Spectroscopic Analysis of Essential Elements in Different Varieties of Wheat Cultivated in Sindh, Pakistan

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Summary: Employing standard analytical methods and the atomic absorption technique, essential elements residues are estimated in eight different wheat varieties which were collected from different areas of Sindh. Analysing a certified sample obtained from the Federal Seed Certification and Registration Department has validated the procedure. Several wheat samples of known origin, variety and crop year have been analysed to determine the content of sodium, potassium, calcium, magnesium, iron, zinc and Mn by means of AAS. The resulting compositions of the different samples have been used to assess species, origin and variety of the examined wheat. Considerable amount of essential elements were present in each variety. The values of each element were compared with certified samples, which is at the 98% confidence limit.

Introduction

The determination of mineral content is an important parameter in the evaluation of the nutritional value of food. Nevertheless, none of these studies have dealt with the ash composition of food. In the International Scientific Technical Network (STN) little or no reliable data relative to mineral components of wheat has been included. Determination of alkaline and alkaline-earth metal contents are even less frequently carried out. For example, the Italian, Istituto Nazionale della Nutrizione, [1] reports only the percentage of Fe and Ca present in two species of wheat: *Triticum durum* (TD) and *Triticum aestivun* (TA).

Voltammetric methods [2] were used to quantitatively assess the presence of Cd, Cu, Co, Ni and Pb in milk powder, wheat, flour and biological materials. The amount of Cu and Zn present in raw and cooked vegetables was determined using atomic absorption spectroscopy (AAS) and x-ray fluorescence spectroscopy [3]. Benzo et al. [5] carried out determinations of Mn, Fe, Cu and Zn in tropical cereals, fruit and vegetables using AAS. The presence of some metals in meat, meat products, liver and animal fats were also revealed [7].

Recently, much attention has been focused on the metal content in food due to the deterimental consequences to human health, as well as the availability of metals as enzyme activators or inhibitors. Knowledge of the oligoelemental composition of wheat is important from a nutritional point of view, as wheat is a major part of the diet in Asia as well as in Europe.

Controlled quantities of sodium and a fixed potassium/sodium ratio are recommended in cases of some heart diseases, and assimilation of Zn is thought to be helpful in the treatment of some liver disease [8]. Maintenance of the appropriate blood Ca level involves bones, kidneys, intestine and parathyroid glands [9]. On the other hand, Ca plays an important role in the pathogenesis of gallstones [10]. As Mg is an essential factor in the glucose transport mechanism through cell membranes, it is often important to determine its level in plasma and erythrocyte [11].

Yang *et al.* [12] determined seven metals (Al, Ca, Cu, K, Fe, Mg and Zn) in thirteen different types of Belgian bread and bread products in order to distinguish between white and whole meal bread.

Armanino and Festa [13] analysed several samples of TA and TD for ash, fat, proteins and humidity. These results were studied using the program Parvus [14], to assess species, origin, variety and year of the harvesting of each sample. As metals are present in food at very low concentrations, it is necessary to develop a sensitive and accurate

Table 1A. Results of important macro-elements (mg/kg) obtained from the Certified and Collected wheat varieties of the Sindh

Varieties	Na (ppm) [a] x (s)		t-test	K (ppm) [a] x (s)		t-test	Ca (ppm) [a] x (s)		t-test	Mg (ppm) [a] x (s)		t-test
	Rep.[c]	Cert[b].		Rep.[c]	Cert[b].		Rep.[c]	Cert[b].		Rep.[c]	Cert[b].	
Anmol	568.9±32.37	563.91±38.53	4.30	3697.4±65.26	3702.1±51.59	-3.63	258.61±8.40	256.45±11.1	4.15	1430.06±15.25	1432.1±16.5	-3.09
TJ-83	619.58±38.5	624.02±38.11	-4.30	3742.8±79.92	3749.3±114.0	-3.99	273.38±9.94	275.22±10.5	-3.45	1392.42±31.24	1390.4±24.85	2.27
Abadgar-93	951.33±4.38	955.35±46.73	-3.65	3773.00±39.0	3767.9±65.26	4.25	239.54±5.46	240.16±8.52	-1.41	1428.88±10.39	1430.4±13.14	-2.68
Mehran-89	745.74±34.1	742.07±28.04	3.95	3742.8±39.81	.3746.8±39.00	-3.84	243.23±12.8	244.46±9.29	-2.22	1499.45±21.13	1502.8±25.41	-4.19
Soughat-90	642.94±38.9	638.67±31.92	4.31	3689.9±51.59	3685.30±39.00	4.07	344.12±7.35	342.14±8.76	4.19	1522.98±23.93	1519.5±2564	4.25
Sarsabaz	839.19±34.1	835.52±28.04	3.95	3705.00±38.0	3709.00±31.01	-4.09	344.73±9.50	345.35±8.4	-1.24	1530.04±27.06	1526.4±29.49	4.16
Kiran	708.34±34.1	704.69±28.04	3.93	3682.3±52.32	3676.8±75.52	4.17	223.55±9.50	224.16±8.4	-1.22	1467.70±17.09	1465.3±18.22	3.37
SKD-10/9	769.1±31.92	773.12±34.12	-4.20	3538.9±38.01	3544.00±62.28	-4.32	320.74±7.35	319.28±8.13	3.15	1434.76±21.41	1435.9±19.67	-1.56

[a]The results are expressed in mg/kg (ppm). For each variety the average value (x), obtained from at least six determinations, and standard deviations (s) are reported.
[b]Certified samples were obtained from office of seed certification and registration department i.e. Hyderabad, Sikrand and Sukkur Sindh, Pakistan
[c]Representative samples were collected from different districts of agricultural research stations/centres i.e. NIA,Tandojam (Hyderabad district), Agricultural research institute Sikrand (district Nawabshas)

Table 1B Results of important micro-elements (mg/kg) obtained from the Certified and Collected wheat varieties of the Sindh

Varieties	Fe (ppm) [a] x (s)		t-test	Zn (ppm) [a] x (s)		t-test	Mn (ppm) [a] x (s)		t-test
	Rep.[c]	Cert[b].		Rep.[c]	Cert[b].		Rep.[c]	Cert[b].	
Anmol	29.39±2.65	30.25±1.62	-3.53	39.57±1.37	39.8±1.3	-1.19	32.58±2.15	32.91±1.79	1.41
TJ-83	34.71±2.10	34.49±1.75	0.95	31.04±1.50	30.74±1.54	1.46	36.64±1.76	36.32±1.64	-1.47
Abadgar-93	30.23±2.81	30.44±3.18	-0.73	32.17±0.98	32.75±0.53	-4.01	38.10±2.88	38.75±2.62	2.35
Mehran-89	40.26±2.74	39.26±2.74	3.62	35.34±1.30	35.27±1.42	0.36	30.11±1.23	30.31±1.23	1.08
Soughat-90	29.80±1.55	29.59±1.94	0.95	39.34±2.97	39.49±2.84	-0.53	28.36±1.62	28.68±1.11	1.64
Sarsabaz	27.02±1.34	26.81±1.05	1.15	45.23±1.27	45.83±1.7	-2.95	34.37±1.55	34.21±1.71	-0.75
Kiran	22.33±1.26	22.54±1.62	-1.05	42.13±0.89	42.21±0.78	-0.53	28.03±1.87	27.87±1.55	-0.73
SKD-10/9	35.13±2.21	34.13±2.21	4.04	42.51±0.98	42.74±1.18	-1.33	20.04±1.11	20.24±1.11	1.14

[a]The results are expressed in mg/kg (ppm). For each variety the average value (x), obtained from at least six determinations, and standard deviations (s) are reported.
[b]Certified samples were obtained from office of seed certification and registration department i.e. Hyderabad, Sikrand and Sukkur Sindh, Pakistan
[c]Representative samples were collected from different districts of agricultural research stations/centres i.e. NIA,Tandojam (Hyderabad district), Agricultural research institute Sikrand (district Nawabshas)

procedure. In this paper Na, k, Ca, Mg, Fe, Zn and Mn Ni have been determined in wheat of known origin, species, variety and year of production.

The main goal of this work is to determine the accurate concentration of essential elements present in wheat of Sindh. This allows the AAS for the determination of all essential and trace elements in the same run.

Results and Discussion

The above described procedure was employed analyses six samples of each wheat variety from Nuclear Institute of Agriculture Tandojam, Sikrand, Kotdiji, and Ghotki Sindh, Pakistan obtained without any chemical or biological treatment. The Tandojam, Sikrand, Kotdiji and Ghotki species consisted of two type (certified & representative samples) to each location, respectively. The amount of Na, K, Ca, Mg, Fe, Zn and Mn was obtained from the average of eighteen determinations. The contents of the essential metals (i.e. Na, K, Ca, Mg, Fe, Zn and Mn) were obtained from AAS measurements.

Tables 1A and 1B report the most significant results of the analysis of the investigated samples. The reliability of our method is shown by the low standard deviation value obtained (in table 1A and 1B)

This study can also be of interest in determining the amount of each element present in wheat of different wheat varieties, origin and species, and metals, which prevail in the corresponding solutions.

The detail experimental data for each element in collected samples is in such a way that the maximum concentration of Na was observed in Abadgar-93 $(951.33\pm40.38)^c$ and the minimum concentration of Na was observed in Anmol i.e. $(568.18\pm32.37)^c$. The level of K was found to be high such as $(3772.96\pm39.00)^c$ in Abadgar-93 while as low value was observed in SKD-10/9 i.e. $(3538.85\pm38.01)^c$. The high level of Ca was found to be in Sarsabaz $(344.73\pm9.50)^c$ and the low value was observed in Kiran $(223.55\pm9.50)^c$. Magnesium is an essential element for maintaining the body health, the level of Mg is found to be $(1530.04\pm27.06)^c$ in Sarsabaz and the lower amount was detected in Tj-83 $(1392.42\pm31.24)^c$. The level of Fe was maximum in Mehran-89 i.e. $(40.26\pm2.74)^c$ while as comparatively low concentration was observed in Kiran i.e. $(22.33\pm1.26)^c$. Similarly high concentration of the Zn was detected in Sarsabaz $(45.23\pm1.27)^c$ and the minimum concentration was found in TJ-83 $(31.04\pm1.50)^c$. Manganese is one of the important macro element which play very important role in many biochemical reactions and its maximum concentration was found in Abadgar-93 $(38.10\pm2.88)^c$ and its low content (i.e. $20.04\pm1.11)^c$ was found in SKD-10/9 variety.

All values for different elements in wheat varieties were found to be within the permissible limit given by FAO and WHO.

Experimental

Reagents

The nitric acid (65% w/v) and hydrogen peroxide (35% w/v) were supra pure reagents (Merck), high-purity water (electrical resistively greater than 10MΩ cm) was produced with a Milli-Q system Millipore, MA, USA).

Apparatus and instrument

Glassware was cleaned by soaking with the contact over night in a 10% (w/v) nitric acid solution and then rinsed with deionized water.

A Hitachi Model 180-50 atomic absorption spectrophotometer was used, sodium, potassium, calcium, magnesium, iron zinc and Mn hollow-cathode lamps (made by Mtiorika company) were operated at lamps current of 9.5, 9.5, 7.3, 7.0, 9.5, 9.5 and 9.5mA respectively. The spectrophotometer output was connected to a Hitachi recorder Model 180-50, 056 with a range of 5mV. The signals measured were the heights of the absorbance peaks. The detail is given in table 2.

Calculations and statistical evaluation

Working standard solutions of sodium, potassium, calcium, magnesium, iron and zinc were prepared from stock standard solution (1000 ppm), in 2N nitric acid and calibration curves were drawn for each element using Atomic Absorption Spectrophotometer Hitachi Model 180-50. The calibration curves obtained for concentrations versus absorbance data were statistically analysed using fitting of straight line by least square method as given in table 3. These seven elements were determined in wheat grains. The results of these measurements are presented in table 1A and 1B.

A blank reading was also taken and necessary corrections were made during the calculation of percentage concentration of various elements.

Method of investigation

The analyses were carried out on certified samples obtained from FSC&RD wheat Samples from the offices of the Federal Seed Certification and Registration Department Hyderabad, Sikarand and Sukkur while as the samples were collected from the agricultural land situated at NIA, Tandojam, WRS, Sikarand, Basic Seed farm, Kotdiji and Basic Seed farm Ghotki, Sindh. Pakistan. Their variety and crop year were also known.

Procedure

Six samples of each wheat varieties *Anmol, TJ-83, Abadgar-93, Mehran, Soughat-90, Sarsabaz, Kiran,* and *SKD10/9* which were grown in four different locations (NIA, Tandojam, Wheat Research Station Sikrand, Basic seed farm Kotdiji and Basic seed farm Ghotki) of the Sindh, Pakistan. Crops were harvested at maturity after 18-20 weeks. The

Table 2.Instrumental conditions for the AAS measurement of Na, K, Ca, Mg, Fe and Zn.

Elements	Wave length (nm)	Slit width (nm)	Lamp Current (mA)	Burner height (mm)	Oxidant (Air) kg/cm^2	Fuel (Acetylene) kg/cm^2	Signal out put
Na	590	0.4	9.5	7.5	1.60	0.25	100%
K	766.8	2.6	9.5	7.5	1.60	0.3	100%
Ca	422.2	2.6	7.3	12.5	1.60	0.4	100%
Mg	285.5	2.6	7.0	7.5	1.60	0.2	100%
Fe	248.3	0.2	9.5	7.5	1.60	0.3	100%
Zn	214.0	1.3	9.5	7.5	1.60	0.2	100%
Mn	279.8	0.4	9.5	7.5	1.60	0.2	100%

Table-3.:Statistical data for standards of elements

Elements	Concentration range ppm (x)	Absorbance	Statistical calculation y = m x + c		
			m	c	r^2
Na	0 – 0.25	0 – 0.084	0.3344	0.0001	0.9996
K	0 – 1	0 – 0.207	0.2069	0.0006	0.9999
Ca	0 – 5	0 – 0.256	0.0508	0.0024	0.9993
Mg	0 – 1	0 – 0.885	0.8856	0.0017	0.9999
Fe	0 – 1	0 – 0.096	0.0976	-0.0016	0.9989
Zn	0 – 0.5	0 – 0.138	0.2761	-0.0004	0.9999
Mn	0 - 1	0 - 0.196	0.1962	0.0005	0.999

grains were separated from their spikes by single heads thresher model No. AAM-8, which were randomly collected and made the representative samples for analysis. These representative samples were washed well with distilled water and dried at 105 ^{0}C for 2 hours in an oven. All varieties were ground in a domestic grinder (Arno. Sao Paulo, SP, Brazil). Subsequently, portions of these wheat variety samples were dried at 60 ^{0}C until constant mass. Triplicate 2gram samples of each variety were weighed into separate 100ml flasks and treated with 5ml of nitric acid. 5ml of nitric acid were also added to empty conical flasks serving as blank. The flasks were covered with watch glasses, and their contents were heated to reflux gently on an electric hot plate. After refluxing for one hour, the contents of flasks were treated with 5ml more of nitric acid, 2ml of 30% hydrogen peroxide was added, and the heating at gentle reflux was continued for an other hour. The watch glasses were removed from the flasks, and the heating was continued until the volumes of their contents were reduced to 2-3ml. The contents of the flask were cooled, diluted with high purity water, and filtered through whatman # 42 paper into 25ml volumetric flasks. The contents of flasks were brought to volume with high purity water and examined by atomic absorption spectrometry for their sodium, potassium, calcium, magnesium, iron, zinc and manganese levels. These analysis was carried out at the Centre of Excellence in Analytical Chemistry Laboratory, located in university of Sindh, Jamshoro, Pakistan.

Conclusions

The experiments carried out provide evidence that the extraction of Na, K, Ca, Mg, Fe, Zn and Mn from wheat by wet digestion method is the traditional reflux systems. The results obtained from representative samples which were collected from four districts (Nawab shah, Khairpur (Mirs) Ghotki and Hyderabad) of the Sindh province, Pakistan are in good agreement with the results of Federal Seed Certification & Registration Department certified samples.

It was concluded that the up take of elements dependents on botanical factor with many other factors such as the amount of elements in agricultural soil and water etc. So up take of elements varied variety to variety of same species.

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