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Determination of trace elements in some fruits collected in Vietnam and Korea by Neutron Activation Analysis on Dalat and HANARO research reactors

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Abstract: The k_0 -based neutron activation analysis (k_0 -NAA) has been applied for determination of trace multi-element in 5 fruits: Orange, tomato, persimmon, pear and apple. The samples were collected in Vietnam and Korea, and dried-frozen in laboratory at a temperature of -65^oC, weighed approximately 50 mg or 100 mg each sample, and put in clean polyethylene bags for short and long time irradiations, respectively. The NIST-1547 (Peach Leaves) and IAEA-V-10 (Hay Powder) were used for the purpose of quality control. Both analytical and standard samples were irradiated in the 500 kW Dalat research reactor (Vietnam) and the 20 MW HANARO research reactor (Korea). Concentration of 16 elements: Al, As, Au, Br, Ca, Cl, Co, Eu, Fe, K, La, Mg, Mn, Na, Rb and Zn were determined. By comparison the concentrations of trace elements in the investigated Vietnam and Korea's fruits, revealed that they are mostly similar between two places. However, the Ca concentration in orange from Vietnam was approximately 2.5 times higher than that one from Korea, whereas the Ca concentrations in all of fruits that collected in Vietnam were mostly higher than those collected in Korea, ranging between 1.4 to 2.2 times.

Keywords: Neutron activation analysis, trace elements in fruits, Dalat research reactor, HANARO research reactor.

I. INTRODUCTION

Fruit is one of the types containing many fiber, vitamins and minerals, moreover, fruit is also a significant source of trace elements that are necessary to the body when we eat fruit every day but which of kinds of fruit were chosen? Concentrations of trace elements in individual fruits like? Does fruit of Korea differ from Vietnam's fruit a lot? How is the difference? This is the content that the authors care. The k_0 -based neutron activation analysis (k_0 -NAA) was applied to answer for the above questions.

In this paper, we have collected some very popular fruits in the market of Vietnam

and Korea, including 5 types of fruit: orange, tomato, persimmon, pear and apple which are the popular fruits containing many vitamins, fiber and minerals, e.g. Ca, Fe, K, Mg, Mn, Zn and other elements needed for the development of the body.

Orange helps to increase the stamina, also to prevent the arteriosclerosis and reduce the cholesterol. Thanks to the huge quality phytosterols which is good for the heart with large amount of the flavonoids which helps the body against cancers of mouth, skin, lung, breast, stomach and colon, prevent the constipation and the gallstones diseases. Orange is an anti-oxidant substance also help to protect the skin from the sunbeam's damage and prevent ageing. Particularly, the orange with very high level of calcium that is an essential element for the bone's growth.

Tomato is rich in Vitamin A, C, K, B6, folate, thiamin, magnesium, niacin, copper and phosphorus. The greater in tomato is very low cholesterol, saturated fats, sodium and chlorine so that it will improve our eyesight, prevent the cancer, the lighten skin, reduce the sugar in blood, promote the sleep, the anti-osteoporosis, and especially thanks to the iron and the vitamins, which help for hair healthy and shiny if we eat tomato regularly.

Ripe persimmon is not only one of fruits containing twice more fiber than other normal fruits, but it is a relative rich anti-oxidant substance with vitamins A, C, protein and a great source of Fe, Ca and Mg. Persimmon could cure digestive disorders due to natural colloidal pectin in the flesh, but it also makes skin beautiful. On the other hand, persimmon is also a diuretic and it can reduce the risk of kidney stones.

Pears contain more flavonoids and fiber, so if we eat more pear it will reduce the risk of heart disease and support the digestive system, strengthen the immunity system, and reduce the fever quickly.

Apple can prevent the constipation very good, the anti-bacterial, the anti-created stones, the bile circulation, the relieve headaches, reduced the fat. When we eat the apples it will reduce the stroke risk for elderly.

Apart from the effects presented above we want to determine the concentrations of trace elements in five fruits: Orange, tomato, persimmon, pear and apple.

Samples were taken for washing and drying, dried-frozen at temperature of -65° C, and analyzed for 16 elements: Al, As, Au, Br, Ca, Cl, Co, Eu, Fe, K, La, Mg, Mn, Na, Rb and Zn by the k_0 -NAA method [1, 2, 3]. The research and standard samples were irradiated on the Dalat research reactor (500 kW, Vietnam) and the HANARO research reactor (20 MW, Korea). The quality control of analytical results was based on the reference materials, i.e. the NIST-SRM-1547 (Peach Leaves) and the IAEA-CRM-V-10 (Hay Powder).

II. EXPERIMENTAL

A. Sampling and Sample preparation

After collecting, the samples were taken to the laboratory, washed with water, then to rinse out again with distilled water. Using of a knife to cut and remove the peel outside and particles inside either. Left part of the flesh is cut into thin slices, fresh weight of samples were weighed. The samples were dried-frozen at a temperature of -65°C for 144 hours, cooled in the desiccator to room temperature. The dry samples were milled into fine powder and weighed to calculate the moisture content. Usually the sample masses are approximately 50 mg or 100 mg used for short and long time irradiation, respectively. The samples were sealed in the clean vials for short irradiation or the polyethylene boxes for long irradiation with transfering the sample to a new counting vial after irradiating. The moisture contents after freeze-drying are listed in Table I.

Fruits	% Moisture (Vietnam's Fruit)	% Moisture (Korea's Fruit)		
Orange	88.47	88.70		
Tomato	94.00	96.40		
Persimmon	73.06	83.50		
Pear	87.08	86.80		
Apple	87.58	86.60		

Table I. Moisture content of fruit samples collected in Vietnam and Korea.

Table I shows that the moisture content of orange, tomato and persimmon of Vietnam is of 0.01% lower than those ones of Korea. Conversely, pear and apple's moisture of Vietnam is approximately 0.01% higher than those ones of Korea.

B. Irradiation and measurement

The short time irradiations were carried out in the 7-1 Channel. The mean thermal neutron flux in the irradiation position is about $4.22 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, f = 9.7, and $\alpha = -0.031$. Irradiation time was 5 minutes, decay time was 5 minutes, the first counting time was 300 seconds to determine the elements: Al, Ca and Mg, after that the samples were decayed for 30 minutes, then measured for 1,800 seconds to determine the elements: Cl, K, Mn and Na. Long time irradiations were carried out in the rotary rack. The mean thermal neutron flux in the irradiation position is about 3.76×10^{12} $n \cdot cm^{-2} \cdot s^{-1}$; f = 30.1 and α = 0.102. Irradiation time was 10 hours, decayed for 2-3 days, measured the first time for 3,600 seconds to determine the elements: As, Au, Br and La, after that the samples were decayed for about two-three weeks, measured for the second time for 10,800 seconds to determine the elements: Co, Eu, Fe, Rb and Zn. Table 2. shows the nuclear parameters for radionuclide used in the analysis of fruits. The gamma-ray spectrometer using GMX-30190 HPGe detector (relative efficiency of 30% and resolution of 1.9 keV at 1332.5 keV) was used to measure the samples after activation. In order to calculate the concentrations of the required elements, we have used the "Ko-Dalat" and " k_0 -IAEA" software [4]. Figures 1 and 2 display the gamma-ray spectra of the samples irradiated for short and long times, respectively.



Fig.1. A gamma-ray spectrum of short time irradiation.

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Fig.2. A gamma-ray spectrum of long time irradiation.

Elements	Radionuclides	Half-life [5]	Gamma-ray Energy (keV) [5]
Al	Al ²⁸	2.24 m	1778.9
As	As ⁷⁶	26.32 h	559.1
Au	Au ¹⁹⁸	2.70 d	411.8
Br	Br ⁸²	35.30 h	776.5
Ca	Ca ⁴⁹	8.72 m	3084.5
Cl	Cl ³⁸	37.24 m	2167.7
Со	Co ⁶⁰	5.27 у	1332.5
Eu	Eu ¹⁵²	13.33 y	1408.0
Fe	Fe ⁵⁹	44.50 d	1099.3
K	K ⁴²	12.36 h	1524.6
La	La ¹⁴⁰	40.27 h	1596.2
Mg	Mg ²⁷	9.46 m	1014.4
Mn	Mn ⁵⁶	2.58 h	1810.7
Na	Na ²⁴	14.96 h	1368.6
Rb	Rb ⁸⁶	18.66 d	1076.6
Zn	Zn ⁶⁵	243.9 d	1115.6

Table II. Nuclear parameters for radionuclides used in the analysis of the fruits by the k_0 -NAA.

Both reference materials of the NIST 1547 (Peach Leaves) and the IAEA-V-10 (Hay Powder) were used for the purpose of the quality control. The reference materials and the samples were irradiated on the Dalat research reactor and the HANARO research reactor. The analytical results of 16 elements: Al, As, Au, Br, Ca, Cl, Co, Eu, Fe, K, La, Mg, Mn, Na, Rb and Zn were determined with the concentrations, uncertainties and detection limits. The analytical results of the reference materials which revealed that the difference between the analytical results and certified values is mostly lower than 15% for the elements of interest. Comparing the levels of trace elements in fruits were surveyed in Vietnam and Korea, it shows that they are similar between two places. However, there are some elements with a significant difference.

III. RESULTS AND DISCUSSION

For quality control of the analytical results, we used the certified reference materials, i.e. the NIST-1547 (Peach leaves) and the IAEA-V-10 (Hay Powder) which have similar matrices with the research samples. The evaluation qualified criteria are based on the calculation of *U*-score as following:

$$U\text{-score} = \frac{x-X}{\sqrt{\sigma_x^2 + \sigma_x^2}}$$

where,

x : the experimental result

X : the certified value

 σ_x : the uncertainty of experimental result

 σ_X : the uncertainty of certified value

If:

|U-score | < 1.64: experimental result does not differ from the certified value.

1.64 < | U-score | < 1.95: experimental result may not differ from the certified value.

1.95 | U-score | <2.58:unknown experimental result has differ from the certified value or not.

2.58 | U-score | < 3.29: experimental result may differ from the certified value

3.29 < |U-score | have difference between the certified value and experimental result

The results of *U*-scores of the reference materials are displayed in Tables III and IV.

Elements	Experiment	al results	Certified	values	Experimental	17
	Concentration	Uncertainty	Concentration Uncertainty		/ Ĉertificate	U-scores
Al	260	11	249	8	1.04	0.65
Br	11.3	0.2	11.0	1.7	1.03	0.20
Co	0.078	0.005	0.070	0.015	1.11	0.50
Eu	0.23	0.01	0.170	0.049	1.35	1.22
Fe	213	5	218	14	0.98	-0.36
K	22000	1000	24300	300	0.92	-1.85
La	9.2	0.1	9.0	1.4	1.02	0.14
Rb	22.0	0.4	19.7	1.2	1.12	1.80
Zn	17	2	17.9	0.4	0.92	-0.85

Table III. The analytical results for the NIST 1547 (Peach Leaves).

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Elements	Experiment	al results	Certified	values	Experimental /	U-scores
	Concentration	Uncertainty	Concentration	Uncertainty	Ĉertificate	
Br	9.0	2.3	8.0	0.6	1.13	0.18
Ca	24000	1500	21600	600	1.13	1.79
Со	0.175	0.017	0.13	0.04	1.35	1.03
Fe	221	22	186	6.5	1.19	1.51
K	20300	450	21000	279	0.96	-0.00
Mg	1360	65	1360	13.4	0.99	- 0.00
Mn	48.0	0.8	47	0.6	1.02	0.80
Na	600	140	500	14.5	1.24	0.94
Rb	7.7	0.7	7.6	0.06	1.01	0.70
Zn	29.0	0.1	24	0.16	1.21	0.19

Table IV. The analytical	results for the IAEA	-V-10 (Hay Powder)
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The analytical results of almost elements in Tables III and IV, have |U-score | < 1.64, except K in NIST 1547 and Ca in IAEA-V-10. However, the |U-score | is still lower than 1.95 so that most of results are not different from the certified values. By comparison the concentration of elements which were determined by the k_0 -NAA in the reference materials with their certified values, show that overall results are in good agreement and proven that the k_0 -NAA is capable of providing accurate results with the | U-score | values is lower than 1.95 for the almost elements of interesting

Table V. Concentration of elements in Korea and Vietnam's fruits (mg/kg).

Fla	Orange		Tomato		Persimmon		Pear		Apple	
ments	Korea	Vietnam	Korea	Vietnam	Korea	Vietnam	Korea	Vietnam	Korea	Vietnam
Al	0.96	25.59	26.50	41.98	ND.	9.07	2.63	10.70	2.01	6.30
Ca	571	1410	135	<1135	419	<519	663	31	249	ND.
Cl	279	187	4290	3751	745	41	43	18	18	14.46
K	10900	8007	37500	25210	12600	736	9910	1129	7940	721
Mg	978	682	2080	<809	561	ND.	1380	110	451	<259
Mn	4.7	4.1	28.2	24.0	20.0	6.4	8.3	0.4	2.5	0.3
Na	111.0	83.7	239.0	344.3	21.1	6.4	13.8	7.8	11.9	8.4
As	0.07	< 0.032	0.87	< 0.51	ND.	< 0.28	ND.	< 0.27	ND.	0.22
Au	ND.	0.04	0.00	0.18	0.00	0.28	0.00	0.06	0.00	0.06
Br	1.54	1.38	3.13	9.33	1.34	2.58	ND.	0.88	ND.	1.18
Co	0.03	0.21	0.09	< 0.34	0.02	0.02	0.10	0.06	0.03	0.02
Eu	ND.	ND.	0.54	ND.	1.62	ND.	1.09	ND.	0.65	ND.
Fe	8.0	44.4	37.2	23.0	8.2	10.5	9.0	13.8	6.5	21.3
La	ND.	0.0	ND.	< 0.087	ND.	< 0.052	0.0	< 0.054	ND.	0.2
Rb	4.7	55.9	16.6	335.9	5.5	27.3	3.1	30.9	0.7	69.8
Zn	8.1	27.6	19.9	27.9	ND.	25.4	ND.	11.0	ND.	6.3

The experimental results of 16 elements in Vietnam and Korea's fruits were presented in Tables V, indicate that they are mostly similar between two places. However, the Ca concentration in orange from Vietnam is of 2.47 times higher that one from Korea's orange, whereas Ca concentration in pears of Vietnam is of 21 times lower than that one in Korean's pear. Mn concentration in the fruits of Vietnam is mostly higher than that one in Korea's fruit ranging between 1.4 to 2.2 times. As in orange and tomato of Korea are higher those ones of Vietnam but As in persimmon, pear and apple of Korea are very low levels in comparison with the Vietnam's ones. K in the fruits of Korea is almost higher than that one in the fruits of Vietnam ranging between 1.36 to 17.1 times, while Eu was not found in 5 fruits in Vietnam, but it was recorded in four fruits of Korea except for orange. Zn in orange and tomato of Vietnam is 2.24 times and 1.07 times higher than that one in Korea, respectively. Zn in persimmon, pear, apple of Korea was not detected at all. [6].

IV. CONCLUSION

In this study we have analyzed 16 elements, i.e. Al, As, Au, Br, Ca, Cl, Co, Eu, Fe, K, La, Mg, Mn, Na, Rb and Zn. Comparing the levels of trace elements in 5 surveyed fruits of Vietnam and Korea, it shows that there are similarities between two places. However, there are some elements, which have difference quite evident. Thus through the tables of the results, it has demonstrated to us that the quality of a fruit depends on its trace element content and nutritional value, but not on the place where the fruit grows. It could also help the people realize, understand and choose for themselves the fruits accordingly.

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