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Macro and Micro Elemental Analysis of *Anethum Sowa* L. (Dill) Stem By X-Ray Fluorescence Spectrometry

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Abstract

Anethum sowa L. (Dill) stem portions were analyzed for its macro and micro elemental concentration by XRF spectrometry collected from different places of Bangladesh. The plants were collected when those were 35 cm in height i.e. within 40-45 days of sowing. Results of proximate analyses showed that the stem parts contained highest level of moisture (93.67), ash (1.62) and dry matter (30.77%) on fresh weight basis (g/100g). The highest level of mineral contents were Ca(478.50±6.22), K(336.65±3.26), Cl(153.92±3.26), Na(114.86±1.38), S(96.65±1.76), Mg(63.96±1.15), P(49.41±0.74), Al(41.75±0.71), Fe(34.57±1.33), Si(31.03±0.18), Ni (11.98±0.22) and Ti (3.75±0.28) in mg/100g on fresh weight basis. Cu, Sr, Rb, Zn, Ba and Zr were present in small amount and Y, Cu and Mn were present in trace amount. However, the toxic elements like Co, Pb, As and Hg were not found in the present study. Presence of higher amounts of mineral contents in the stem parts could potentially be consumed as supplement as human diets or livestock feed as well as pharmaceutical preparation.

Key words : *Anethum sowa* L., XRF spectrometry, Dill, Condiment, Macro and micro elements, Elemental composition.

Introduction

Medicinal herbs have a long history of use in traditional medicine. There are some evidences over recent decades that medicinal herbs possess important pharmacological properties. Many bioactive compounds with known effects on human physiology and diseases have been identified through studies of plants used in traditional medicine. As a medicinal herb, *Anethum sowa* L.(Dill, Indian Dill and Bengali-Shulfa) belongs to

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the family *Apiaceae* (*Umbelliferae*) and comes under genus *Anethum*. There are two species under cultivation i.e. European dill (*Anethum graveolens* L. Syn. Peucedanum graveolens Benth & Hook) and the closely related to Indian Dill (*Anethum sowa* L.). The entire plant is glabrous aromatic and is grown as annual crop during the winter season. The plant is native to Asia and Mediterranean region of Europe and Africa and USA. It is found growing wild in Southern Russia, Southern France and North Africa. Dill is indigenous to the northern plains of India, Pakistan and Bangladesh. People of this region grown the green herb as pot-herb for it's fresh aromatic herb and fruits. It's fruits are longer but less fragrant than *Anethum graveolens* L. The Dill herb grows up to 2.5ft. in height and like fennel, have small feathery leaves, which stand on sheathing foot-stalks with linear and pointed leaflets. Stem is erect, branched, cylindrical, straited, smooth and pale green (Anonymous 1985; Chopra *et al.*, 1992; Spices Board 2005; Bentley *et al*., 1983). The green herb and its oil are also used for flavoring and seasoning of various foods, pickles vegetables and also in soap and perfume industry. Different parts of this plant have a wide range of application in traditional and folk medicine and in various medicinal preparations. Biological and pharmacological studies of this plant revealed antimicrobial, antioxidative and anti-spasmodic activities (Baslas *et al.*, 1971; Halva *et al*., 1987; Paakkonen *et al*., 1989).

Medicinal and aromatic plants gained more importance in agronomy, pharmacy, pharmaceuticals preparation and in day-to-day life. At present, for the prevention of several diseases, there is an increasing interest for the importance of dietary minerals. The trace elements, together with other essential nutrients, are necessary for growth, normal physiological functioning and maintaining of life; they must be supplied by food, since the body cannot synthesis them. The exact classification of trace versus macro minerals is not clear but traces are often considered as minerals required by the body in amounts less than 100 mg per day and make up less than 0.01% of bodyweight (Anna *et al*., 2006). Srikumar (1993) gave a classification of the elements contained in vegetables. Potassium, sodium, calcium, magnesium and iron were classed as macro elements. Zinc, copper, manganese and selenium as trace elements and cadmium, lead, mercury and arsenic as toxic elements. According to Kleszczewska *et al*., (2001) the elements classified in the last group have no biological functions. Major minerals serve as structural components of tissues and function in cellular and basal metabolism, water and acid-base balance, clotting of blood and formation of bones and teeth etc. (Macrae *et al.*, 1993a ; Nielsen 1984; Smith 1998; Ozcan 2004; Gupta *et al*., 2000 and Rajurkar *et al.*, 1997).

Several studies have been carried out on fatty acid and Dill oil (essential oil) composition as well as vitamins, alkaloids, glycosides & other active components of the herb and their pharmacological effects. A little has been reported about minor and trace elemental composition of the herb. Nevertheless, there is a dearth of information on the mineral content of Dill stem. However, most of the data are reported for dry form and therefore, their values in the fresh stage i.e. the normal form that we usually consumed remain unknown. The stem parts of Dill plant, which are not usually consumed at the matured stage, were found to be rich in nutritive mineral components. As far as we know, no such studies on Dill stem have been undertaken. Therefore, the aim of the study was to determine the contents of some macro and micro elements in fresh Dill stem parts and to evaluate their nutritional property, bioavailability as well as calculate the contribution of these elements in daily dietary intake and correlate with medicinal properties for several purposes of pharmaceuticals and ayurvedic preparation. Another aspect of the study was to explain variation in elemental contents of the plant grown in different places of Bangladesh.

Materials and Methods

Sample collection and preparation

Dill samples were collected from four different places (Sirajgonj Tarash, Natore Gurudashpur, Dhaka Botanical-Garden and Dhaka Keranigonj) of Bangladesh during the month of December to March in 2002-2003. A voucher specimen (DACB Accession Number-31,282) of the plant has been preserved in the Bangladesh National Herbarium Centre, Dhaka. The collected samples were kept in airtight plastic bags, sealed and transported to the laboratory. The moisture content of the fresh stem samples was immediately measured. The stems were separated from the herb, and allowed to air dry in a sheltered area at 25-30^{O}C. The air-dried samples were ground to powder by mechanical means and finally stored in air-tight high-density polyethylene bag at ambient temperature for subsequent analyses.

Determination of moisture content

The moisture content of Dill stems was determined by the oven drying method at 105^{O}C until constant weight (about 6 hours) (AOAC 1984) was achieved.

Determining the mineral composition.

i) Preparation of samples for XRF analysis

A certain amount of Dill stem powder was burned to ashes at 450±50^{O}C temperature by muffle furnace until constant weight (approximately 4 hours). The ash was cooled and powdered by means of morter & pastle. Then the powder was sieved through 100 mesh sieve and dried at 105^{O}C in an oven before the analysis. The moisture content (at 105^{O}C) of the ash powder was recorded for XRF data imputation. The ash powder of the specific grain size was taken to the mini-press and applying 12 tons pressure for 1 minute. The sample powder was compressed into solid thin pellet. The ratio of sample : boric acid : stearic acid = 10:20:1 was required for preparation of the pellets. All the solvent and chemicals used were of A.R. grade Sigma/E. Merck.

ii) 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 analyses were carried out in which calculation and fixed calculation methods were used. The 'PW 2404 XRF' 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 pellets. The 'XRF' analytical information data of Dill stem of different regions are shown in Table I.

Statistical analysis.

Results were expressed as mean value ± standard deviations of three separate determinations. The significant differences between means were calculated by one way analysis of variance (ANOVA).

Results and Discussion

The comparative results of the elemental and proximate analyses of Dill stem of different places of Bangladesh are presented in Table-II and Table-III respectively. Dry weight values (g/100g) of elemental compositions are shown in Table-IV from XRF instrument data sheet. Results are expressed on their fresh weight basis. The average results of proximate compositions (Table-II) of green Dill stem showed that the moisture (93.67) and ash (1.62) content are found in the highest amount in Sirajgonj (Tarash) sample, while the lowest amount of moisture (69.23) found in Dhaka (Botanical Garden) and ash (0.83) in Natore (Gurudashpur) samples (g/100 g on fresh weight basis) and their corresponding dry matter values were vise-versa. On the other hand, the ash values determined on dry weight basis found the highest (25.59) in Sirajgonj (Tarash) while the lowest (3.24) in Natore (Gurudashpur) sample. The ash value implies that Dill stem is a fairly good source of minerals.

The Dill stem contained significant amount of important mineral elements. The elements presents in descending order by quantity

Table I : XRF analytical information data of Dill stem of different places of Bangladesh

Parameters	Sirajgonj (Tarash)	Natore (Gurudashpur)	Dhaka (Botanical garden)	Dhaka (Keranigonj)
RMS	0.00	0.000	0.000	0.000
Sum before normalization	57.2%	63.5%	67.0%	57.4%
Normalized to	99.4%	98.7%	98.5%	99.8%
Sample type	Pressed powder	Pressed powder	Pressed powder	Pressed powder
Initial sample weight (g)	S_1= 4.056 S_2=4.050 S_3=4.047	S_1= 4.009 S_2=4.001 S_3=4.012	S_1= 3.902 S_2=3.914 S_3=3.911	S_1= 4.044 S_2=4.039 S_3=4.052
Weight after pressing (g)	S_1= 4.463 S_2=4.457 S_3=4.454	S_1= 4.411 S_2=4.403 S_3=4.414	S_1= 4.309 S_2=4.321 S_3=4.318	S_1= 4.451 S_2=4.446 S_3=4.459
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_+

Note: S_1, S_2 and S_3 values represent the values for three individual samples.

Table II: Proximate composition of Dill stem of different places of Bangladesh (g/100g).

Parameters	Sirajgonj (Tarash)	Natore (Gurudashpur)	Dhaka (Botanica garden)	Dhaka (Keranigonj)
Moisture	93.67	74.32	69.23	81.90
Dry matter	6.34	25.68	30.77	18.10
Ash (on dry weight basis)	25.59	3.24	3.32	8.58
Ash (on fresh weight basis)	1.62	0.83	1.02	1.55

Note: Each value represents the average value from three experiments.

(mg/100g on fresh weight basis), were Ca, K, Cl, Na, S, Mg, P, Al, Fe, Si, Ni and Ti. (Table III). The highest amount of Ca(478.50), P(49.42), Al(41.75), Fe(34.57) and Ti(3.75) were found in Sirajgonj (Tarash) sample and the lowest amount of Ca(311.28), Fe(3.89) and Al(3.42) in Dhaka (Keranigonj), P(19.12) in Natore (Gurudashpur), and also Ti(1.62) in Dhaka (Botanical Garden) samples. On the other

Table-III: Mineral element compositions of the stem of *A. sowa* (Dill) of different places of Bangladesh (mg/100g on fresh weight basis, calculated from their dry values).

Compound Formula	Elements	XRF Line	Crystal	Sirajgonj (Tarash)	Natore (Guruda-shpur)	Dhaka (Botanical garden)	Dhaka (Keranigonj)
O	O	-	-	496.11±3.03	262.87±1.65	348.29±2.09	456.80±2.44
Na_2O	Na	K*a*	PX1	48.93±1.49	14.36±0.168	17.96±0.28	114.86±1.38
MgO	Mg	K*a*	PX1	56.59±1.01	34.72±0.90	63.96±1.15	34.24±0.94
Al_2O_3	Al	K*a*	PE	41.75±0.71	9.65±0.25	11.07±0.44	3.42±0.15
SiO_2	Si	K*a*	PE	ND	ND	31.03±0.18	8.40±0.67
P_2O_5	P	Ka_1	Ge	49.42±0.74	19.12±0.57	39.62±0.19	32.52±1.23
SO_3	S	K*a*	Ge	53.82±1.76	30.92±0.80	25.49±1.14	96.65±1.76
Cl	CI	K*a*	Ge	104.54±3.58	14.16±0.50	14.13±0.64	153.92±3.26
K_2O	K	K*a*	LiF200	253.44±3.60	113.20±3.71	104.64±3.04	336.65±3.26
CaO	Ca	K*a*	LiF200	478.50±6.22	322.85±3.30	334.58±3.17	311.28±2.57
TiO_2,	Ti	K*a*	LiF 200	3.75±0.28	ND	1.622±0.10	ND
Fe_2O_3	Fe	K*a*	LiF220	34.57±1.33	5.23±0.01	12.83±0.62	3.89±0.46
NiO,	Ni	K*a*	LiF220	ND	3.50±0.60	11.98±0.22	ND
ZnO,	Zn	K*a*	LiF220	ND	ND	0.83±0.01	ND
Rb_2O	Rb	K*a*	LiF220	Tr	0.31±0.00	Tr	0.47±0.00
SrO	Sr	K*a*	LiF220	0.49±0.0	0.79±0.00	0.611±0.01	0.47±0.00
ZrO_2,	Zr	Ka_1	LiF220	Tr	0.10±0.00	0.142±0.00	Tr
BaO,	Ba	K*a*	LiF220	Tr	ND	1.79±0.00	Tr
Y_2O_3 , CuO MnO,	Y, Cu, Mn	Ka_1, K*a*	LiF220	Tr	Tr	Tr	Tr

Note: Where minimum detection limit is 0.01%, Tr stands for trace amount and ND for not detectable. Each value is the mean ± SD of three determinations.

hand K(336.65), Cl(153.92), Na(114.86) & S(96.65) found the highest amount in Dhaka (Keranigonj) sample and the lowest amount of K(104.64), S(25.49) & Cl(14.13) in Dhaka (Botanical Garden) and also Na(14.36) in Natore(Gurudashpur) sample. Moreover, Mg (63.96), Si (31.03) & Ni (11.98) were found in the highest amount in Dhaka (Botanical Garden) sample and the lowest amount of Mg (34.24) & Si (8.40) in Dhaka (Keranigonj) and Ni (3.50) in Natore (Gurudashpur) samples. However, Ti was not detected in Natore (Gurudashpur) and Dhaka (Botanical Garden), Ni was not detected in the sample of Sirajgonj (Tarash) and Dhaka (Keranigonj), Zn was not detected

Table IV : Mineral element compositions of the stem of A. sowa (Dill) of different places of Bangladesh (g/100g on dry weight basis, calculated from their values as oxides).

Compound Formula	Elements	XRF Line	Crystal	Sirajgonj (Tarash)	Natore (Guruda-shpur)	Dhaka (Botanical garden)	Dhaka (Keranigonj)
	O	-	-	30.42±0.18	31.1922±0.19	33.6144±0.20	29.35±0.14
Na_2O	Na	K*a*	PX1	3.00±0.09	1.7044±0.02	1.7336±0.02	7.38±0.08
MgO	Mg	K*a*	PX1	3.47±0.06	4.1202±0.10	6.1726±0.11	2.20±0.06
Al_2O_3	Al	K*a*	PE	2.56±0.04	1.1450±0.03	1.0685±0.04	0.22±0.01
SiO_2	Si	K*a*	PE	ND	ND	2.9953±0.02	0.54±0.04
P_2O_5	P	Ka_1	Ge	3.03±0.05	2.2691±0.07	3.8241±0.02	2.09±0.07
SO_3	S	K*a*	Ge	3.30±0.10	3.6685±0.09	2.4597±0.11	6.21±0.11
Cl	CI	K*a*	Ge	6.41±0.22	1.6797±0.06	1.3638±0.06	9.89±0.20
K_2O	K	K*a*	LiF200	15.54±0.22	13.4329±0.44	10.0993±0.29	21.63±0.21
CaO	Ca	K*a*	LiF200	29.34±0.38	38.3094±0.39	32.2910±0.31	20.00±0.16
TiO_2,	Ti	K*a*	LiF 200	0.23±0.01	ND	0.1566±0.01	ND
Fe_2O_3	Fe	K*a*	LiF220	2.12±0.08	0.6206±0.01	1.2388±0.06	0.25±0.03
NiO,	Ni	K*a*	LiF220	ND	0.4159±0.07	1.1564±0.02	ND
ZnO,	Zn	K*a*	LiF220	ND	Tr	0.0801±0.00	ND
Rb_2O	Rb	K*a*	LiF220	Tr	0.0364±0.00	Tr	0.03±0.00
SrO	Sr	K*a*	LiF220	0.03±0.0	0.0933±0.00	0.0590±0.00	0.03±0.00
ZrO_2,	Zr	Ka_1	LiF220	Tr	0.0124±0.00	0.0138±0.00	Tr
BaO,	Ba	K*a*	LiF220	Tr	ND	0.1730±0.00	Tr
Y_2O_3, CuO,MnO,	Y, Cu, Mn	Ka_1, K*a*	LiF220	Tr	Tr	Tr	Tr

Note: Where minimum detection limit is 0.01%, Tr stands for trace amount and ND for not detectable, each value is the mean ± SD of three determinations.

in Sirajgonj (Tarash), Natore (Gurudashpur) and Dhaka(Keranigonj) samples. Similarly, Si was not detected in Natore (Gurudashpur) and Sirajgonj (Tarash) samples. Very small concentrations of Zn (0.83), Rb (0.31-0.47), Sr (0.47-0.79) & Zr (0.10-0.142) and Ba (1.79) were determined in all the places under investigation. Y, Cu & Mn were present in trace amount in all the sample of the said places. The toxic elements like Co, Cd, As, Cr, Pb & Hg were not detected in the investigation. In our study some variations is observed in our data. These variations may be due to on such factors as type of genetic variety, maturity, collection time, climatic condition in various geographical location, composition of the soil, water and fertilizer used as well as permissibility, selectivity and absorbility of plants for the uptake of these elements. All the effects caused the final level of mineral components in a plant. (Sovljanski *et al*., 1989; Claudia P. *et al.*, 1998).

In the present study the highest concentration of Ca, P, Al and Fe were observed in Sirajgonj(Tarash), K, Cl, Na and S in Dhaka (Keranigonj) and Mg , Si and Ni in Dhaka (Botanical Garden) samples. Mineral values of Dill stem obtained in this investigation are comparable to other *Umbelliferae* species stem part like Parsley (*Petroselinum crispum*) stem contained Na (22.0), K(479.0), Ca(51.0), Mg(17.0), P(18.0) and Fe (0.7) mg/100g on fresh weight basis (**Claudia P *et al*.,1998**). In general, research findings have indicated that Dill stems contain substantial amount of mineral elements. The high amount of these elements could provide alternative sources of mineral intake. However, the bioavailability of these minerals, specially phosphorous, remains a problem, as it is more often than not in a complexed form.

Mineral elements play vital roles in many important processes in the body, such as Fe, Zn, Na, K and Ca are important in human nutrition. The body requires Fe for the synthesis of the oxygen transport proteins hemoglobin and myoglobin and for the formation of heam enzymes and other Fe containing enzymes, which are particularly important for energy production immune defence and thyroid function. The body normally regulates Fe absorption so as to replace the obligatory iron losses of about 1-1.5 mg per day. Fe deficiency anemia can decrease mental and psychomotor development in children increase both morbidity and mortality of mother and child at childbirth, decrease work performance and decrease resistance to infection. In this study the Fe (3.89-34.57 mg) content in Dill stem is an agreeable limit (DRI 1997). Ca is the major component of bone and assists in teeth development (Brody 1994). Where low intake of Ca can be detrimental to health, since low intake is one of the risk factors in the bone disease osteoporosis. Ca is required for the normal growth and development of the skeleton. Adequate Ca intake during adolescence is critical in achieving optimal peak bone mass and reducing the rate of bone loss associated with aging (Frossard *et al*., 2000). On the other hand, Na, K and Ca play an important role in the electrophysiology of cardiac tissue. Ca-ions increase the force of contraction of the heart. (Rajurkar *et al*., 1997). Na maintains the osmotic equilibrium between the extra cellular fluid and the tissue cells and maintains the pH of blood within normal limit. It is also concerned with the conduction of nervous impulses, muscle contractility and control of heart muscle conduction (Gupta *et a*l., 2000). Mg, Fe and P are essential for most metabolic processes. This is nutritionally significant considering the fact that, potassium plays a principal role in neuro-muscular functions. (**Ibironke *et al*, 2006**). Zn is an important constituent of several enzymes and plays vital role in clinical, biochemical and immunological effects (**Fell and Lyon 1994; Dell and Sunde, 1997**). The important of these elements cannot be overemphasized because many enzymes require them as cofactors (**Akpanabiatu *et al.*, 1998**). In the present communication, the mineral element composition of Dill stem is an agreeable limit for our daily dietary allowance (**Table -V**).

authors. In comparison with other *Umbelliferae* species stem part, Dill stem accumulated encouraging amount of mineral elements. Precision of the measurements was taken by analysis of three sub samples of each region. Mean elemental contents vary over a wide range, attributed to varying geo-environmental conditions and local soil characteristic from one place to another. The ANOVA results proved that there was not a significant variation between the single analytical procedures employed. Due to the increasing interest in finding the biological

Table V: The mineral elemental composition present in Dill stem is compared with daily dietary allowance.

Mineral elements (mg/100g)	Amount present determined in the study (mg/100g on fresh weight basis)	Daily dietary allowance for human adult (DRI, 1997) (mg)	Daily dietary allowancefor infants (DRI, 1997) (mg)
Na	14.36-114.86	500	120-200
Mg	34.24-63.96	320-420	75
P	19.12-49.41	800	275
CI	25.49-96.65	750	300
K	104.64-336.65	2000	700
Ca	311.28-478.50	1200	270
Fe	3.89-34.57	10-18	10
Zn	0.83	15	5
Cu	Tr	1.5-3	0.6-0.7
Mn	Tr	2.5	0.6-1.0

Conclusion :

The total concentration of macro and micro elements were measured in Dill stems from four different places of Bangladesh by XRF spectrometry for the first time by the

roles of nutrients and their function in chronic diseases, vis-à-vis knowledge of dietary nutrient intake is needed to optimize human health. The nutritional assessment of food intake is of permanent interest to food chemist. Dietary sources of essential elements are important for correct physiological functions of the human body. The high quantity of K, Mg and Ca together with the quantity of Na plus the content of the essential elements Fe, Mn, Zn and Cu allow the stems of Dill is to be considered as excellent sources of bioelements. The results indicate that analyzed dill stem should be considered as sufficient amount of mineral element supplement to meet the daily dietary allowance (DRI 1997). Inorganic elements remain complexes with organic ligands and made them bioavailabe to the body system. Physiological effect of each mineral should be evaluated in connection with the minerals daily taken from other foods. At any rate, it is considered that stems of Dill play a meaningful roll in human nutrition as useful mineral sources. The high level of these macro and micro-elements in stem part make it useful as supplements as human diets or livestock feed and also be used as raw materials in pharmaceuticals and ayurvedic formulation.

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