Assessment of microelements in six varieties of sesame seeds using ICP-MS

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Abstract. Sesame seeds are being used since long time worldwide and particularly in China as a food ingredient. However, insufficient information is available with micro mineral concentrations in different varieties of sesame seeds. The study compared the mineral composition in six varieties of black and white sesame seeds in China. Eleven trace elements (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Mo and Ba) were quantified on inductively coupled plasma-mass spectrometry (ICP-MS) after closed-vessel microwave digestion. In general, average levels of Mn, Fe, Cu, Zn and Ba in selected varieties ranged 1.07-7.40 mg/100 g, based on dry weight of the samples. Nevertheless, V, Cr, Co, Ni, Se and Mo were found at lower concentrations (<0.14 mg/100 g). The average concentrations of Mn, Fe and Zn in black sesame varieties were higher than that of the white varieties. No significant variation was noted for V, Cr, Co, Ni, Cu, Se, Mo and Ba contents between black and white sesame seeds. On the whole, black varieties of sesame exhibited similar levels of investigated elements, which could be helpful to suggest the consumption value of sesame seeds based on mineral contents.

1. Introduction

Sesame is a commonly growing plant species in tropical, subtropical and southern temperate regions of the world, particularly in India, Sudan, China, and Burma, which contribute approximately 60% of the total world production[1]. White varieties of sesame are common in West and Middle East, while the black varieties are popular in the Far East[2]. Sesame seeds are important sources of oil, protein, carbohydrates and ash, which are essential components of human nutrition[3]. Oil extraction and sesame meal are among the major usage of sesame seeds worldwide. Due to high proteins content, sesame seeds are preferably used along with bread, porridge, soup, etc. and in pharmaceuticals as a soap fat and synergist for insecticides[4]. Recently, the photochemical profile, antioxidant and antiproliferation activity of black and white sesame seeds were reported by our group[5,6].

Sesame seed supply many kinds of minerals and this rich assortment of minerals can translates into many medicinal properties. In China, black sesame seeds' paste is considered to be a favorable food for children and as traditional Chinese medical herb against hair loss and flabby limbs weak[7]. The minerals or microelements such as Ca, K, Mg, Na and P in sesame seeds are well recorded in nutrient database of USDA (United States Department of Agriculture, NDN.12023). However, there are limited studies on the comparative assessment of the microelements of white and black sesame seeds grown in China.

Several analytical techniques, such as flame atomic absorption spectrometry (FAAS), inductively
coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS), are available for the quantification of trace elements in food samples[8-10]. Obviously, the determination of microelement concentrations based on modern techniques is necessary to evaluate the nutrition and safety on dietary exposure. The present study was aimed to quantify and compare eleven micro-mineral elements (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Mo and Ba) in black and white sesame varieties using inductively coupled plasma mass spectrometry (ICP-MS).

2. Materials and Methods

2.1. Sample collection and preparation
Six varieties of black and white sesame seeds (*Sesamum indicum* L.) were collected from China and instantly transferred to the laboratory for further processing. Three black sesame varieties Zhenzhou1, Fenheizhi3, 05H27 was abbreviated as B1, B2 and B3 respectively, meanwhile three white sesame varieties Jizhi157, Fenzhi2 and Jizhi1 was abbreviated as W1, W2 and W3 respectively. Samples were dried at 105 °C in a drying cabinet with air-circulation (PH-050A) until a constant weight. About 0.5 g of each sample was added to polytetrafluoroethylene vessel containing digestion mixture (2.5 mL HNO₃ and 1 mL H₂O₂) and was digested in a closed microwave system (Cem-MARS Xpress) following the procedure as: 25 to 140 °C in 15 min then hold for 5 min; 140 to 160 °C in 10 min hold for 35 min; then cool to room temperature. After digestion, the solutions were dilute with ultrapure water to 50 mL and mixed. The blank was also prepared likewise.

2.2. Instrumental analysis
Standards’ stock solutions (V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Se, Mo and Ba, ≥ 99.95%) were purchased from Accustandard, while HNO₃ was obtained from Sigma. Working standards were prepared fresh in 5% of HNO₃ (67% v/v), whereas sample solutions were prepared using analytical grade reagents and ultrapure water (18.2 MΩ·cm) with concentration series of 0.5, 1.0, 3.0, 5.0, 10.0 μg/L. Identification and quantification of micro-minerals in the samples were carried out by ICP-MS spectrometer (Agilent 7500cx, Japan)[11]. The final concentrations were expressed as mean ± SD mg/100 g of the sample on dry weight basis.

2.3. Statistical analysis
Analytical data were processed for statistical analysis using ANOVA and Tukey’s test (SPSS 13.0, Inc., Chicago, IL), and were presented as the mean ± SD for triplicates. Statistical significance was set at p < 0.05. Basic statistical parameters and correlation coefficients were also calculated for metal data.

3. Results and discussion

3.1 Distribution of selected metals in sesame seeds
Measured levels of selected metals in black and white seeded sesame varieties are presented in Fig. 1. In general, the concentration of iron (Fe) metal was the highest, followed by Zn, Cu, Mn and Ba, while the rest of the metals were in less than 0.2 mg/100 g concentration on dry weight basis in all varieties. Black seeded sesame varieties exhibited similar levels for metal content compared to white varieties as a whole. Among black sesame varieties, Zhenzhou1 (B1) exhibited highest concentration of Fe at 8.250±0.43, followed by Mn at 3.467±0.24 and Ba at 2.917±0.18 mg/100 g DW, with a significant difference at p<0.05. Zinc and copper levels were maximum in Fenheizhi3 (B2) at 7.083±0.47 and 2.775±0.224 mg/100 g DW respectively. In the white seeded varieties significant level of Fe metal was calculated in Jizhi1 (W3) at 9.798±0.05 mg/100 g DW, followed by Zn and Cu contents in Fenzhi2 (W2) at 4.891±0.25 and 2.605±0.73 mg/100 g DW, Mn and Ba concentrations in Jizhi1 (W3) at 1.614±0.01 and 1.155±0.01 mg/100 g DW showing significant difference at p<0.05. Measured levels for Cr and V metals were lowest among all varieties of black and white sesame seed.
| Variety | V  | Cr  | Mn  | Fe  | Ni  | Co  | Cu  | Zn  | Se  | Mo  | Ba  |
|---------|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| B1      | 0.008±0.007 | 0.013±0.005 | 3.467±0.240 | 8.250±0.430 | 0.001±0.008 | 1.900±0.270 | 0.050±0.030 | 0.026±0.070 | 0.076±0.080 | 2.937±0.100 | 21.42 |
| B2      | 0.005±0.006 | 0.008±0.004 | 1.720±0.140 | 6.476±0.280 | 0.152±0.010 | 2.015±0.270 | 5.468±0.300 | 0.059±0.014 | 0.145±0.080 | 8.777±0.150 | 16.98 |
| B3      | 0.004±0.006 | 0.008±0.004 | 1.320±0.120 | 5.736±0.120 | 0.139±0.008 | 2.015±0.380 | 4.575±0.080 | 0.056±0.010 | 0.133±0.080 | 8.965±0.017 | 15.26 |
| W1      | 0.004±0.006 | 0.008±0.004 | 1.315±0.010 | 5.230±0.140 | 0.122±0.008 | 2.405±0.370 | 4.365±0.200 | 0.167±0.010 | 0.116±0.010 | 1.104±0.100 | 15.63 |
| W2      | 0.006±0.007 | 0.010±0.009 | 1.973±0.160 | 7.457±0.330 | 0.100±0.009 | 2.775±0.240 | 7.083±0.670 | 0.166±0.010 | 0.091±0.010 | 1.151±0.110 | 19.72 |
| W3      | 0.014±0.008 | 0.015±0.008 | 1.614±0.010 | 9.798±0.050 | 0.147±0.010 | 2.775±0.520 | 5.728±0.130 | 0.050±0.130 | 0.137±0.110 | 2.976±0.390 | 26.55 |

Min 0.004(W2) 0.007(W1) 1.437(W2) 5.323(W2) 0.100(B2) 0.009(B2) 2.185(W1) 4.586(W1) 0.051(W1) 0.137(W1) 0.77(B2) 16.08
Max 0.014(W3) 0.015(W3) 3.467(B1) 9.798(W3) 0.284(B1) 0.031(B1) 2.775(B1) 7.083(B2) 0.011(B1) 0.147(B3) 2.917(B1) 26.55
Mean(b) 0.005 0.010 2.386 7.395 0.179 0.017 2.237 5.728 0.110 1.157 19.66
Mean(w) 0.007 0.010 1.512 6.965 0.143 0.011 2.285 4.721 0.115 0.132 1.074 16.88
Mean 0.006 0.010 1.949 7.180 0.161 0.014 2.281 5.225 0.107 0.136 1.126 18.27

Data are presented as means ± SD, n=3 replicates, mean values with different superscripts in a row are significantly different at P<0.05. Mean(b) represents the mean of three black sesame seed varieties, Mean(w) represents the mean of three white sesame seed varieties.

Fig. 1. Eleven mineral elements in six varieties of sesame seeds (mg/100g, dry weight).

Comparative assessment of the present results with reported levels of metals in sesame varieties by different workers (Table 1), revealed that measured levels of Fe, Cu, Mn, Cr and Mo in sesame varieties were in agreement [12-19]. It has been reported that black sesame varieties contain high contents of Mn and Fe compared to white[15,20], which was in accordance with the average concentration in our findings, however, the contents of Fe in W3 (white sesame) varieties showed the highest value 9.798±0.05 mg/100g in all six varieties. Bhattachary et al. reported that white sesame varieties contain more Fe contents than corresponding black varieties[12]. According to these results, it can be inferred Fe value in black sesame seeds were not higher than that in the white sesame seeds. Zn levels in our study is lower than the report by Obiajunwa et al.[19], but in the same range of those reported by Cao et al.[21]. Such variations might be attributed to the difference in varieties, growth environment, pretreatment and analytical methods used. Alege et al. indicated that majority of the minerals in sesame were respond to soil fertility[16]. According to Bhardwaj et al.[22], planting date would have an influence on the contents of some minerals and reported that earlier planting of sesame resulted in significantly higher contents of Mn, Cu, Zn, and B. However, Se contents in sesame seeds reported by Cao et al.[21] and in nutrient database of the USDA were 100 to1000 times high compared to the present concentrations, which need more investigation.
Table 1. Nine Mineral composition of sesame seeds reported in the literature (mg/100g).

| Cr    | Mn    | Fe    | Ni    | Cu    | Zn    | Se    | Mo    | Ba    | Color | Reference |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----------|
| 0.01-0.02 | 1.41-1.63 | 5.14-9.85 | 0.12-0.16 | 1.69-3.34 | 4.43-5.15 | 0.01-0.02 | 0.11-0.15 | 0.95-1.16 | White | Current work (average value) |
| 0.01 | 1.65-3.71 | 6.19-8.68 | 0.10-0.30 | 1.63-3.01 | 4.15-7.55 | 0.01-0.03 | 0.07-0.15 | 0.69-3.09 | Black |
| ND | 3.53-3.64 | 10.80-10.90 | ND | 2.00-2.08 | 7.90-8.81 | ND | ND | ND | Black [22] |
| ND | 3.30-3.46 | 10.40-11.30 | ND | 2.15-2.20 | 8.60-8.87 | ND | ND | ND | White |
| ND | 1.13-1.73 | 5.63-6.63 | ND | ND | 7.65-7.67 | 0.02 | ND | ND | White [14] |
| 0.01-0.06 | 1.15-2.62 | 6.33-25.43 | ND | 1.51-1.98 | 2.83-3.63 | ND | 0.05-0.14 | ND | NM [17] |
| ND | 2.45 | 5.01 | ND | ND | 7.40 | 0.06 | ND | ND | Black [15] |
| ND | 5.88-5.92 | 6.20-6.22 | ND | ND | 8.77-8.79 | 0.02-0.04 | ND | ND | White |
| 0.08 | 1.62 | 18.60 | ND | 1.74 | 4.55 | 3.87 | ND | 1.47 | Black [21] |
| ND | ND | 10.60 | ND | ND | 3.80 | ND | ND | ND | Black [18] |
| ND | ND | 10.60 | ND | ND | 3.60 | ND | ND | ND | White |
| ND | 7.80 | 12.10 | ND | 4.4 | 16.10 | ND | ND | ND | Black [20] |
| ND | 3.50 | 11.10 | ND | 5.1 | 17.00 | ND | ND | ND | White |
| 0.6-1 | 2.3-3.3 | 9.8-12.0 | 0.3-0.5 | 1.7-2.4 | 6.9-10.8 | ND | ND | ND | NM [19] |

ND: not detected. NM: not mentioned in the reference.

3.2 Health benefits of mineral content in sesame seeds

Minerals contents and particularly the essential metals executed significant contribution in human body for normal function of metabolism, reproductive and immune systems. Fang et al. reported that trace elements and antioxidant enzyme activity are crucial for brain in maintaining normal neurological functions[23]. Though antioxidant activities of black and white sesame seeds and their hull fraction have attracted great attention in recent years[24-26]. However, these studies were mainly focused on phytochemicals profiling, such as vitamins and lignin contents in sesame. The present study was aimed to quantify selected metals in black and white sesame varieties, which would be informative for the nutritional and safety evaluation of different sesame varieties and further development of sesame resources.

Mn, Fe, Cu, Zn and Se are known components of proteins, enzymes and redox systems for humans, deficiency or excessive intake in humans can lead to several disorders or diseases[27-28]. The Recommended Dietary Allowance (RDA) in the U.S. for adults is 8-11 mg/day for Zn, 8-18 mg/day for Fe, 0.9 mg/day for Cu, 1.8-2.3 mg/day for Mn, 0.055 mg/day for Se (Food and Nutrition Board of the Institute of Medicine). The current RDA for children (4–8 year old) is 5 mg/day for Zn, 10 mg/day for Fe, 0.44 mg/day for Cu, 1.5 mg/day for Mn, 0.03 mg/day for Se. The RDA for Ba is not available for the estimated average requirements cannot be developed. One hundred gram black or white sesame seeds can meets nearly 50% Zn, 40% Fe, 250% Cu, 85%-108% Mn and 30% Se for adults according to the suggested RDA. In view of the health safety of the Cu element, no more than 5 g/day sesame seeds are supposed nutritional and beneficial to health for daily consumption.

3.3 Correlation of metal levels in selected sesame seeds

Correlation coefficient was used to analyze similarity in metal levels among the six varieties of black and white sesame as mentioned in Table 2. A highly significant positive associations were noted for:
Fe with V ($r = 0.943$) and Cr ($r = 0.935$), followed by Se with Ni and Co ($r = 0.778$) for each, Mn ($r = 0.736$) and Ba ($r = 0.678$) respectively, and Zn with Cu ($r = 0.666$). Conversely, strong negative correlations were also noted in Mo-Mn ($r = -0.804$), Cu-Ni ($r = -0.761$), Mo-Co ($r = -0.644$) and Cu-Co ($r = -0.592$).

Whether varieties, geographical factors and other factors lead to these findings is not clear. The response of mineral elements in sesame to different environmental conditions such as geography, nutrient source, planting dates is critical to the nutrition and planting of sesame seeds, but is not the scope of the present study.

### Table 2. Correlation coefficient ($r$) matrix of trace elements in six sesame seed varieties.

|     | V  | Cr | Mn  | Fe  | Ni  | Co  | Cu  | Zn  | Se  | Mo  | Ba  |
|-----|----|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| V  | 1.000 |  |  |  |  |  |  |  |  |  |
| Cr | 0.951 | 1.000 |  |  |  |  |  |  |  |  |
| Mn | 0.205 | 0.470 | 1.000 |  |  |  |  |  |  |  |
| Fe | 0.943 | 0.935 | 0.392 | 1.000 |  |  |  |  |  |  |
| Ni | 0.252 | 0.507 | 0.863 | 0.297 | 1.000 |  |  |  |  |  |
| Co | 0.258 | 0.530 | 0.925 | 0.329 | 0.972 | 1.000 |  |  |  |  |
| Cu | -0.234 | -0.366 | -0.398 | -0.174 | -0.761 | -0.592 | 1.000 |  |  |  |  |
| Zn | -0.347 | -0.427 | -0.152 | -0.103 | -0.586 | -0.511 | 0.666 | 1.000 |  |  |  |
| Se | -0.356 | -0.057 | 0.736 | -0.243 | 0.778 | 0.778 | -0.515 | -0.260 | 1.000 |  |  |
| Mo | 0.095 | -0.114 | -0.804 | -0.109 | -0.491 | -0.644 | -0.154 | -0.159 | -0.549 | 1.000 |  |
| Ba | 0.284 | 0.536 | 0.946 | 0.383 | 0.888 | 0.964 | -0.386 | -0.382 | 0.678 | -0.795 | 1.000 |

### 4. Conclusion

In total 11 elements were quantified in six varieties of black and white sesame by ICP-MS techniques combined with microwave assisted acid digestion. Fe, Zn, Mn, Ba and Cu metals were found at high concentrations in all varieties. Black sesame varieties exhibited similar levels of metals compared to white varieties as a whole. Our findings suggested that black sesame varieties *Zhenzhou1* (B1) and *Fenheizhi3* (B2) are excellent sources of essential metals and could be highly significant for consumers having Fe, Zn, Mn and Cu deficiencies. *In vivo* investigation on antioxidant properties bioactivities of essential metals is recommended for further investigation.

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