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Elemental Analysis of *Anethum sowa* L. (Dill) Root by XRF Spectrometry

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Abstract

Anethum sowa L. (Dill) were collected from different places of Bangladesh and subjected to quantitative estimation of the elements present in roots of the herb. The elemental analyses were done by XRF (PW 2404 PANAlytical) method. The maximum percentage (%) of the elements found in the root samples were: 24.71, 24.43, 10.30, 9.21, 5.16, 5.11, 3.72, 3.46, 3.08, 2.36, 0.32 and 0.16 for K, Ca, Si, Na, Cl, Mg, Al, S, P, Fe, Ti and Mn respectively. Rb, Sr and Zr were present in small amount and Ni, Cu, Zn, Y and Ba were present in trace amount. However Co, Pb, As and Hg were not found in any of the samples under investigation. This analyses may be helpful for the use of *Anethum sowa* L. root in pharmaceutical preparation and in ayurvedic form of medicine.

Keywords: *Anethum sowa* L, Dill, Elemental composition, XRF Spectrometry.

Introduction

Anethum sowa L. (Dill, Indian Dill and Bengali-Shulfa) belongs to the family *Apiaceae* (*Umbelliferae*) and comes under genus *Anethum*. There are two species under cultivation i.e. European Dill (*Anethum graveolens* L.) and the Indian Dill (*Anethum sowa* L.). It is an annual or biennial herb and cold weather crop. It is grown in the subtropical and temperate regions in India and Bangladesh. People of this region use the green herb as a pot herb and as a flavoring agent specially in the winter season. It is also largely cultivated in Southeast Asia, Japan, Northern Europe, and Bordering Mediterranean Sea. The herb grows ordinarily 2-2.5ft. high and very like fennel, though smaller, having the small feathery leaves, which stand on sheathing foot-stalks with liner and pointed leaflets. Roots are tapped and branched (Anonymous 1985; Chopra R.N. *et al.,* 1992).

Green leafy vegetables are good source of minerals as well as vitamins (Slupski J., *et al.,* 2005; Snehalatha N.R. *et al.,* 1998). Dill is a green leafy vegetable that belongs to the carrot family, has an attractive flavour. It has an ancient history of food flavouring and medicinal uses since antiquity. It has been used as a basic component in canning, soups, sauces, flavouring salads, seafood and also soap, perfume and in food industry (Cancur O. *et al.,* 2006). The green herb, seeds and its roots are used as folkloric medicine e.g aromatic, carminative especially useful in flatulence, colic and hiccups of infants and children (Woolf 1999). Recently, it has been reported that it is a potential source of antioxidant and also has anti microbial and antispasmodic properties (Sing G. *et al.* ,2005).

In the last few decades, dietary minerals are receiving attention for there usefulness in prevention of several diseases. The major minerals (such as Ca, P, Mg, S, K, Cl and Na) which are structural components of tissues, function in cellular and basal metabolism, water and acid base balance. Minor (trace) minerals (such as Zn, Si, Mn, Cu, F, I and Cr) are very important for hormone, vitamin and enzyme activity (Macrae R. *et al.,* 1993; Ozcan M. 2005). Most of the studies were published on Dill (seed & leaf) on the effects of dehydration on sensory qualities or some physical and chemical changes such as texture, colour, flavour, aroma, taste of foodstuff (Ozcan M. 2005). But there are only a few studies (Udagawa Y. 1995) on the mineral content of Dill root to the best of our knowledge. The elemental composition of Dill root in this plant has not yet been studied and reported in Bangladesh.

Due to various above stated applications of Dill, it would be interesting to analyze the mineral elemental content of Dill root parts. Therefore the aims of this study were (1) to determine and explain the variation of elemental contents in dill

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root parts from different places of Bangladesh (2) to calculate and evaluate their nutritional property (in respect of mineral content) which can be used in pharmaceuticals and ayurvedic preparations.

Materials and Methods

Sample collection and preparation

A. sowa herb samples were collected form four different places (Tarash, Sirajgonj; Gurudaspur, Natore; Dhaka Botanical-Garden (Dhaka City) and Keranigonj, Dhaka) of Bangladesh before flowering stage. A voucher specimen (DACB Accession Number-31,282) of the plant has been preserved in the Bangladesh National Herbarium Centre, Dhaka, Bangladesh. The collected herb samples were kept in airtight plastic bags, sealed and brought to the laboratory. The roots of the herb were separated and chopped. The moisture content of the fresh root parts was immediately measured. The root samples are then subjected to steam distillation for collection of essential oil. The essential oil free root samples were sun dried and ground to powder by mechanical means and finely stored in airtight high density polyethylene bag for further analyses.

Determination of moisture content

The moisture content was determined by the oven method (AOAC 1984) at 105°C until constant weight (About 6 hours).

Determining the mineral composition.

i) Preparation of samples

The ash content was determined (AOAC 1984) by muffle furnace of a known weight of dry Dill root samples at 450±50°C temperature until the constant weight (approximately 4 hours) was achieved. The ash was powdered by morter & pestle and passed through 100 mesh sieve. The ash sample dried at 105°C in an oven before XRF analysis. The moisture content (at 105°C) of the ash powder was recorded for XRF data imputation. The ash powder of the specific grain size was taken to the minipress machine and applying a 12 tone hydraulic press to compress the sample powder into solid thin pellet for 1 minute exactly. The pellet preparation ratio is sample: boric acid : stearic acid = 10:20:1 All the solvent and chemicals used were of A.R. grade of E. Merck.

XRF measurements

The mineral concentrations were determined by XRF Spectrometer. Model no: PW 2404, Instrument type: Wavelength dispersive, Measuring type: Sequential, Manufacturer: PHILLIPS at present, PANAlytical, The Spectris Technology, The Netherlands. The 'PW 2404 XRF'

Table I : XRF analytical information data on dill root of different places in Bangladesh

Parameters	Sirajgonj (Tarash)	Natore (Gurudashpur)	Dhaka (Botanical Garden)	Dhaka (Keranigonj)
RMS	0.000	0.000	0.000	0.000
Sum before normalization	50.6%	61.4%	60.3%	54.7%
Normalized to	98.0%	99.4%	98.5%	99.6%
Sample type	Pressed powder	Pressed powder	Pressed powder	Pressed powder
Initial sample weight (g)	S_1=2.649 S_2=4.009 S_3=4.019	S_1=4.015 S_2=4.011 S_3=4.021	S_1=2.738 S_2=4.063 S_3=4.006	S_1=4.032 S_2=4.012 S_3=4.027
Weight after pressing (g)	S_1=3.050 S_2=4.410 S_3=4.420	S_1=4.422 S_2=4.418 S_3=4.428	S_1=3.145 S_2=4.470 S_3=4.413	S_1=4.437 S_2=4.417 S_3=4.432
Correction applied for medium	No	No	No	No
Correction applied for film	None	None	None	None
Used compound list	Oxides	Oxides	Oxides	Oxides
Result database	iq_+	iq_+	iq_+	iq_+

S_1, S_2 and S_3 are represents for three individual sample taken.

spectrometer was equipped with an X-Ray tube anode Rh tube and also maximal 4 filter. X-ray generator: 4 KW with 60 KV, 125 mA (in steps). The generator is solid state based on 'Switch Mode Power Supply' design to respond fast the changes sought in X-Ray tube power. Detectors: The Scintillation Detector, Duplex (Xenon filled detector for mid range in tandem with flow counter). The P10 gas (is normally 90% Ar and 10% CH_4 ; gas output pressure 80 kPa) used in flow detector as the quench gas. A minipress was used for making the pellets. The 'XRF' analytical information data of Dill root of different regions are shown in Table I.

Statistical analysis

Statistical analysis of the elements were performed by means of the SPSS version 13.0 software for windows. Results were expressed as mean value ± standard deviation (n=3) of three separate determinations. The significant differences ($P<0.01$) of the mean values were calculated for each element in the different areas were compared by one way ANOVA.

Results and Discussion

The comparative results of the proximate parameter are shown in Table II. The considerable variations were observed in one cultivar to others. Sirajgonj Tarash and Dhaka-Btoanical Garden (Dhaka City) samples were the highest (88.31%) and the lowest (64.99%) moisture content respectively. The ash content (Dry weight basis) was the highest (12.73%) in Sirajgonj-Tarash and the lowest (3.42 %) in Dhaka-Keranigonj samples. On the other hand, the ash value calculated on fresh weight basis found the highest (1.55%) in Natore-Gurudashpur and the lowest (0.74%) in

Table II: Results of proximate analyses (g/100g) of Dill root of different places in Bangladesh

Parameter	Sirajgonj (Tarash)	Natore (Gurudashpur)	Dhaka (Botanical Garden)	Dhaka (Keranigonj)
Moisture[a]	88.31	71.49	64.99	78.46
Dry matter	11.69	28.51	35.01	21.54
Ash[b]	12.73	5.44	4.03	3.42
Ash[a]	1.49	1.55	1.41	0.74

[a]On fresh weight basis in g/100g, [b]On dry weight basis in g/100 g , Each value represents the average value from three experiments.

Dhaka-Keranigonj samples. The differences observed may be due to variety, cultivar and agronomic practice differences.

The elemental concentrations of Dill root are shown in Table III. Results are expressed on dry weight basis (g/100g of ash). The significant amounts of important elements are present in the following order: K > Ca > Si> Na> Cl> Mg>Al> S>P> Fe> Ti> Mn> Sr> Rb> Zr. A comparison of elemental contents of Dill roots among four different places shows that six elements like Ca (24.43), Na (9.21), Mg(5.11), S(3.46), P(3.08) and Mn (0.16) (in g/100g of ash) were detected the highest amount in Dhaka-Keranigonj sample. Similarly the highest amount of Si (10.30), Al (3.72) and Ti (0.32) (g/100g of ash) were present in Natore Gurudashpur and K (24.71), Cl (5.16) and Fe (2.36) were in Sirajgonj-Tarash samples. On the other hand the lowest amount of Na (3.68), Si (6.22), Cl (1.16) & Mn (0.12) were present in Dhaka Botanical-Garden ; Mg (3.95) and Ca (17.88) in Sirajgonj-Tarash ; K (14.22), S (1.56) and P (1.84) in Natore- Gurudashpur and Al (2.22), Ti (0.19) and Fe (1.80) in Dhaka-Keranigonj sample (g/100g of ash on dry weight basis). A look at Table III shows that, major mineral like Ca, Na, Mg, P and S are the most enriched in Dhaka-Keranigonj and Fe, Cl and K in Sirajgonj-Tarash samples. The minor and trace element like Al, Si, and Ti were present in high concentration in Natore Gurudashpur sample. Si was not found in Sirajgonj-Tarash and Dhaka-Keranigonj samples. Similarly Mn was not found in Natore-Gurudashpur sample. Minor amounts of alkali and alkaline earth metals (Na, K, Mg and Ca), together with Cl^{-} ions, must be in balance in extra cellular fluid, which is responsible for muscular irritability. Mg has been particularly shown to play a significant role as a regulatory cation direct and indirect traumatic brain injury.

Recently, it has been reported that trace amounts of Rb and Cs help in the breakdown of starch to glucose (Choudhury and Grarg *et al.,* 2007). However the mineral constituents of Dill root (Table III) varied among the cultivars, but K and Ca constituted the major mineral. K content ranged from 14.22 g/100g in Natore-Gurudashpur to 24.71 g/100g in Sirajgonj Tarash sample and Ca content ranged from 17.88 g/100g in Sirajgonj-Tarash to 24.43 g/100g in Dhaka-Keranigonj samples. All cultivars contained good amounts

Table III : XRF spectrometry result of the elements present in Anethum sowa L. root (g/100g of ash on dry weight basis) of different places in Bangladesh.

Compound formula	Concent -ration as element form	XRF line	Crystal	Sirajgonj (Tarash)	Natore (Gurudashpur)	Dhaka (Botanical garden)	Dhaka (Keranigonj)
-	O	-	-	28.28±0.357	35.83±0.355	33.78±0.208	31.57±0.447
Na_2O	Na	Kα	PX1	7.01±0.085	3.76±0.13	3.68±0.187	9.21±0.081
MgO	Mg	Kα	PX1	3.95±0.095	4.61±0.108	4.08±0.075	5.11±0.078
Al_2O_3	Al	Kα	PE	2.99±0.091	3.72±0.055	2.59±0.097	2.22±0.036
SiO_2	Si	Kα	PE	ND	10.30±0.182	6.22±0.193	ND
P_2O_5	P	Kα	Ge	2.10±0.072	1.84±0.069	2.25±0.07	3.08±0.06
SO_3	S	Kα	Ge	3.04±0.105	1.56±0.036	3.02±0.087	3.46±0.087
Cl	CI	Kα	Ge	5.16±0.095	1.81±0.026	1.16±0.043	2.86±0.086
K_2O	K	Kα	LiF220	24.71±0.416	14.22±0.098	19.33±0.115	15.42±0.081
CaO	Ca	Kα	LiF220	17.88±0.088	19.02±0.208	19.77±0.104	24.43±0.155
TiO_2	Ti	Kα	LiF220	0.25±0.017	0.32±0.026	0.26±0.017	0.19±0.02
MnO	Mn	Kα	PX1	0.13±0.01	ND	0.12±0.01	0.16±0.01
Fe_2O_3	Fe	Kß	LiF220	2.36±0.072	2.35±0.055	2.15±0.095	1.80±0.036
Rb_2O	Rb	Kß	LiF220	Tr	0.02±0.00	0.04±0.00	0.03±0.00
SrO	Sr	Kß	LiF220	0.04±0.00	0.05±0.00	0.04±0.00	0.06±0.00
ZrO_2	Zr	$K\alpha_1$	LiF220	<<	0.01±0.00	0.02±0.00	<<
BaO, NiO, CuO, ZnO, Y_2O_3	Ba, Ni, Cu, Zn, Y	Kα, & $K\alpha_1$,	LiF220 Tr	Tr	Tr	Tr	

Note : Where minimum detection limit is 1 ppm, Tr stands for trace amount and ND for not detectable. Each value is the- mean ± SD of three determinations. P<0.01 and n=3 (Individual element tested)

of K, Ca, Na and Mg. The results are very high to those already reported (Udagawa Y. 1995) values (P 0.96%, K 3.85%, Ca 1.22% and Mg 0.67 % of dill root ash). This result revealed that Dill root accumulated a significant amount of minerals in Bangladeshi geo-environmental condition. Besides these, elements like Sr (0.04-0.06), Rb (0.02-0.04) and Zr (0.01-0.02) (g/100g) were present in small amounts and the element of Ni, Cu, Zn, Y and Ba were present in very trace amounts in all the samples. In addition to the toxic elements like Co, Cr, Pb, As and Hg were not found within the detection limit of the instrument in the samples under investigation.

Element uptake by a plant is its characteristic property and may depend on plant species maturity, the use of fertilizers, irrigation water and different climatological/geo-environmental factors (Choudhury and Grary *et al.,* 2007; Claudia *et al*., 1998; Guierrero *et al.,* 1998 and Peterson *et al.,* 1979). The most variation in elemental content observed in Dill root sample of different places might be due to the said factors. So far authors knowledge go there is a limited report on the elemental analysis of Dill root. However up till now the elemental composition of Dill root had not been reported earlier in Bangladesh by using modern analytical techniques like XRF.

Conclusion

Three samples of each places were analyzed for elemental composition by wave length dispersive XRF Spectrometry. 20 elements were found within the measuring limit of the instrument. Mean elemental contents vary over a small wide range, attributed to varying geo-environmental conditions and local soil characteristic from one places to another. The

ANOVA results revealed that there was not a significant variation ($p<0.01$) of each elemental content among the areas in that analytical procedure. Dill root is a rich source of major mineral constituent of Na, K, Ca, Mg, P, S and Cl along with minor (trace) minerals such as Fe, Zn, Si, Mn and Cu. Root parts of the Dill herb is not usually consumed, it is wasted mostly. The present investigation will help us to understand the metabolic system in plants body in which elements play significant role. It will also be helpful to pave the way for formulating ayurvedic and pharmaceutical preparation of medicine which will be required for treating the diseases caused by the deficiency of various elements. Moreover the proposed analytical method (XRF Spectrometry) offers an interesting perspective for elemental analysis within the detection limit (1 ppm) of the instrument. It enables us to avoid the time and labor consuming steps decreasing analysis cost and risk of contamination and also simplifies laboratory work as well as accuracy of the results.

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