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Trace Element Analysis of Black Foods by ICP-AES

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A method for determination nineteen trace elements of Se, Zn, Ni, B, Mn, Fe, Mg, Be, Ca, Cu, Ba, Na, K, P, As, Pb, Cd, Cr and Al in five black foods (black bean, black rice, black sesame, black tree fungus and seaweed) by inductively coupled plasma atomic emission spectrometry has been suggested and sufficient experimental conditions of microwave digestion have been studied. The accuracy of the method was validated using the Chinese reference material GBW08517 Sesame and GBW08502 rice. The multi-element standard solutions (5 mg/kg) as a correction technique was explored. Results showed concentrations of all elements displayed a wide variability among those black foods, except for Se, Pb, Cr, Be and Ba. The predominant element was K, followed by P, Ca, Mg and Na. The medium content was Al, Fe, B, Zn, Mn and Cu. Meanwhile, high levels of As, Pb and Cr were found in seaweed. Therefore, it is important to have a good quality control for black foods in order to protect consumers from health risks for consumption.

Key Words: Black foods, Trace elements, Microwave digestion, ICP-AES.

INTRODUCTION

At present, black foods have attracted more and more attention to common diet because they contain abundant beneficial components such as proteins, fat, vitamins and trace elements. Among these products, black bean, black rice, black sesame, black tree fungus and seaweed are the most popular agricultural products consumed for medical purposes or maintaining good health[1]. International Agricultural Research (CGIAR) Micronutrients Project has been to assess the feasibility of improving the micronutrient content of common beans, especially the mineral contents[2]. The mineral composition of food legumes is a more or less variable factor and influenced by a number of interrelated factors, such as genetic diversity, grain colours, climate, soil characteristics (content of organic matter, pH and clay mineralogy), cropping strategies, transport, storage and preparation. These factors vary from one region to another and even within the same country[3-5].

The human body requires both metallic and nonmetallic elements within certain permissible limits for growth and good health. Mineral and vitamin deficiencies affect a greater number of people in the world than does protein-energy malnutrition. Their diets consist mostly of staple foods, primarily agricultural products. For most people, these staple foods are already primary sources of micronutrients they are able to consume, particularly minerals. Therefore, determination of element compositions in black foods and related products is essential for understanding their nutritive importance, determination of minerals in black foods becomes increasingly significant and some techniques have been described recently.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is the most used technique in the determination of minerals because of the capability for rapid multi-element detection over a wide concentration range with relatively low detection limits[6,7]. Compared to other techniques such as neutron activate analysis (NAA)[8] or inductively coupled plasma mass spectrometry (ICP-MS)[9], ICP-AES is relatively inexpensive. Flame atomic absorption spectrometry (FAAS)[10,11], electrothermal atomic absorption spectrometry (ETAAS)[12,13] are a single-element technique and time-consuming if many elements are to be determined in each sample. However, the low level of minerals in samples is not compatible with detection limits exhibited by this technique and major constituents, such as organic compounds and inorganic salts, may cause some matrix effects. In order to achieve accurate and reliable results, one usually requires an efficient preconcentration of minerals was tested by microwave digestion procedure.

The objective of this study is to establish the levels of some mineral and trace elements (Se, Zn, Ni, B, Mn, Fe, Mg, Be, Ca, Cu, Ba, Na, K, P, As, Pb, Cd, Cr and Al) in black foods that are widely and habitually consumed for nutrition purposes in China. On the other hand, it is well known that not only the

determination of trace element concentrations in these black foods is very important, but also a reliable analytical procedure is a critical step in the studies on trace element analysis for preventing heavy metal poisoning.

EXPERIMENTAL

The black foods used in the experiment including samples of black bean, black rice, black sesame, black tree fungus and seaweed were bought from the agricultural product market in Xinxiang, China and authenticated by Benguo Liu (School of Food Science, Henan Institute of Science and Technology, Xinxiang, China).

All reagents were of analytical-reagent grade. 65 % HNO_3 and 72 % $HClO_4$ were used for digestion procedures, Zn, B, Mn, Fe, Mg, Be, Ca, Cu, Ba, Na, K, Al multi-element stock solutions 1000 mg/L (Merck, Darmstadt, Germany) and Se, As, Pb, Cd, Cr, Ni multi-element stock solutions 100 mg/L (Merck, Darmstadt, Germany) served for preparation of multi-element calibration solutions. Phosphorus stock solution (ρ = 1000 mg/L) was prepared by dissolving appropriate amount of ammonium dihydrogenphosphate (purity 99.99 %) (Shanghai, China) in ultra-pure water. For preparation of all solutions and samples, An Ultra-pure Water System (SG Ultra Clear system, Wasseraufbereitung und Regenerierstation GmbH, Germany) was used to produce ultrapure water with specific conductivity down to 0.055 μS/cm for the analysis of trace elements. All multi-element calibration standard solutions were prepared in 2 % (v/v) nitric acid by dilution of multi-element stock standard solutions as already stated.

Before use all labware was subjected to a cleaning procedure. It was soaked in 25 % HNO_3 overnight and washed in an ultrasonic bath during 20 min. Then the labware was rinsed with distilled and finally with ultra-pure water.

Standard reference materials of trace elements in sesame GBW08517 and rice GBW08502 (the Chinese CRM/RM Information Center, China), was used.

All microwave digestion reactions were conducted in a microwave-accelerated reaction system MARS-5 (CEM, USA) equipped with high-pressure PTFE vessels (internal volume of 10 mL, maximum operating temperature of 300 ºC). To reduce sample carry over between digestions, the digestion vessels were cleaned by first microwaving them with a mixture of 25 mL 14.2M HNO_3 and 2 mL 30 % H_2O_2 for 3 min at 400 W (120 ºC) followed by 10 min at 800 W (150 ºC). The PTFE vessels were then rinsed thoroughly with ultrapure water. After repeating this procedure twice, the digestion vessels were then air dried and used stored.

All trace elements were determined by ICP-AES (Optima 2100 DV, Perkin Elmer, USA) measurement, with a cyclone axial spray chamber; nebulizator Ar flow, 0.80 L/min; generate RF-power, 1300 W; RF, 40.68 MHz; analytical wavelength (nm), Se (196.02), Zn (213.86), Ni (231.60), B (249.67), Mn (257.61), Fe (259.93), Mg (279.08), Be (313.04), Ca (317.93), Cu (324.75), Ba (455.40), Na (589.59), K (766.49), P (213.69), As (193.69), Pb (220.35), Cd (226.50), Cr (267.71) and Al (396.15). Radial viewing mode was used. A manual sample uptake was adopted to obtain stable signal intensity.

General procedure: High-pressure microwave wet digestion and three procedures including microwave assisted extraction were used for the preparation of black food for the determination of trace elements. The samples were digested using a microwave digestion system as follows. A 0.30 g sample was placed in a PTFE vessel, 10 mL of HNO_3 and 2 mL of $HClO_4$ for predigestion were added. The predigestion process was kept at room temperature for atleast 12 h to allow for the digestion program. The digestion program consisted of three steps: powder: 800 W, ramp: 120 °C for 5 min, hold for 5 min; powder: 800 W, ramp: 150 °C for 3 min, hold for 10 min and powder: 1600 W, ramp: 210 °C for 5 min, hold for 15 min. When the digestion program finished, a 20 min ventilation step (no microwave power) cooled the vessels for reducing the pressure inside to ambient values. After digestion, the solution was evaporated to dryness, the residue was transferred into a volumetric flask and made up to 25 mL with ultrapure water. Blank solutions were prepared in the same way as the samples.

Detection method: Trace elements were determined by ICP-AES (radial configuration). Zn, B, Mn, Fe, Mg, Be, Ca, Cu, Ba, Na, K, Al multi-element calibration standard solutions (0.00, 1.00, 5.00, 10.00, 20.00 and 40.00 mg/kg) were prepared by diluting 1000 mg/kg multi-element stock solutions and Se, As, Pb, Cd, Cr, Ni multi-element calibration standard solutions (0.00, 0.50, 1.00, 2.00, 4.00 and 8.00 mg/kg) were prepared by diluting 100 mg/kg multi-element stock solutions, respectively. P calibration standard solution (0.00, 1.00, 10.00, 20.00, 40.00 and 60.00 mg/kg) was prepared by diluting phosphorus stock solution (ρ = 1000 mg/L). The determination of all trace element concentrations was based on different calibration graphs obtained from six-level calibration standard solutions.

RESULTS AND DISCUSSION

Linearity, limit of detection and limit of quantification: Linearity, limit of detection (LOD) and the limit of quantitation (LOQ) for all the analysis elements by ICP-AES method were investigated under the above optimum analysis conditions. Calibration curves were obtained for analysis elements using a series of multi-element calibration standard solutions, LOD and LOQ were calculated using 3 SD/b and 10 SD/b (SD is the standard deviation of the curve and *bis* the slope of the curve). A good linear relationship between the corresponding sensitivities and the concentrations of the analysis elements was achieved. The calculated regression equation, correlation coefficients (r), LOD and LOQ by ICP-AES method are shown in Table-1.

Determination of accuracy and precision of the method: The accuracy and precision of the method were tested with two standard reference materials GBW08517 (sesame) and GBW08502 (rice). The results indicated that the concentrations of trace elements determined by the present ICP method were in agreement (within ± 10 %) with the certified values, except in the cases of Be for GBW08517 and As for GBW08502, for which the determined values were different from the certified values (Table-2). Boron and Al are not present in the GBW08517 and GBW08502.

TABLE-1
LINEARITY AND DETECTION LIMITS FOR THE ANALYSIS ELEMENTS

Element	Regression equation*	Correlation coefficient (r)	LOD (mg/kg)	LOQ (mg/kg)
As	Y = 787.1X + 3.5	0.999535	0.0730	0.2421
Se	Y = 1193X + 61.1	0.999215	0.0990	0.3267
P	Y = 6170X + 2394.7	0.999888	0.0925	0.3085
Zn	Y = 128715X + 234.3	0.999958	0.0047	0.0155
Pb	Y = 4518X + 56.8	0.999823	0.0678	0.2237
Cd	Y = 61823X + 2115.4	0.999964	0.0044	0.0145
Ni	Y = 27258X + 164.6	0.999913	0.0232	0.0765
B	Y = 92690X + 1138.3	0.999986	0.0079	0.0260
Mn	Y = 183000X + 5077.1	0.999943	0.0018	0.0059
Fe	Y = 170200X + 1537.2	0.999992	0.0073	0.0240
Cr	Y = 27055X + 284.7	0.999982	0.0089	0.0293
Mg	Y = 2783X + 123.4	0.999974	0.0421	0.1389
Be	Y = 3403000X + 35852.4	0.999034	0.0008	0.0026
Ca	Y = 20482X + 9733.9	0.999359	0.0310	0.1023
Cu	Y = 47523X + 1625.6	0.999965	0.0068	0.0224
Al	Y = 23420X + 404.6	0.999959	0.0622	0.2052
Ba	Y = 21880000X - 119903.1	0.999997	0.0018	0.0059
Na	Y = 2098000X - 192720	0.999210	0.0782	0.2580
K	Y = 756400X - 74360.9	0.999095	0.0515	0.1699

*Y = sensitivity (cps), X = concentration of compound (mg/mL).

TABLE-2
ANALYSIS OF GBW08517 AND GBW08502 REFERENCE MATERIALS (n = 6)

Element	GBW08517 (mg/kg)		RSD (%)	Element	GBW08502 (mg/kg)		RSD (%)
	Certified value	Measure value			Certified value	Measure value	
As	13.9 ± 2.4	17.28	1.39	As	0.051 ± 0.003	0.061	2.63
Se	0.062 ± 0.009	0.058	1.85	Se	0.045 ± 0.008	0.043	1.74
P	6700	7249	2.3	P	a		
Zn	27.9 ± 0.9	26.46	1.06	Zn	14.1 ± 0.5	14.45	0.88
Pb	1.41 ± 0.12	1.57	1.87	Pb	0.75 ± 0.05	0.81	1.59
Cd	1.14 ± 0.11	1.16	0.76	Cd	0.02 ± 0.002	0.19	0.42
Ni	0.71 ± 0.09	0.72	0.98	Ni	a		
B	a			B	a		
Mn	a			Mn	9.8 ± 0.2	9.89	0.19
Fe	a			Fe	5.1 ± 0.2	5.46	1.94
Cr	0.63 ± 0.08	0.61	2.26	Cr	a		
Mg	29.5	30.44	0.47	Mg	120± 5	128.65	2.66
Be	0.022	0.054	2.24	Be	a		
Ca	3360	3568	2.84	Ca	55 ± 3	59.62	1.04
Cu	5.01 ± 0.32	5.47	1.62	Cu	2.6 ± 0.2	2.56	1.38
Al	a			Al	a		
Ba	81.1 ± 6.0	84	2.69	Ba	a		
Na	a			Na	8.4 ± 0.6	9.42	1.69
K	a			K	656 ± 15	683.76	2.96

n: Number of assay for each of the medicinal herb sample; a: not certified.

Another study made to assure that the accuracy and precision of the method were good, the 5 mg/kg multi-element calibration standard solutions as a correction technique were determined. The results showed the relative standard deviations of all the elements tested were not more than 5 % and good agreement of measured values for all elements when compared to the multi-element calibration standard solution, which indicated the agreement (within ± 10 %) with the certified value.

Concentration of analysis trace elements in black foods: The optimized procedure was applied to the analysis of black bean, black rice, black sesame, black tree fungus, seaweed. Each sample was read six times with the average reported. At the end of each run, the multi-element calibration standard solutions (5 mg/kg) were run as a sample to ensure ICP stability and an absence of carryover from other samples. The concentrations of nineteen trace elements determined in each of five black foods are collectively listed in Table-3.

It is observed that most elemental concentrations vary by one to two orders of magnitude except Pb (7.75-9.12 mg/kg), Cr (1.75-2.17 mg/kg) and Be (2.57-4.91 mg/kg). Where variations are in a wide range. Potassium content was very high in all black foods, the seaweed contained the highest level of K, which was about 18 times the level found in the black rice. Sodium content of the black foods was in the range of 416-13144.84 mg/kg, Na content of the seaweed was about two orders of magnitude the level found in the black sesame, These electrolytic or structural elements play an important role in the fluid balance[14].

TABLE-3
CONTENTS OF TRACE ELEMENTS IN DIFFERENT BLACK FOODS (mg/kg) n = 6

Element	Black bean	Black rice	Black sesame	Black tree fungus	Seaweed
As	ND	0.91	ND	1.42	8.928
Se	6.33	7.00	15.16	9.02	4.17
P	3535.83	2955.83	5073.33	1390.83	5618.02
Zn	30.08	17.16	49.75	8.84	96.23
Pb	0.69	0.84	1.83	1.75	3.12
Cd	ND	ND	ND	ND	1.19
Ni	15.16	ND	1.416	ND	4.96
B	74.75	15.08	18.41	83.25	34.12
Mn	23.83	31.58	28	7.84	ND
Fe	81.33	71.66	70.33	186.67	4.36
Cr	2.17	1.75	1.91	1.89	1.98
Mg	1865	1161.66	3028.33	828.58	4991.07
Be	4.41	4.58	4.84	4.91	2.57
Ca	2553.33	896.66	11633.34	159	2174.60
Cu	14.75	10.58	21.51	5.58	34.62
Al	115.41	45.08	70.25	88	794.64
Ba	9.41	3.75	26.25	5.61	8.63
Na	299.91	236.75	416	1902.5	13144.84
K	13725	1997.5	5120.83	5168.30	36339.28

n: Number of assay for each of the medicinal herb sample; ND: not detected.

Phosphorus in the five black foods was in the range of 1390.83-5618.02 mg/kg. The highest P was determined in seaweed, its content was about 4 times the level found in the black tree fungus. Magnesium content of the black foods was in the range of 828.58-4991.07 mg/kg, Mg content of the seaweed was about 6 times the level found in the black tree fungus.

Calcium in the black foods varied in a wide range of 159-11633.34 mg/kg, the highest Ca was determined in the black sesame whereas the lowest was in the black tree fungus. Calcium has reached the similar value in black bean and seaweed. Fernandez *et al.*[15], determined the Mg and Ca content of black and green teas in the range of 5 and 22 mg/L. Lozak *et al.*[13], reported data on Ca and Mg present in row mint leaves as 15.331 and 5778 mg/kg, respectively.

Copper content of the seaweed was about 2 times the level found in the black tree fungus, Cu in the black foods varied in a wide range of 5.58-34.62 mg/kg. The content of Al in the black foods, which is known as one of the toxic elements, varied between 45.08 mg/kg (black rice) and 794.64 mg/kg (black tree fungus). Muller *et al.*[16], indicated that most investigated foodstuff (vegetables, meat and dairy products) contained less than 5 mg/kg of Al (fresh weight) and high concentrations were determined in cocoa-cocoa products (33 mg/kg), spices (145 mg/kg) and black tea leaves (899 mg/kg). These authors indicated that in general, the Al content of frequently consumed food increased in the following order: beverages > food of animal origin > food plant origin[17]. López *et al.*[13], analyzed Al in 72 samples of 17 different spices and aromatic herbs. The Al content ranged from 5.20-35.30 mg/kg.

Boron and zinc concentrations in the black foods indicated similar maximum levels, they were determined in the range of 15.08-83.25 and 8.84-96.23 mg/kg, respectively. Boron levels were relatively higher than Zn level of black bean and black tree fungus. Zinc levels were relatively higher than B level of seaweed and black sesame.

Manganese in the black foods was in the range of 7.84-31.58 mg/kg. The highest Mn was determined in black rice, Mn content in the seaweed was not found. Berrylium in the black foods was found as in the range of 2.57 mg/kg (seaweed) and 4.91 mg/kg (black tree fungus), Be concentrations in the black foods indicated similar levels.

For all of the black foods, Ba concentration was not found as high as Fe and it varied between 3.75 mg/kg (fennel) and 26.25 mg/kg (senna tea), Ba content in black sesame was about 4 times the level found in the black rice.

Lead in black bean was the minimum at 6.91 mg/kg while it was the maximum at 9.12 mg/kg in seaweed. As element was not detected in black bean and black sesame. It was found in the other black foods in the range of 0.91-89.28 mg/kg. The highest As was in seaweed whereas the lowest was in black rice. Except for seaweed, Cd content was not observed in the other black foods. Chromium concentration of the black foods was in the range of 1.75-2.17 mg/kg with the highest value of black bean. Except in the seaweed, Cr was not detected in the other black foods. Garcia *et al.*[18], indicated that presence of Cr in spices and aromatic herbs is higher than other foods and beverages. Fuh *et al.*[19], determined Pb, Cd and Cr concentrations in 13 herbs in Taiwan. Average Pb, Cd and Cr concentrations are 28.05, 1.11 and 8.46 mg/kg, respectively. The content of Se in the black foods, which is recognised as being essential for human and animal health elements, varied between 4.17 mg/kg (seaweed) and 15.16 mg/kg (black sesame).

For all the elements, the predominant element was K followed by P, Ca, Mg and Na. The medium content was Al, Fe, B, Zn, Mn, Cu and Ba. It was observed from the test results that all black foods contained significant values of elements presented a wide variability with crop cultivars, soil and climatic conditions of the area, among other factors. Therefore, it is important to study the mineral composition of black foods for each area separately.

On the other hand, all the black foods, which are widely consumed in China, contained both essential and toxic elements in a wide range. Some of them can be used as beneficial sources for Se, P, Zn, B, Mn, Fe, Mg, Ca, Cu, Na and K. At the same time, they may also contain high levels of some toxic elements such as As, Pb, Cd and Al over the standard limited values for medicinal purposes. Therefore, long-term consumption of seaweed should also be of concern for the accumulation of some toxic elements such as Cr, As, Pb and Al in target organs, especially the kidney and liver. It is necessary to study in further detail the toxicity of these black foods contaminated with high levels of some toxic metal ions. Although the daily intakes of these elements from black foods in the present study are below the standard limits and may not constitute a health risk from toxic elements originating from these agricultural products, it is absolutely essential to have good quality control of food raw materials and to determine the presence of some contaminants, especially toxic elements, to avoid overconsumption and their cumulative toxicities in long-term use.

Recovery test of the method: The method of standard addition was considered as a validation method[20]. In order to

demonstrate the validity of present method, a recovery study was carried out. A synthetic black bean sample solution was prepared for the performance of the recovery test. As can be seen in Table-4, the results are considered satisfactory; recoveries being within the range: 95.39-104.93 %.

TABLE-4
RECOVERY OF ALL THE ELEMENTS IN BLACK BEAN

Element	Base value (mg/kg)	Quantity added (mg/kg)	Quantity found (mg/kg)	Recovery (%)	RSD (%)
As	ND	0.5	0.49	98.26	3.12
Se	6.33	5	11.45	102.34	1.58
P	3535.83	200	3745.45	104.81	4.60
Zn	30.08	20	50.13	100.26	1.89
Pb	0.69	0.5	1.17	95.39	2.65
Cd	ND	0.5	0.49	97.65	0.65
Ni	15.16	10	25.12	99.66	1.82
B	74.75	50	124.44	99.37	2.43
Mn	23.83	20	43.88	100.23	0.85
Fe	81.33	50	132.19	101.72	1.04
Cr	2.17	2	4.21	102.20	0.99
Mg	1865	200	2062.52	98.76	1.32
Be	4.41	5	9.33	98.47	0.96
Ca	2553.33	200	2763.19	104.93	3.41
Cu	14.75	10	24.92	101.66	1.78
Al	115.41	100	218.70	103.29	2.22
Ba	9.41	10	19.06	96.54	1.68
Na	299.91	200	505.65	102.87	3.95
K	13725	200	13932.26	103.63	2.88

ND: Not detected.

Conclusion

Elemental contents vary in a wide range in the five black foods, in some cases even by one or two orders of magnitude. This study is to give important reference value to people due to individual differences by adjusting the food to complement the different trace elements. Due to the different bioavailability of minor and trace elements in soil to black foods used for medical purposes concentrations in medicinal herbs available on the market place are very variable, black foods may be contaminated easily during growing and processing. It is important to have a good quality control for black foods in order to protect consumers from contamination.

Based on the results obtained in the present work (Table-3), it can be concluded that the proposed digestion techniques is suitable for the application of microwave assisted extraction for the decomposition and dissolution of black food for trace element determination by ICP-AES. In addition, purposed method is useful for routine control analysis of these products because of its rapidity, sensitivity and versatility.

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