

METAL CONTENTS IN *GLYCINE MAX* (L.) MERR. FROM SEVEN PROVINCES OF CHINA

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Abstract

The black soybean (*Glycine max* (L.) Merr.) native to China contains rich protein, fat and vitamins. A total of 24 trace elements in black bean from Zhejiang, Heilongjiang, Hebei, Inner Mongolia, Henan, Hainan and Fujian provinces of China were determined by ICP-MS and AAS. Black beans were found to contain beneficial trace elements such as K, Mg, Ca, Zn, Fe and Mn for human health. The heavy metal concentration in black beans are much low, which proves that black bean is a safe food. The qualities of black beans from the north provinces are higher than south provinces.

The black soybean (*Glycine max* (L.) Merr.) which originated from northeast of China has been considered as the world's healthiest foods. It contains high protein, fat, vitamin, microelement and thick fibre. The protein content is more than 40% of dry weight (DW) and the composition of indispensable amino acid structure is better than that of soybean (Cong 2008). Fat content of black bean is about 15.9% DW and most of which is unsaturated. Black soybean is rich in microelement such as zinc, copper, magnesium, selenium and phosphorus. It is also rich in vitamin A, vitamin E, riboflavin, melanoma, etc. (Cong 2008).

The nutrient content of agricultural products depends greatly upon agro ecological condition and soil nutrients of the area (Liu *et al.* 2001). In China, the soil types vary in different provinces (Chen *et al.* 2013). So, the objective of the present study was to find nutritional components in black beans from different provinces of China.

Dried seeds of black beans were collected from seven provinces of the People's Republic of China (Table 1). After collection, the beans were rinsed 3 - 5 times with deionized water and dried in an oven to obtain constant weight. The seeds were then crushed to powder with the help of a micro plant sample pulverizer (TEST FZ102, Tianjin of China). The powder was sieved using 100 mesh to facilitate digestion.

Multi element mixed standard samples of Ag, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V and Zn were bought from SPEX of USA (100 mg/l). Internal standards (10 mg/l) In, Pt and Ru were also bought from SPEX of USA. Standard of boron (100 mg/l) was bought from National standard material center. Standard substances of poplar leaves GBW07604 (GSV-3) and tea GBW07605 (GSV-4), nitrate (GR, Jing Rui company of Suzhou), perchloric acid (GR, Shanghai Jinlu Chemical Co. Ltd.), liquid argon (> 99.99%) and purified water (>18 MΩ) were also used.

Parameters of inductively coupled plasma mass spectrometry (ICP-MS) (X-7, Thermo Electron Corporation of USA): Hoisting speed of sample 1.0 ml/min, atomizer cooling temperature 3°C, argon gas pressure 0.6 MPa. The other main parameters of ICP-MS have been presented in Table 2.

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By using an electronic balance (Ohaus AR1140, USA, ± 0.0001 g) 1.0 g of black bean sample was accurately weighed. To it 10 ml of HNO_3 was added and digested on a temperature controlled electric heating plate (Lab Tech, EG35B). PTEF (polytetrafluoroethylene) was carried out at 120°C for 2 hrs by adding 10 ml H_2O_2 , and digesting at 190°C continuously (Graphite cover heating digestion instrument, Lab Tech, EHD36 with glass digestion tube).

Table 1. Geographical location of the seven provinces of PRC from where the samples were collected.

Provinces	Abbreviation	Latitude	Longitude
Zhejiang	(ZJ)	27°12'58"-31°31'13"	118°-123°
Heilongjiang	(HLJ)	43°25'-53°33'	121°10'59"-135°05'
Hebei	(HB)	36°01'58"-42°37'13"	113°04'58"-119°52'01"
Inner Mongolia	(NMG)	37°24'58"-53°23'13"	97°12' 58"-126°04'13"
Henan	(HEN)	31°23'58"-36°22'58"	108°37'13"-111°05'58"
Hainan	(HAN)	18°10'11"-20°10'11"	108°37'13"-111°05'58"
Fujian	(FJ)	23°30'58"-28°22'13"	115°50'58"-120°40'13"

Table 2. Other parameters of ICP-MS.

Item	Parameter	Item	Parameter
Forward power/w	1200.00	Analogue detector/V	2260
Cool /L/min	13.00	PC detector/V	3685
Nebuliser /L/min	0.88	Focus/V	19.60
Auxiliary /L/min	0.75	Horizontal/V	3.00
Sampling depth/mm	25.00	Vertical/mm	311.00

Parameters of Avanta atomic absorption spectrophotometer (GBC Co., Australia) have been presented in Table 3. After digestion 10 ml purified water was added and the liquor changed to yellow or colorless. Heating was continued until a volume of approx. 2 ml reached for removing acids, cooling and setting the volume to 10 ml with purified water for determination.

Table 3. The main parameters of AAS.

Elements	Wave length (λ)/nm	Current intensity (I)/ mA	slit/nm	Fuel/l/min
K	766.5	5	0.5	1.9
Mg	285.2	4	0.5	1.6
Ca	422.7	6	0.5	2.0
Fe	248.3	8	0.2	2.0
Cu	324.7	3	0.5	1.8
Mn	279.5	5	0.4	1.9
Na	589.0	6	0.5	1.6
Zn	213.9	4	0.5	2.0

Concentration of 24 elements present in black beans from 7 provinces of China have been presented in Table 3. The results showed black beans contained many beneficial trace elements for human health, the descending order of trace elements in black beans are $\text{K} > \text{Mg} > \text{Ca} > \text{Zn} > \text{Fe} > \text{Mn} > \text{Ti} > \text{Cu} > \text{Na} > \text{Sr} > \text{Mo} > \text{Ba} > \text{Ni}$, and other elements were all lower than 1.0 mg/kg, especially the contents of heavy metals such as Pb, and Cr were very low than National standard (National Standard of the People's Republic of China 2005).

The descending order of Na concentration in seven provinces is NMG > FJ > HB > HEN > HLJ > ZJ > HAN; Mg: HB > HAN > NMG > HLJ > HEN > FJ > ZJ; K: HAN > HB > HEN > NMG > ZJ > HLJ > FJ; Ca: HLJ > HB > NMG > ZJ > HAN > HEN > FJ; Ti: HAN > HEN > HLJ > HB > ZJ > FJ > NMG; V: ZJ > NMG > HLJ = HEN > HB > HAN > FJ; Cr: ZJ = HAN > NMG > HLJ > HEN > HB > FJ; Mn: HLJ > NMG > HB > FJ > HEN > ZJ > HAN; Fe: HLJ > HEN > FJ > HB > HAN > ZJ > NMG; Co: FJ > HB > NMG = HLJ > HEN > HAN > ZJ; Ni: ZJ > HLJ > HAN > NMG > FJ > HEN > HB; Cu: NMG > HB > HLJ > HEN > HAN > ZJ > FJ; Zn: HLJ > HB > FJ > HEN > NMG > ZJ > HAN; Se: HEN > HAN > NMG > HLJ > HB > FJ > ZJ; Sr: NMG > HLJ > ZJ > HB > HAN > HEN > FJ; Mo: NMG > HB > HEN > HLJ > HAN > ZJ > FJ; Ba: HLJ > ZJ > FJ > HB > NMG > HAN > HEN (Table 4).

Table 4. Contents of 24 kinds of elements in black beans from 7 provinces of China (mg/kg).

Elements	ZJ	HLJ	HB	NMG	HAN	HEN	FJ
Na	8.76	10.1	35.4	51.3	6.02	14.3	44.8
Mg	1955	2268	3142	2517	2541	2227	2164
K	14187	13118	16893	15194	17462	15266	12573
Ca	878	1691	1464	976	656	627	151
Ti	11.5	15.6	15.2	10.0	17.8	15.7	11.0
V	0.042	0.019	0.016	0.021	0.013	0.019	<0.007
Cr	0.11	0.084	0.056	0.086	0.11	0.075	0.042
Mn	19.7	31.0	23.1	24.3	18.0	20.9	22.8
Fe	26.6	67.5	38.7	24.7	37.2	43.5	43.2
Co	0.057	0.14	0.15	0.14	0.085	0.1	0.19
Ni	7.59	5.02	0.53	2.61	4.11	0.67	1.51
Cu	8.87	10.3	13.2	14.0	8.90	10.0	6.34
Zn	36.0	53.7	49.1	36.9	34.1	43.3	48.6
As	0.012	0.013	0.019	0.014	0.015	0.01	0.006
Se	<0.007	0.038	0.032	0.044	0.053	0.062	0.014
Sr	7.07	7.40	4.51	25.4	3.39	2.57	2.42
Mo	0.27	1.39	7.54	18.6	1.10	4.77	0.23
Ag	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Cd	0.0068	0.03	0.037	0.045	0.04	0.026	0.013
Sn	0.015	0.06	0.013	0.021	0.059	0.041	0.048
Sb	0.01	0.0068	0.0067	0.0052	0.0085	0.0069	0.004
Ba	5.53	10.5	2.49	2.39	1.84	1.12	4.94
Tl	0.0035	0.00049	0.0019	0.00047	0.0014	0.00073	0.00073
Pb	0.18	0.16	0.18	0.17	0.18	0.17	0.15

The results obtained in the present research shows that black beans contain many beneficial trace elements such as K, Mg, Ca, Zn, Fe and Mn for human health. Heavy metals in black beans are much lower than National standard, which proved that black bean is a safe food. The quality of black beans from the north provinces are higher than south provinces, especially, black beans from HLJ contains more Ca, Mn, Zn, Fe, Sr and Ba. On the other hand, black beans from HB contains more Mg, K, Ca, Co, Cu, Zn and Mo and from NMG contains more Na, Mn, Cu, Sr and Mo.

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