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A pilot study to measure levels of selected elements in Thai foods by instrumental neutron activation analysis

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Abstract A pilot study was carried out to evaluate the scope of instrumental neutron activation analysis (INAA) for measuring the levels of selected elements in a few commonly consumed food items in Thailand. Several varieties of rice, beans, aquatic food items, vegetables and soybean products were bought from major distribution centers in Bangkok, Thailand. Samples were prepared according to the protocols prescribed by the nutritionist for food compositional analysis. Levels of As, Br, Ca, Cd, Cl, Cr, Cu, Fe, K, Mg, Mn, and Zn were measured by INAA using the irradiation and counting facilities available at the Thai Research Reactor with the maximum in-core thermal neutron flux of 3×10^{13} cm^{-2} s^{-1} of the Thailand Institute of Nuclear Technology in Bangkok. Selenium was determined by cyclic INAA using the Dalhousie University SLOWPOKE-2 Reactor facilities in Halifax, Canada at a thermal neutron flux of 2.5×10^{11} cm^{-2} s^{-1}. Both cooked and uncooked foods were analyzed. The elemental composition of food products was found to depend significantly on the raw material as well as the preparation technique.

Keywords INAA · Cyclic INAA · Thai food · Nutrition · Toxic elements

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Introduction

Measurement of concentrations of toxic elements and nutrient minerals in food is important for human health. Some elements like Fe, Cu, Zn, and Mn are necessary where as As and Cd are toxic. Moreover, the essential elements like Cu and Se can have toxic effects at high levels. Elements in food may occur naturally or be introduced by human activities such as preservatives, packaging and cooking. Many countries have established regulations on the maximum permissible levels of toxic elements in food items and minimum daily intake of nutritionally important elements for life and growth.

For these reasons, various analytical techniques have been applied to food analysis. Some of the more commonly used techniques are atomic absorption spectrometry [1], graphite furnace atomic absorption spectrometry [2], inductively-coupled plasma mass spectrometry [3], and inductively-coupled plasma optical emission spectrometry [4].

Neutron activation analysis (NAA) is an effective technique for the simultaneous analysis of major, minor and trace elements which play an important role in human health. Thus the INAA technique was chosen for the pilot study for the determination of some selected elements in Thai food. Only one particular element, namely Se which usually occurs in food at ultralow levels, was analyzed by CINAA.

In this work a pilot, prelude to a comprehensive, study recently initiated to determine the major, minor and trace element content of Thai food items for the purpose of updating the food composition table of Thailand is presented. Concentrations of As, Br, Ca, Cd, Cl, Cr, Cu, Fe, K, Mg, Mn, Se and Zn were measured by two types of NAA in raw as well as cooked food items, namely rice, bean, aquatic animal, vegetable, soybean and soybean products, commonly consumed by Thai people.

Experimental

Five selected food categories in this study comprised of varieties of rice, bean, soybean products, vegetables and aquatic animals. These food items were collected from local markets in Bangkok, Thailand using the protocols recommended by the nutritionist for food compositional analysis reported elsewhere [5].

Rice and bean samples chosen consisted of local varieties commonly consumed by Thai people. In Asian countries, soybean is recognized as one of the protein-rich food items available widely at a low cost. Several types of soybean product were prepared for normal consumption. To demonstrate the impact of human activities in food processing to the elemental concentrations in food, soybean products were chosen as an example. These are various types of tofu as well as soy protein shown in Table 1. Since most Thai people usually consume cooked vegetables on a daily basis, we also cooked vegetables and analyzed them in the study.

Aquatic food comprised of both marine and fresh water type. Cooked shrimp, prawn, mollusk and fish commonly found in local market were selected for this study. After collection and preliminary preparation, these samples were cleaned with tap water followed by deionized water, and then freeze dried, powdered and kept in a cool dry place until analysis. Details of the food preparation also followed the protocol recommended by the nutritionist for food compositional analysis [5]. Description of samples in each food category is presented in Table 1.

For the determination of As, Br, Ca, Cd, Cl, Cr, Cu, Fe, I, K, Mg, Mn, and Zn by INAA, the samples in dry powder form were irradiated at the TRIGA type research reactor, TRR1/M1, in the Thailand Institute of Nuclear Technology, Bangkok, Thailand with a maximum in-core thermal neutron flux of 3×10^{13} cm^{-2} s^{-1}. Depending on the half-lives of the neutron activation products, food samples were irradiated for 25 s (short), 12 h (medium) and 36 h (long) followed by gamma-ray spectrometry of suitable radionuclides. Details of method validation, samples preparation as well as irradiation and gamma-ray counting are described in our earlier work [5, 6]. The radionuclides used in this study are presented in Table 2. The concentration of each element was obtained using various certified reference

Table 1 Description of samples analyzed in 5 selected food categories

Sample category	Food items	Sample category	Food items
Rice	Brown jasmine rice	Bean	Black-eyed bean
	White jasmine rice		Green bean
	White glutinous rice		Red bean
	Black glutinous rice		Red kidney bean
	Black-sapphire jasmine rice		Soybean
	Pink jasmine rice		Peanut
Soybean product	Tofu, white, soft-type, packed in box		Egg tofu, soft, packed in pouch
	Tofu, white, firm-type, packed in box		Tofu, dried, deep fried
	Tofu, white, soft, packed in pouch		Soy protein
Aquatic animals		Vegetable	
Marine	Shrimp, salted, dried	Seeds, pod and fruit	Chilli pepper, roasted
	Shrimp, banana, boiled		Lady’s finger, young pods, boiled
	Prawn, giant tiger, boiled		Horse-radish, young pods, boiled
	Blue spot gray mullet, boiled		Gourd/cucumber, bitter, Thai variety
	Giant sea perch, boiled		Parkia speciosa, seeds
	Cockle/ark shell, blanched		
	Oyster, Pacific, blanched		
	Mussel, green, steamed		
Fresh water	Clam, undulated surf, stir-fried	Leaves and tender tips	Classia, leaves and tender tips, boiled
	Prawn, Lanchester’s freshwater, raw	Flower	Indian mulberry, leaves, steamed
	Striped snake-head fish, steamed		Sesbania/Cork wood, young leaves, boiled
	Red Tilapia (Tabtim), boiled		Horse-tamarind, tender tips
	Snail, pond/river, boiled		Cowslip creeper, flowers, blanched
			Cabbage, Chinese/
			Flowering white cabbage, flower
			Cauliflower

Table 2 Nuclear parameters of the elements of interest

Element	Radionuclide	Half-life	γ-Ray used (keV)
As	^{76}As	26.3 h	559.1
Br	^{82}Br	1.47 days	776.5
Ca	^{49}Ca	8.7 min	3084.4
Cl	^{38}Cl	37.2 min	2167.7
Cu	^{66}Cu	5.1 min	1039.3
Fe	^{59}Fe	44.5 days	1099.2
I	^{128}I	25.0 min	442.9
K	^{42}K	12.36 h	1524.6
Mg	^{27}Mg	9.45 min	1014.4
Mn	^{56}Mn	2.58 h	846.8, 1810.8
Na	^{24}Na	14.95 h	1368.6
Se	^{77}Se	17.6 s	161.9
Zn	^{64}Zn	243.8 days	1115.5

materials as comparator standards. NIST standard reference materials (SRMs), namely SRMs 1568a, 1573a, 8704, 1566b, 1577b, 1549, and NRCC CRM DORM-1 and NMIJ CRM 7302-a were used to cover all types of food category used in this study.

Selenium content of food items was measured using the CINAA irradiation facilities and counting equipment at DUSR in Canada. Dried powdered samples in pre-cleaned polyethylene vials were irradiated at the inner site of DUSR at a neutron flux of 2.5×10^{11} cm^{-2} s^{-1}. The optimum CINAA timing parameters used were: 20 s irradiation time, 10 s decay time, 20 s counting time, 1 min between consecutive cycles, and 5 cycles [7]. The 161.9 keV gamma-ray of the ^{77m}Se nuclide was measured using gamma-ray spectrometry consisting of an EG&G Ortec HPGe p-type coaxial detector. The selenium comparator standards were made from plasma emission spectroscopy standard solution with a certified purity of >99.999 % supplied by SPC Canada Ltd. Due to the time limitation of this project, vegetables could not be analyzed for Se by CINAA.

Results and discussion

Method validation

The INAA and CINAA methods were validated by analyzing several NIST SRMs, namely SRMs 1568a, 1573a, 8704, 1566b, 1577b, 1549, and NRCC CRM DORM-1 and NMIJ CRM 7302-a. Our results are in good agreement with the certified values within ±5 % deviation or better. The details of the results are shown in a previous paper [6]. For the sake of completeness of this paper the results of selected certified reference material NIST SRM 1568a (Rice Flour) are shown in Table 3.

Table 3 Elemental concentrations in NIST SRM 1568a rice flour

Element	Certified value (mg kg^{-1})	This work (mg kg^{-1})
As	0.29 ± 0.03	0.28 ± 0.01
Ca	118 ± 6	117 ± 17
Cu	2.4 ± 0.3	2.5 ± 0.19
K	1280 ± 80	1270 ± 29
Mg	560 ± 20	550 ± 26
Mn	20.0 ± 1.6	19.7 ± 0.7
Zn	19.4 ± 0.5	19.7 ± 0.9

Elemental composition of Thai food items

Elemental concentrations in selected food samples were measured using short, medium and long irradiations. The mass fractions of elements found in these samples can be divided into two groups, namely minor and trace levels. The results presented here are on dry-weight basis. The minor nutrients in food are Ca, Cl, K, Mg and Na and their concentration ranges are presented in Table 4. Trace elements found in the chosen food categories are As, Br, Cr, Cu, Fe, I, Mn and Zn and their ranges are presented in Table 5.

The dominant elements found in rice and beans are Ca, K and Mg. Aquatic animals are rich in most elements. The overall mass fractions of most elements, except K, in aquatic animals are found at higher levels compared to other categories of food. Thus this protein-rich diet of rice, beans and aquatic animals is an important source of minerals for humans. It should be noted that the results presented here are higher than those reported by another researcher [8]. This may be due to the fact that our samples cover several kinds of cooked aquatic food, e.g. crustacean, mollusk and fish.

The concentrations of Cu and Zn in various categories of vegetables are shown in Table 5. These values are also higher than that reported by another researcher [3]. Arsenic and iodine were below the detection limits of 0.01 and 0.38 mg kg^{-1}, respectively, under the experimental conditions used. We found higher levels of Br and Fe while lower levels of Ca, Na and K in cauliflower compared to those of Singh [9]. The levels of Cr in all of our samples were below the detection limit of 0.40 mg kg^{-1}, thus are not reported here. We observed that vegetables are rich in Ca, Cl and K.

In order to demonstrate the effect of human activity on elemental composition in food, we selected soybean products as an example. A single sample of each soybean

Table 4 Range of minor elements in selected food categories by INAA (mg kg^{-1})

Element	Ca	Cl	K	Mg	Na
Rice	<15–200	176–347	640–2,800	50–1,500	NA
Bean	540–2,800	<5–640	6,500–19,900	1,400–2,600	NA
Aquatic animals	<15–70,000	235–103,976	<15–10,900	343–8,619	285–66,250
Vegetable					
Seeds	1,200–11,000	1,109–55,072	13,000–44,900	2,000–4,900	20–730
Leaves	2,200–20,700	207–15,610	1,600–20,600	800–7,800	27–5,862
Flowers	2,400–22,000	2,990–32,866	29,700–42,400	1,700–4,300	104–5,813
Soy product	<15–2,900	10–31,111	3,700–27,100	<40–5,407	29–50,569
LOD	15	5	15	40	0.58

NA not analyzed

Table 5 Range of trace elements in selected food categories by INAA (mg kg^{-1})

Element	As	Br	Cu	Fe	I	Mn	Zn
Rice	<0.01–0.21	<0.12–0.75	<0.85	<18	<0.38	8–56	21–27
Bean	<0.01	<0.12–13.5	<0.85–16.4	<18–160	<0.38	12–34	8–58
Aquatic animals	0.9–7	8–265	<0.85–231	<18–1,234	0.42–15	<0.58–212	18–500
Vegetable							
Seeds	<0.01	2–29	<0.85	<18–85	<0.38	10–290	35–138
Leaves	<0.01	1–47	<0.85	76–186	<0.38	16–170	37–105
Flowers	<0.01	4–70	<0.85	<18—212	<0.38	19–51	58–150
Soy-product	<0.01	<0.12–104	<0.85–18	82–104	<0.38–4	<0.58–47	40–64
LOD	0.01	0.12	0.85	18	0.38	0.58	0.27

product was studied here. The minor nutrients and trace element levels in each soybean product are presented in Tables 6 and 7, respectively. It is evident that elemental composition of various types of soybean products differs according to their preparation steps. It appears that some calcium minerals must have been added to soft soybean packed in boxes. On the other hand, our results show that soft egg tofu is very low in Ca; it is then possible that this product is made from a raw material other than soybean. We found the elemental composition of soy protein to be quite similar to soybean. It can perhaps be concluded then that the preparation steps of this soybean product were subjected to minimal chemical additives.

Selenium in food by CINAA

Due to time limitations the CINAA method was applied to the determination of Se in only four categories of food to demonstrate the effectiveness of this technique in food analysis. The range of Se content and limit of detection in all groups are shown in Table 8. This technique was found to be very effective and highly accurate for analyzing food samples with low levels of Se with high throughput. Additional study of soybean products did not show significant difference in Se content. Thus, we may conclude that Se was not a contaminant during the preparation of these soy-products.

Table 6 Minor elements in soybean and soybean products by INAA (mg kg^{-1})

Element	Ca	Cl	K	Mg	Na
Soybean	2,700	46	17,200	2,310	11
Tofu, soft, packed in box	10,400	1,962	8,400	2,214	108
Tofu, firm, packed in box	2,900	9,123	5,800	5,407	3,941
Tofu, soft, packed in pouch	3,400	194	14,600	2677	847
Egg tofu, packed in pouch	<15	31,111	2,7100	<40	30,569
Tofu, deep fried	2,100	10	3,700	1,761	252
Soy protein	2,900	293	15,400	2,246	29
LOD	15	5	15	40	0.58

Table 7 Trace elements in soybean and soybean products by INAA (mg kg^{-1})

Element	As	Br	Cu*	Fe	I*	Mn	Zn
Soybean	<0.01	2	15	75	0.92	32	58
Tofu, soft, packed in box	<0.01	1	16	86	0.84	42	63
Tofu, firm, packed in box	<0.01	104	18	82	0.75	45	57
Tofu, soft, packed in pouch	<0.01	1	17	104	0.36	38	62
Egg tofu, packed in pouch	<0.01	16	<0.85	67	3.94	<0.58	40
Tofu, deep fried	<0.01	<0.12	<0.85	100	1.47	42	64
Soy protein	<0.01	0.57	<0.85	87	0.16	47	55
LOD	0.01	0.12	0.85	18	0.05	0.58	0.27

* Analyzed at the Dalhousie University SLOWPOKE-2 Reactor (DUSR) facility

Table 8 Selenium content and detection limit in selected food categories (mg kg^{-1})

Food category	Selenium concentration*	Limit of detection*
Rice	<0.04–0.07	0.04
Bean	0.03–0.36	0.03
Soybean	0.13	0.05
Tofu, soft, packed in box	0.24	0.05
Tofu, firm, packed in box	<0.05	0.05
Tofu, soft, packed in pouch	0.16	0.05
Egg tofu, packed in pouch	1.02	0.05
Tofu, deep fried	0.09	0.05
Soy protein	0.09	0.05
Aquatic animals	0.70–3.52	0.05

* Analyzed at the Dalhousie University SLOWPOKE-2 Reactor (DUSR) facility

Conclusions

The INAA and CINAA methods used in this study indicate the effectiveness of nondestructive analytical technique for the determination of minor and trace elements in various types of food items. The techniques proved to be accurate, sensitive with ease of operation and able to do multielement analysis of food items regardless of their categories. Thus these techniques will be invaluable for the elemental analysis of many food items in our significantly larger nation-wide study. The data obtained from the larger study of nutrient and minerals in food will enhance the estimation of the average daily dietary intakes through various types of food by Thai population groups. Then the malnutrition due to elemental deficiency can be overcome by proper selection of food in our daily meals. In addition, the potential toxicity in food due to presence of harmful elements can be evaluated beforehand. The NAA techniques will be invaluable tools for nutritionists to fill the gaps in the food composition table.

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