Letter to the Editor

Determination of Trace Elements in Edible Nuts in the Beijing Market by ICP-MS*

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Nuts have received increased attention from the public in recent years as important sources of some essential elements, and information on the levels of elements in edible nuts is useful to consumers. Determination of the elemental distributions in nuts is not only necessary in evaluating the total dietary intake of the essential elements, but also useful in detecting heavy metal contamination in food. The aim of this study was to determine the mineral contents in edible nuts, and to assess the food safety of nuts in the Beijing market. Levels of Li, Cr, Mn, Co, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Cs, Ba, Pb, Th, and U in 11 types of edible nuts and seeds (macadamia nuts, lotus nuts, pistachios, sunflower seeds, pine nuts, almonds, walnuts, chestnuts, hazelnuts, cashews, and ginkgo nuts) as well as raisins were determined by inductively coupled plasma mass spectrometry (ICP-MS). The accuracy of the method was validated using standard reference materials GBW10014 (cabbage) and GBW10016 (tea). Our results provide useful information for evaluating the levels of trace elements in edible nuts in the Beijing market, will be helpful for improving food safety, and will aid in better protecting consumer interests.

Edible nuts are commonly consumed products around the world since they are rich in important nutrients such as essential minerals, vitamins, proteins, carbohydrates, and unsaturated fatty acids[1-2]. Previous studies have shown that edible nuts have beneficial effects on human health, such as cancer prevention and reduction of risks of type 2 diabetes and coronary heart disease[3-5]. These studies raise the likelihood that their consumption will be recommended as an important component of diets. However, potential negative health effects from toxic elements, as well as transfer of metal contaminants through handling, food processing, and packaging, contribute to the wider issue of general food safety[6].

In the last few years, people have gradually become concerned about essential and trace elements in nuts and seeds, and a number of studies have focused on the contents of trace elements in various types of edible nuts[4-10]. However, there are far fewer reports on trace elements in various types of nuts in China than in other countries. Seventeen different elements were determined in 11 commonly consumed nuts and seeds, as well as in raisins, that were purchased from markets in Beijing in order to investigate the trace elements in edible nuts on the market in China. Several commercially available brands of each nut or seed variety representing the most frequently consumed products in China were selected for this study. Processed, pre-packed nuts/seeds were examined first. Trace element contents in edible nut samples were determined by inductively coupled plasma mass spectrometry (ICP-MS) and microwave digestion methods.

Macadamia nut, lotus nut, pistachio, sunflower seed, pine nut, raisin, almond, walnut, chestnut, hazelnut, cashew, and ginkgo nut samples were collected from supermarkets and retail stores in Beijing. The samples were in sealed packages. These products and types were selected based on popularity. The samples were pulverized into a fine powder, and dried nut products were subsequently homogenized. Three replicate samples each weighing 0.3 g were added to microwave vessel containing 5 mL of HNO_3 (Suprapur, Merck) and 2 mL of H_2O_2 (Suprapur, Merck), and heated in an oven to 205 °C over 15 min, held at that temperature for 5 min, and then cooled over 30 min. The resulting digested mixture was allowed to cool to room temperature, resulting in a clear, colorless solution. After digesting, the solution was transferred to a perfluoroalkoxy (PFA) cup and heated at 150 °C to

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near dryness, and the residue was diluted to 25 mL with ultrapure water (Milli-Q elements) in a plastic volumetric vessel.

A Finnigan sector field high-resolution ICP-MS instrument (Element 2, Thermo Finnigan, Bremen, Germany) was used. Ultrapure water (18.2 MΩ cm) was produced with a Milli-Q system (Millipore, USA). Prior to measurement, ^{115}In and ^{209}Bi (Spex, USA; 10 μg/mL) were added to all solutions as internal standards. All acids used in the chemical analyses were ultrapure grade (HNO_3 65% v/v, Merck) and inspected for possible trace metal contamination.

ICP-MS was performed with a carrier gas flow rate of 0.98 mL/min, auxiliary gas flow rate of 0.8 mL/min, cooling gas flow rate of 16.0 mL/min, and RF power of 1200 W. Before detection, the sensitivity and resolution of the apparatus were tuned using standards offered by Thermo.

Extreme care was taken to avoid contamination in the preparation of the samples and in analytical determination. All of the materials were soaked overnight in 20% HNO_3 (v/v). Then, materials were rinsed with ultrapure water and air-dried with special care before use. A reagent blank was prepared for each digestion to assess possible contamination from the sample preparation.

The evaluated determination procedure was employed to determine the contents of Li, Cr, Mn, Co, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Cs, Ba, Pb, Th, and U in μg/g in the collected samples. Limit of detection is defined as the concentration corresponding to three times the standard deviation of ten blanks. The limit of detection values of the elements in μg/g were 0.0028 for Li, 0.00091 for Cr, 0.013 for Mn, 0.0020 for Co, 0.026 for Cu, 0.044 for Zn, 0.0029 for As, 0.038 for Se, 0.0016 for Rb, 0.0016 for Sr, 0.0023 for Mo, 0.0013 for Cd, 0.00067 for Cs, 0.010 for Ba, 0.011 for Pb, 0.000091 for Th, and 0.00047 for U.

In order to validate the accuracy, reliability, and sensitivity of the determination methods used to evaluate the contents of trace elements, certified reference materials (CRMs) GBW10014 (cabbage) and GBW10016 (tea) were used. The CRMs were purchased from the General Administration of Quality Supervision, Inspection and Quarantine of the PRC, and stored under specified controlled conditions to ensure stability.

The results of the CRMs are shown in Table 1. The obtained results are in good agreement with certified values. For quality control purposes, internal controls and reference materials were tested together with the samples on a daily basis.

Table 1. Certified Reference Materials (GBW10014 cabbage and GBW10016 tea)

Elements	GBW10014 Cabbage		GBW10016 Tea	
	Certified Value (μg/g)	Determined Value (μg/g)	Certified Value (μg/g)	Determined Value (μg/g)
Li	0.54±0.08	0.57±0.04	0.14±0.02	0.139±0.003
Cr	1.8±0.3	1.8±0.5	0.45±0.10	0.43±0.13
Mn	18.7±0.8	17.6±0.8	500±20	460±7
Co	0.089±0.014	0.090±0.01	0.22±0.02	0.21±0.01
Cu	2.7±0.2	2.4±0.5	18.6±0.7	16.7±0.1
Zn	26±2	25.5±1.3	51±2	56±2
As	0.062±0.014	0.059±0.013	0.09±0.01	0.089±0.024
Se	0.2±0.03	0.26±0.04	0.098±0.08	0.12±0.01
Rb	19.6±1.0	20.3±1.5	117±5	107.8±2.8
Sr	48±3	48.1±0.5	9.1±1.2	8.9±0.24
Mo	0.71±0.07	0.69±0.05	0.040±0.012	0.041±0.010
Cd	0.035±0.006	0.035±0.002	0.062±0.004	0.063±0.009
Cs	0.082±0.012	0.080±0.005	0.32±0.06	0.30±0.005
Ba	12±2	12.1±4.3	9.6±0.5	9.2±1.0
Pb	0.19±0.03	0.19±0.05	1.5±0.2	1.47±0.02
Th	0.009±0.003	0.008±0.001	0.038±0.012	0.037±0.015
U	0.02±0.003	0.021±0.006	0.01±0.002	0.0092±0.004

Table 2. Contents of the Trace Elements (μg/g) in the Analyzed Samples (mean±sd)

Elements	Macadamia Nuts	Lotus Nuts	Pistachios	Sunflower Seeds	Pine Nuts	Raisins	Almond Nuts	Walnuts	Chestnuts	Hazelnuts	Cashews	Gingko
Li	0.030±0.030	0.010±0.010	0.040±0.020	0.10±0.020	<LOD	0.19±0.013	0.090±0.10	0.010±0.010	<LOD	0.040±0.050	0.010±0.010	0.030±0.010
Cr	0.090±0.060	0.060±0.090	0.15±0.080	0.20±0.050	<LOD	0.0019±0.0020	0.31±0.38	<LOD	5.6±0.24	0.22±0.020	2.2±2.0	0.31±0.12
Mn	11.6×10±17	36±1.1	6.0±1.2	14±2.0	44±2.9	1.5±0.020	14±4.5	10±0.12	20±3.2	33±9.8	13±5.8	6.3±2.2
Co	0.020±0.010	0.070±0.020	0.010±0.0020	0.060±0.010	0.010±0.0040	<LOD	0.060±0.020	0.020±0.0010	0.060±0.030	0.13±0.060	0.050±0.030	0.030±0.020
Cu	3.2±0.99	7.6±0.69	7.2±2.0	12±1.6	7.1±0.81	2.6±0.17	7.0±1.8	8.8±0.15	4.1±0.97	10±2.5	17±5.3	4.6±0.63
Zn	8.6±1.5	11±0.28	15±3.3	27±3.8	38±8.6	0.91±0.36	24±4.0	20±1.1	9.9±2.7	15±0.82	41±12	12±2.0
As	0.33±0.020	0.060±0.010	0.070±0.14	0.21±0.070	0.15±0.010	0.13±0.010	0.23±0.030	0.12±0.040	0.23±0.090	0.31±0.050	0.31±0.19	0.57±0.060
Se	<LOD	0.49±0.25	0.16±0.16	1.1±0.30	<LOD	<LOD	0.57±0.18	<LOD	<LOD	<LOD	<LOD	1.9±0.31
Rb	16±2.6	40±0.14	8.4±0.11	6.3±0.63	3.5±0.21	1.8±0.080	2.9±0.41	5.6±0.37	6.7±1.1	13±4.3	27±10	7.3±1.2
Sr	2.5±0.31	1.4±0.040	1.8±0.4	2.1±0.28	0.060±0.040	4.3±0.18	6.4±0.040	3.4±0.010	0.96±0.15	5.7±1.5	1.1±0.52	0.87±0.17
Mo	0.11±0.020	0.050±0.00	0.070±0.010	0.23±0.040	0.060±0.010	0.10±0.010	0.11±0.050	0.21±0.00	0.030±0.020	0.010±0.010	0.21±0.080	0.080±0.020
Cd	0.050±0.00	0.17±0.010	0.070±0.010	0.17±0.00	0.13±0.020	0.030±0.00	0.040±0.010	0.020±0.00	0.050±0.00	0.24±0.00	0.040±0.010	0.020±0.00
Cs	0.060±0.0050	0.070±0.0010	0.18±0.0030	0.020±0.0020	0.0025±0.00030	0.0016±0.00050	0.0025±0.0020	0.010±0.00	0.030±0.010	0.11±0.050	0.46±0.26	0.030±0.010
Ba	4.2±0.090	1.1±0.13	0.66±0.27	0.54±0.080	0.20±0.14	0.13±0.0040	4.5±0.92	0.45±0.060	2.2±0.10	2.2±0.64	0.72±0.52	0.97±0.44
Pb	0.18±0.020	<LOD	<LOD	0.040±0.15	<LOD	<LOD	<LOD	<LOD	<LOD	0.17±0.14	<LOD	<LOD
Th	0.0034±0.0024	0.0031±0.00020	0.0021±0.00060	0.0047±0.0021	0.0011±0.00030	0.0025±0.00010	0.00090±0.00020	0.00040±0.00010	0.0013±0.00060	0.0070±0.0076	0.0037±0.0018	0.0021±0.00070
U	0.0020±0.00020	0.0032±0.00060	0.0032±0.00020	0.0051±0.00060	0.0021±0.00020	0.0031±0.00010	0.0020±0.00080	0.0015±0.00040	0.0036±0.00060	0.0023±0.00010	0.0027±0.0017	0.0038±0.00080

Note. <LOD=below the limit of detection.

The amounts of trace elements in the different samples are displayed in the Table 2. The contents of the trace elements Li, Cr, Mn, Co, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Cs, Ba, Pb, Th, and U were determined. Previously reported values are shown in Table 3.

Toxic elements are significant contaminants in food. The conventionally adopted toxic metals for human studies are Pb, Cd, and As.

Lead is one of the representative metals whose levels in the environment represent a reliable index of environmental pollution[11]. The World Health Organization (WHO) states that the maximum permissible level of lead in raw plant materials is 10.0 mg/kg[12]. In our study, very little or no Pb was detected in most of the 12 analyzed samples. The standard limit for Pb in nuts in China is 0.2 mg/kg[13]. The Pb contents of these 12 analyzed samples were below the limit.

The contents of As determined in the 12 samples (Table 2) ranged from 0.060 μg/g in lotus nuts to 0.57 μg/g in ginkgo nuts. Arsenic can cause gastrointestinal tract injuries and cardiac function disorders, and is a carcinogen[14]. The U. S. Food and Drug Administration (FDA) limit for As in fruits and vegetables is 1.4 μg/g[4]. The standard limit for As in corn and vegetables in China is 0.5 mg/kg[13]. Most foods contain less than 1.0 μg/g[4] and our experimental As values were in agreement with this value.

According to toxicity studies, cadmium is a toxic element. Cadmium accumulates in the kidneys, spleen, and liver. Blood serum levels increase following mushroom consumption[15]. The WHO states that the maximum permissible level of cadmium in raw plant materials is 0.30 mg/kg[12]. The contents of Cd in this study were 0.020-0.24 μg/g. The detected concentration range of Cd was similar to that in a previous study[6].

Uranium and thorium are long-lived natural radioactive elements that are widely present in soil and rocks. Their radioactive decay products, such as radium and radon, in minerals raise more concerns for human health[16-18]. In our study, the contents of Th and U were 0.00040-0.0070 and 0.0015-0.0051 μg/g, respectively, which were slightly higher than the previously reported values. The standard limits for Th and U in potatoes in China are 0.4 and 0.64 mg/kg[19], respectively. The values from these 12 analyzed samples were below the limits.

Some of the essential trace elements are Cr, Cu, Mn, Mo, Co, Sr, Se, and Zn, which serve as co-factors for many physiological and metabolic functions. The FDA has established reference daily intakes (RDIs) of the essential elements for human nutrition, which were 120 μg for chromium, 2 mg for copper, 2 mg for manganese, 75 μg for molybdenum, 70 μg for selenium, and 15 mg for zinc per day[20]. In our study, the concentrations of Cu, Mn, Mo, Co, Sr, Se, and Zn

Table 3. Previously Reported Literature Data (μg/g)

Element	Brazil	South Africa	Sweden	Spain and Portugal
Zn	2.2-54	38.46-137.86	18-78	25-113
Mn	<0.010-123	3.40-192.6	11-93	26-559
Rb	-	-	3.1-17	-
Cu	<0.015-21.8	18.96-59.44	8.5-16	8-41
Sr	ND-69	-	0.11-2.6	-
Ba	<0.029-1990	-	0.008-15	-
Mo	-	-	0.036-4.2	-
Co	-	-	0.0031-0.056	-
Se	0.10-35.1	ND-36.1	0.0036-0.26	-
Cs	-	-	0.0058-0.044	-
Cd	-	-	0.0047-0.29	-
Pb	-	-	0.00092-0.0079	-
Cr	-	0.94-2.02	0.0039-0.015	-
Li	-	-	0.0018-0.016	-
As	-	0.013-0.024	0.00095-0.014	-
U	-	-	0.00007-0.0027	-
Th	-	-	0.00004-0.0011	-
Ref.	[7-9]	[4]	[6]	[10]

were in ranges similar to those in Swedish nuts. The highest Cr content of 5.6 μg/g was found in chestnuts, which was higher than that in nuts from Sweden but closer to the content in nuts from South Africa. Cr deficiency disrupts metabolism, while an excess of Cr may be toxic[3]. The content of Se ranged from below the limit of detection to 1.9 μg/g in our which was far below that in nuts from Brazil[7-9]. Selenium is classified as an essential element; an intake of <50 μg/d is considered to represent a deficiency, while a Se intake of 50-400 μg/d is the safe range for adults. An acceptable threshold for Se toxicity may be 850-900 μg/d[7].

Barium is a non-essential element for humans. Acute barium poisoning leads to reduced blood pressure, serious heart rate disorders, and cerebral hemorrhaging, eventually leading to death[21]. In our present study, the highest content of Ba (4.5 μg/g) was found in almonds, whereas the lowest content of Ba (0.13 μg/g) was observed in raisins. The contents of Ba in our study were in a similar range to that in Swedish nuts and lower than that in nuts from Brazil[6-7].

There have been a few studies in which the Li, Rb, and Cs contents in nuts were measured. In our experiment, the contents of Li, Rb, and Cs were <0.0028 (limit of detection) to 0.10 μg/g, 1.8-40 μg/g, and 0.0016-0.46 μg/g, respectively. The contents of Li, Rb, and Cs were slightly higher than in Swedish nuts[6].

The worldwide consumption of nuts is increasing as more people recognize that they are rich in important nutrients. In spite of this popularity, the availability of reliable information about the elemental contents of these foods remains rather limited except for a few major inorganic constituents. In this study, contents of Li, Cr, Mn, Co, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Cs, Ba, Pb, Th, and U in edible nuts and seeds such as macadamia nuts, lotus nuts, pistachios, sunflower seeds, pine nuts, almonds, walnuts, chestnuts, hazelnuts, cashews, and ginkgo nuts, as well as raisins, were measured by ICP-MS, which was demonstrated to be a suitable, sensitive, and rapid technique for measuring multiple elements simultaneously.

Heavy metal contamination in food may come from food processing and packaging; therefore, monitoring the nuts in the market is as important as monitoring raw nuts. The samples were collected from supermarkets and retail stores in Beijing for this study. Our results indicate that the content of toxic metal Pb did not exceed the standard limit for Pb in nuts in China, and Cd and As contents in edible nuts were in agreement with reported values. Our data also provide useful information for evaluating the levels of other trace elements such as Li, Cr, Mn, Co, Cu, Zn, Se, Rb, Sr, Mo, Cs, Ba, Th, and U in edible nuts. Monitoring the levels of trace elements in edible nuts in the market will be helpful for improving food safety and better protecting the interests of consumers.

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