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Trace elements in Taiwanese health food, *Angelica keiskei*, and other products

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Abstract

Epithermal and instrumental neutron activation analysis (ENAA & INAA) revealed the presence of more than a dozen elements in fresh leaves, and stems of the Taiwanese health food product, "*Angelica keiskei* AK". AK was sampled from five main planted areas in central Taiwan to ensure diversity. This research employed ENAA to identify Al, As, Br, Cl, I, K, Mg, Mn, Na, Sb, and Sm and INAA to identify Cr, Fe, Rb, Sc, and Zn. Some of these elements are classified as either toxic or essential to humans. The elemental concentrations mentioned above were found to vary from 10^4 to 10^{-2} μg/g, among different planted areas. A quantified index of agreement (AT) was introduced to help to classify the elements. A smaller AT indicated a close consistency of the specific trace element in the AK, while a bigger AT indicated a larger fluctuation, or less agreement. The different ATs in various fresh leaves and stems were considered and the values closely matched previously published data.

Keywords: *Angelica keiskei*; Elemental concentration

1. Introduction

"*Angelica keiskei* AK", a health food, originated in Japan (Umbelliferae, "Ashita-Ba" in Japanese), and it has been widely planted at Puli and Lalashan in Taiwan over the past 20 years (Liu, Liu & Chu, 1992). This plant has been recognized as naturally aromatic and a medicinally important traditional Chinese herb (Okuyama et al., 1991). This herb is used as a diuretic, analeptic, and lactagogue and has been recommended, cultivated, and propagated by the Taiwan Agricultural Research Institute (TARI) (Chen, 1995; Fujita et al., 1992; Liu et al., 1992; Inamori, Baba, Tsujibo, Taniguchi, Nakata & Kozawa, 1991; Okuyama et al., 1991). Fresh leaves and stems are stir-fried, like celery, or eaten as salad in many restaurants and consumed as a raw vegetable, because of their perceived medical properties. Old roots and stems are used to produce tea bags, capsules and health-care products such as *Angelica sinensis*. AK is also included in various traditional Chinese herb mixtures and "secret recipes". It is also added to tea bags and capsules (Yunming tea company, 1999). The vegetable is planted mainly in cool and humid climates at altitudes of 400–1200 meters above sea level at five farms: Chuchi, Lalashan, Minder, Puli, and Taian, all in central Taiwan. (Liu et al., 1992). Each planted areas cover almost 50 acres (Liu et al., 1992). The elements in AK are considered to promote human health and have been extensively studied in recent years. Fujita et al. (1992) have already studied the growth of this plant in Japan as also have Inamori et al. (1991), Okuyama et al. (1991), Murakami et al. (1990), and Kozawa, Morita, Baba, and Hata (1978), but few studies have been directed to elemental analyses of Taiwanese AK. The elemental concentrations in this health food are very interesting. ENAA and INAA are effective techniques for identifying most of the interesting trace elements and are reliable multi-element analytical methods which do not involve pretreatment before irradiation (Chen & ChangLai, 2001; Chen & Pan, 2001; Wei & Chung, 1997; Wang, Duo, Chang, & Yang, 1996; Ibrahim, 1995; Ibrahim, 1994,1987; Wang, Ke, & Yang, 1993). Finally, the index of agreement (AT) was evaluated for comparing the consistency of fresh leaves and stems taken from each planted area.

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2. Materials and methods

2.1. Material

Raw AK, approximately 5 kg of fresh leaves and stems, and 1 kg of other products such as tea bags and capsules, were taken simultaneously from the five planted areas during the winter and spring harvests to ensure diversity, as endorsed by TARI in Taiwan. The collected fresh leaves and stems were first washed with distilled water and then homogenized with a Polytron Homogenizer. They were then carefully freeze-dried before analysis as published elsewhere (Wei & Chung, 1997). Freeze-dried AK tissues were powdered in an all-teflon cylindrical mill and sieved through a 0.9×0.8 mm sieve (Wei & Chung, 1997). Tea bags and capsules were dried materials, and used in their original forms after they were purchased from the five planted areas. Lichen (IAEA-336) was selected as the irradiation standard, and carefully weighed into clean polyethylene (PE) bottles. Samples were dried in an oven at 50 °C to constant weight, and then stored in an electron desiccator (Ibrahim, 1987).

2.2. Experimental methods

2.2.1. Preparation of activated samples

350±10 mg of lichen and AK were weighed for ENAA and 150±10 mg were weighed for INAA. A weighed sample was packed into a 3×3 cm^2 PE bag and then doubly sealed in another PE bag. It was placed in the vertical tube (VT) for long irradiation and pneumatic tube (PT) for short irradiation in the open pool Reactor of Tsing Hua University, as stated in Table 1 (Chen & ChangLai, 2001; Chen & Pan 2001; Wei & Chung, 1997; Wang et al., 1996; Wang et al., 1993). An identical empty PE bag was taken as a blank correction, also double-sealed. Each sample and standard was prepared in triplicate to minimize the statistical uncertainty, as explained elsewhere (Chen & ChangLai, 2001; Chen & Pan 2001; Wei & Chung, 1997). Each irradiated sample was paired with a 10 mg Ni-foil monitor, used to record fluctuations in the neutron flux (Chen & Pan, 2001).

2.2.2. Irradiation filters and irradiation schemes

A large boron-polyethylene (BPE) flexible shield cylinder container with dimensions, 164 mm H × 44 mm D with a 3.2 mm thick wall, (Flex/Boron, Reactor Experiments, UK) and a small cadmium cylinder container with dimensions, 40 mm H × 25 mm D with a 1 mm thick wall were used to screen thermal neutrons. Three irradiation schemes were used: (a) short irradiation ($t_i = 10$ min) when wrapped in a Cd filter in the PT; (b) long irradiation ($t_i = 24$ h) when wrapped in a BPE filter in the VT; (c) long irradiation ($t_i = 24$ h) without any wrapping in the PT. Table 1 details all of the irradiation schemes and decay properties of the nuclides of interest (Chen & Pan, 2001; Knoll, 1989; Shirley & Lederer, 1978).

2.2.3. Counting and analysis

The γ-ray spectra were measured using a calibrated HPGe detector with 15% relative efficiency. The counting system provided an energy resolution of 2.5 keV at 1333.2 keV for ^{60}Co. γ-ray spectra were analyzed using Micro SAMPO90 software on a personal computer connected to a System-100 multichannel analyzer board for spectral acquisition (Chen & Pan, 2001). The statistical errors of each of these counting values did not exceed 15% and dead times were maintained below 10% (Chen & Pan, 2001; Wei & Chung, 1997).

2.2.4. Elemental concentrations

The method of comparison is used to determine the concentrations of each element (Ibrahim, 1994). If C_{std} are elemental concentrations of lichen, then the elemental concentrations of the unknown sample C_{sample} are given by,

$$\frac{C_{sample}}{C_{std}} = \frac{R_{sample}/W_{sample}}{R_{std}/W_{std}} \times f$$

where R_{sample} and R_{std} are the activities of unknown samples and standards; W_{sample} and W_{std} are the masses of unknown samples and standards; and f is the conversion factor of the neutron flux fluctuation (Chen & Pan, 2001).

3. Results and discussion

3.1. General

Figs. 1(a) and (b) present the elemental concentrations, obtained using the ENAA and INAA techniques, of freeze-dried AK taken in tea bags and capsules from five planted areas. The prime sources of systematic error in this Figure were primarily from counting geometries. These were minimized through experimental design, by ensuring identical conditions for both standard and samples (Ibrahim, 1994). Among these elements, only Rb is present in the capsule, as shown in Fig 1a. Otherwise, Rb concentrations in tea bags, fresh leaves and stems, sampled in various different planted areas, cannot be determined due to their being present in low concentrations.

3.2. Capsules and tea bags

Capsules are generally made of old roots, and tea bags are made of old stems and leaves (Yunming tea company, 1999; Liu et al., 1992). The quantities of 16 elements were analyzed, using the γ-ray spectra, as shown in Fig. 1(a) and (b). The Al concentration is the

Table 1
Experimental parameters and irradiation positions for ENAA and INAA in this work (the ^{65}Ni flux monitors are used for neutron fluence measurement)

Neutron shield	Irradiation position	Element	Nuclear reaction	Half-lives[a]	γ-Ray energy (keV)
ENAA					
Cd	PT[b]	Al	^{27}Al (n, γ) ^{28}Al	2.24 m	1778.8
BPE	VT[c]	As	^{75}As (n, γ) ^{76}As	26.32 h	559.2
Cd	PT[b]	Br	^{79}Br (n, γ) ^{80}Br	16.7 m	616.7
Cd	PT[b]	Cl	^{37}Cl (n, γ) ^{38}Cl	37.2 m	1642.7
Cd	PT[b]	I	^{127}I (n, γ) ^{128}I	24.99 m	442.9
Cd	PT[b]	K	^{41}K (n, γ) ^{42}K	12.36 h	1524.7
Cd	PT[b]	Mg	^{26}Mg (n, γ) ^{27}Mg	9.46 m	843.8
Cd	PT[b]	Mn	^{55}Mn (n, γ) ^{56}Mn	2.58 h	846.6
Cd	PT[b]	Na	^{23}Na (n, γ) ^{24}Na	15.0 h	1368.6
BPE	VT[c]	Sb	^{121}Sb (n, γ) ^{122}Sb	2.70 d	564.1
BPE	VT[c]	Sm	^{152}Sm (n, γ) ^{153}Sm	46.7 d	103.2
INAA					
None	VT[d]	Cr	^{50}Cr (n, γ) ^{51}Cr	27.8 d	320.0
None	VT[d]	Fe	^{58}Fe (n, γ) ^{59}Fe	44.6 d	1099.2
None	VT[d]	Rb	^{85}Rb (n, γ) ^{86}Rb	18.7 d	1076.6
None	VT[d]	Sc	^{45}Sc (n, γ) ^{46}Sc	83.8 d	889.2
None	VT[d]	Zn	^{64}Zn (n, γ) ^{65}Zn	244.4 d	1115.5
None		Ni	^{64}Ni (n, γ) ^{65}Ni	2.52 h	1481.8

[a] m, minutes; h, hours; d, days.
[b] Epithermal neutron flux 1.4×10^{11} n cm^{-2}s^{-1}; Irradiation time: 10 miFdecay time: 10 miFCounting time: 5 m.
[c] Epithermal neutron flux 1.1×10^{11} n cm^{-2}s^{-1} ; Irradiation time: 24 hiFdecay time: 1-2 diFCounting time: 20 m.
[d] Neutron flux 2×10^{12} n cm^{-2}s^{-1} ; Irradiation time: 24 hiFdecay time: 30-45 diFCounting time: 2 h.

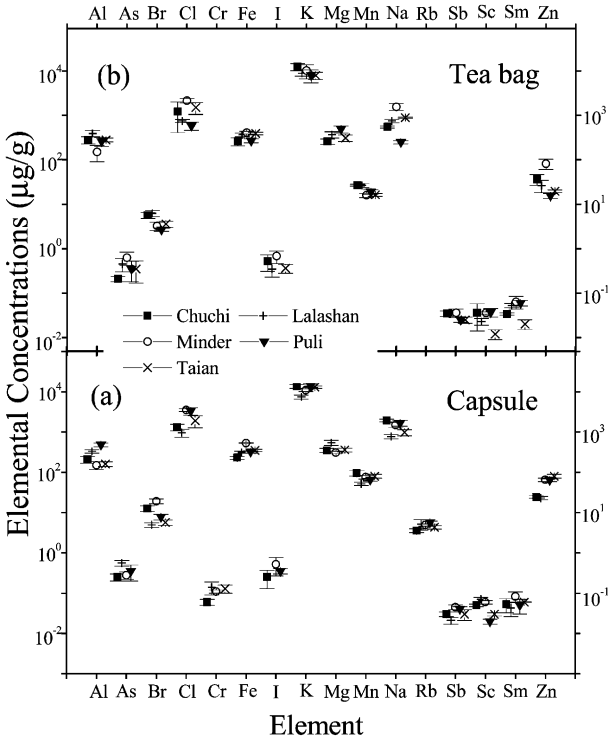

Fig. 1. (a,b). Elemental concentrations of capsules and tea bags in the five planted areas.

highest, in both capsules and tea bags, ranging from 0.74 to 1.72%.

Magnesium and iodine were the first elements to be detected at a level as low as 0.1 μg/g in the capsules. Mertz (1981) demonstrated that iodine is the active component of the thyroid hormones, triiodothyronine and thyroxin. Arsenic was also found in the capsules and tea bags at levels of almost 0.1 μg/g. Concentrations of iron and zinc ranged from 20 to 500 μg/g. Additionally, the elemental concentrations of iron in capsules and zinc in tea bags were found to be higher in Minder than in any other planted area. Arsenic is classified as a toxic element and iron and zinc are essential for human beings (Tanner & Friedman, 1977). Tea bags have the same proportions of AK in the five planted areas but contain different ingredients (Yunming tea company, 1999). The elemental contents in the tea bags have agreed closely with "drinking tea" in the public data of Wang et al. (1993), but the zinc concentration in AK teabags exceeded that in drinking tea, and was four times that of Oolong tea (Wang et al., 1993).

3.3. Fresh leaves and stems

Fifteen elements were present in the analyzed samples at widely differing concentrations, ranging from 10^4 to

10^{-2} μg/g among the various planted areas. The TARI has also been cultivating and propagating this health food over 20 years (Chen, 1995; Liu et al., 1992) in central Taiwan. The number of consumers is continuously increasingly (Liu et al., 1992). Therefore, classifying these elements revealed strong consistency among the concentrations of the trace elements which is interesting and is discussed below.

3.4. Index of agreement for fresh leaves and stems

3.4.1. General

Fresh leaves and stems of Taiwanese AK were purchased from five planted areas. Three samples were obtained from each area. The vegetables were distributed throughout the island and eaten as celery by the general public in restaurants. Table 2 shows a total of 15 elements, analyzed in the fresh leaves and stems. The elemental concentrations are expressed in μg/g, unless otherwise stated (dry weight). The last two columns in the Table present the averaged values ($\bar{x}$) with one standard deviation (σ) over the five planted areas, and the quantified index of agreement (AT, $AT = 100\% \times \sigma/\bar{x}$) (Bevington, 1992; Chen & Pan, 2001). A bigger AT value indicates a larger fluctuation of the specific trace element in AK, or less agreement, because 68% of the total samples fall within one standard deviation of the mean concentrations (Bevington, 1992; Chen & Pan, 2001). Fig. 2 plots the ATs of each element. The ATs can be approximately categorized into three groups:

Group 1: AT < 30; Group 2: 30 < AT < 60; and Group 3 AT > 60. Thus, the trace elements Al, As, Cr, Fe, and Sb are in Group 1; Br, I, K, Mg, Mn, Na, Sc, Sm and Zn are in Group 2; while Cl is in Group 3. However, As, Cr (Group 1) and Mg (Group 2) are treated as Group 3 trace elements because their concentrations are below the minimum detectable concentration in the planted area, causing significant discrepancy between planted areas.

3.4.2. $AT < 30$

The fluctuations of various trace elemental concentrations in Group 1: AT < 30 are less than those in the other groups, including Al, Fe, Sb. The Fe concentration at Puli was higher than in other planted areas and about 1.36 times more than that in Taian. Moreover, it ranges from 280 to 380 μg/g.

3.4.3. $30 < AT < 60$

The variations in the concentrations of the trace elements in Group 2: 30 < AT < 60 exceed those in Group 1. Fig. 2 shows the agreements of Br, I, K, Mn, Na, Sc, Sm, and Zn in this Group. For example, the Zn concentrations ranged from 67 in Puli to 28 μg/g in Minder and those of Mn ranged from 83 in Lalashan to only 33 μg/g in Taian. Finally, the maximum concentration of Br was 17.1 μg/g in Puli.

3.4.4. $AT > 60$

Concentrations of trace elements in Group 3: AT > 60 fluctuate extremely; Cl concentrations range from 0.09% in Puli to 0.51% in Taian. The concentration of arsenic in Lalashan is 0.49 μg/g, but is negligible in Minder and Puli. Determination of whether the toxic elemental contents in this vegetable may be considered a health risk, particularly to children, is crucial. The Cr concentration cannot be determined neither in Minder or Taian, but Cr concentration is

Table 2
Elemental concentrations of fresh leaves and stems (units μg/g or as otherwise stated, dry weight) for five planted areas of *Angelica keiskei*[a]

Element	Planted area						
	Chuchi	Lalashan	Minder	Puli	Taian	Mean value $\bar{x} \pm \sigma$	Agreement
Al	136±10	126±19	107±21	129±29	165±20	133±21	15.9
As	0.28±0.07	0.49±0.10	<MDC	<MDC	0.33±0.07	0.37±0.11	29.9
Br	6.50±1.05	5.70±0.35	9.51±0.45	17.1±1.2	6.56±0.28	9.07±4.72	52.0
Cl(%)	0.23±0.03	0.35±0.07	0.17±0.03	0.09±0.04	0.51±0.23	0.27±0.16	60.9
Cr	0.10±0.03	0.19±0.01	<MDC	0.13±0.03	<MDC	0.14±0.04	27.5
Fe	300±68	360±40	310±80	380±140	280±70	326±42	12.9
I	0.37±0.07	0.35±0.07	0.82±0.17	0.67±0.19	0.30±0.04	0.42±0.17	39.7
K(%)	1.25±0.32	1.01±0.29	1.25±0.32	2.24±0.80	1.19±0.24	1.39±0.49	35.0
Mg	<MDC	<MDC	250±90	<MDC	130±10	190±85	44.7
Mn	50±6	83±25	37±7	63±10	33±12	53.2±20.4	38.4
Na(%)	0.069±0.006	0.140±0.044	0.075±0.004	0.168±0.016	0.163±0.045	0.123±0.048	38.9
Sb	0.039±0.003	0.035±0.004	0.046±0.007	0.025±0.001	0.026±0.005	0.034±0.009	25.9
Sc	0.012±0.001	0.013±0.001	0.014±0.001	0.021±0.014	0.038±0.013	0.020±0.011	55.5
Sm	0.018±0.005	0.030±0.007	0.011±0.008	0.014±0.003	0.016±0.010	0.018±0.007	41.0
Zn	44±3	40±3	28±9	67±12	33±10	42.4±15.1	35.6

[a] Values represent means±SD of 15 samples (five planted areas and three samples per area).

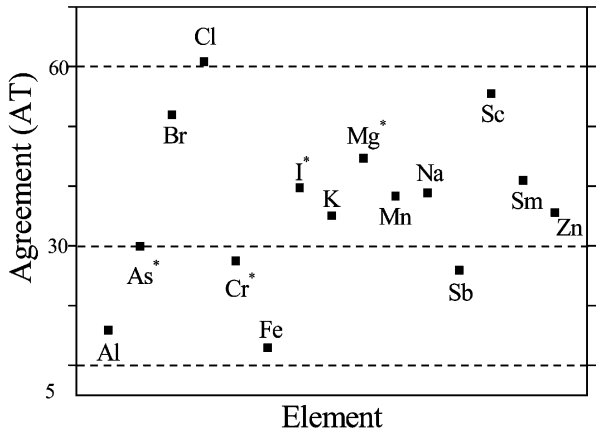

Fig. 2. Agreement (AT) of various trace elements of fresh leaves and stems verified in this study.

consistent with that in other planted areas (The AT of Cr is 27.5).

Experimental results for As, Mn, Fe, and Zn agree closely with the reported values presented in Table 2, but the Zn concentrations in the fresh leaves and stems exceed those in *Angelica sinensis* (Wang et al., 1996), revealing that the accuracy of nuclide measurements based on the ENAA and INAA techniques is satisfactory.

4. Conclusion

AK is consumed, both as a health food and a traditional medicinal herb, and is used as a diuretic, analeptic, and lactagogue in Taiwan. The presence of 16 trace elements, Al, As, Br, Cl, Cr, Fe, I, K, Mg, Mn, Na, Rb, Sb, Sc, Sm, and Zn, in the investigated AK reveals their importance in the medical treatment of the Taiwanese. The ranges of elemental concentrations were found to vary from 10^4 to 10^{-2} μg/g among fresh leaves, stems, tea bags and capsules. Zinc concentrations in the tea bags exceeded those in the drinking teas. Mg and I were the first elements to be detected. AT was used to help classify these elements. Herein, the concentrations of Al, Fe, and Sb showed the smallest AT, because they have similar concentrations in each planted area. Those of As, Cl, Cr, and Mg exhibited the greatest discrepancy in both the fresh leaves and the stems among the five planted areas. The experimental results demonstrate that the ENAA method can be applied successfully to analyze trace elements of Al, As, Br, Cl, I, K, Mg, Mn, Na, Sb, and Sm.

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