahwaz city. The analyses were done by using atomic absorption/emission and flame photometry techniques. Before the final measurement of each element, it was essential to obtain the maximum absorption wavelength or the so called analytical line search of the element in question, and draw its corresponding curve. This was done for each of the elements Zn, Cu, Mn, Mg and Ca; the results are given in Table-1. Having set the experimental conditions precisely, first the standard solutions were fed into the corresponding instrument by increasing concentration sequentially, then, the standard curves were plotted and finally the unknown solutions were fed and absorbance/emission was read on the instrument and the amount of each element was determined.The amount of each of the elements in the leaves and seeds of the *Ziziphus spina* Christi tree grown in Ahwaz city of Iran are given in Table-4 and are shown in Figs. 1 and 2, as well. As mentioned before, the presence of sulphur was determined qualitatively by using sodium fusion test. These results show that the leaves are rich in calcium, magnesium and sodium and the seeds are rich in magnesium, calcium and has sufficient amount of zinc and sodium.

TABLE-4
THE QUANTITATIVE ANALYSIS OF THE ELEMENTS IN THE LEAVES AND THE SEEDS OF *ZIZIPHUS SPINA* CHRISTI TREE GROWN IN AHWAZ CITY

Measured element	Seed (mg/100 g)	Leaf (mg/100 g)
Zinc	8.06	2.85
Copper	1.80	0.50
Manganese	1.90	14.0
Magnesium	270.20	365
Calcium	98.70	203
Sodium	9.10	84

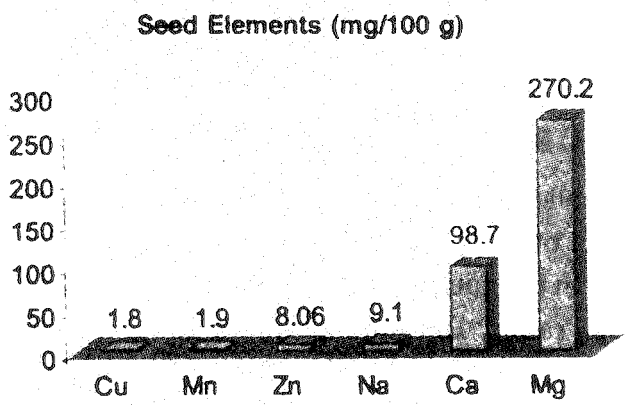

Fig. 1. The quantitative analysis of the elements in the seeds of *Ziziphus spina* Christi tree grown in Ahwaz city

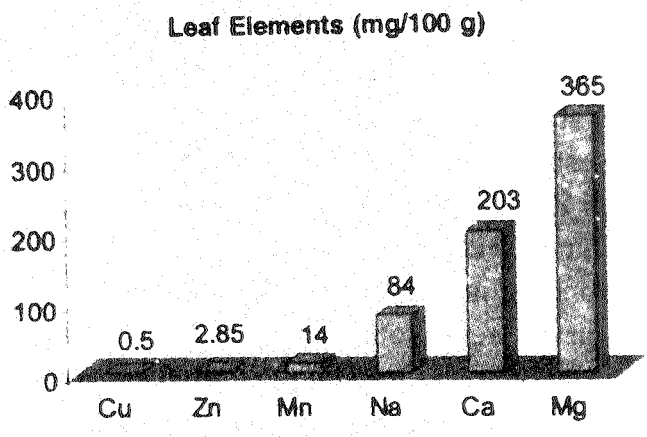

Fig. 2. The quantitative analysis of the elements in the leaves of *Ziziphus spina* Christi tree grown in Ahwaz city

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