NEUTRON ACTIVATION ANALYSIS OF ELEMENTAL CONTENT OF EDIBLE AND MEDICINAL PLANT IRON STICK YAM

Li Xuesong^{1,2}, M.V. Frontasyeva¹, G. Hristozova³, P. S. Nekhoroshkov¹, Inga Zinicovscaia^{1,4}, N. Yushin¹, Atanas Vasilev⁵, O. Chepurchenko¹

¹ FLNP, Joint Institute for Nuclear Research, Russia Federation
² Northwest Institute of Nuclear Technology, Xi'an, China
³ Faculty of Physics, Paisii Hilendarski University, Plovdiv, Bulgaria
⁴ Institute of Chemistry of Sciences of Moldova, Chisinau, Republic of Moldova
⁵ Faculty of Physics, St. Kliment Ohridski University, Sofia, Bulgaria

ABSTRACT

For the first time conventional and epithermal neutron activation analysis (ENAA) was applied to determine the elemental content of iron stick yam (Dioscorea opposita Thunb), an edible and medicinal plant grown in China. It is well known for its high nutritional value and salutary effects: anti-aging, anti-tumor, etc. A total of 30 elements were determined at the reactor IBR-2 of FLNP JINR (Na, Mg, Al, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Se, As, Br, Sr, Rb, Zr, Ag, In, Sb, I, Ba, Cs, La, Ce, Nd, Eu, Gd, Sm, Tb, Dy, Yb, Tm, Hf, Ta, W, Au, Th, and U), 11 of which (S, Cl, Br, Rb, Sb, Cs, Nd, Eu, Sm, Au, and U) have never been reported in previous studies of yam. Abnormally high concentrations of Al, U, Eu and Nd have been found.

Key words: NAA, iron stick yam, elemental content, medicinal plants

INTRODUCTION

Yam is a type of useful food plant belonging to the *Dioscorea* genus which has more than 600 species, mainly distributed in tropical and subtropical areas. To the best of our knowledge, the study of yam started in 1969 [1]. iron stick yam (*Dioscorea opposita* Thunb), also known as Die-hard yam or Tie Gan yam, grows in Wenxian County, China, and is deemed to have anti-aging, anti-tumor, anti-fatigue and immunity enhancing qualities.

The Chinese researchers studied mineral and trace element content in different types of yams for several decades, including iron stick yam. Inductive coupled plasma atomic emitted spectrometry (ICP-AES), atomic absorption spectrometry (AAS), inductive coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF) have been employed to determine a batch of mineral and trace elements in several types of yams [2-7]. Numerous investigations of mineral elements in various kinds of yams were performed in other yam-rich countries. A lot of investigations on mineral elemental content of yam were carried out in Nigeria [8-10], India [11], South Korea [12], and Ghana [13], where AAS and ICP-AES have also been widely used to determine the mineral elemental content.

Despite the fact that over the past, several analytical techniques have been employed complementarily in the elemental content studies, the obtained data are still insufficient.

With the development of nuclear research reactors and high resolution gamma spectrometry, neutron activation analysis (NAA), a multi-element and non-destructive analysis technique, showed itself a reliable analytical method used in many branches of the life sciences [14-17].

In the present work, the elemental content of iron stick yam was determined by NAA for first time and concentrations of 30 elements were determined, among them eleven elements (S, Cl, Br, Rb, Sb, Cs, Nd, Eu, Sm, Au, and U) were never reported in literature before.

MATERIALS AND METHODS

Samples of iron stick yam were collected near the Yellow river (red point in Figure 1a), Wenxian county, Jiaozuo city, Henan province, China.



a. Sampling place of iron stick yam b. Iron stick yam Fig. 1 Iron stick yam from China

Neutron conditions. The IBR-2 reactor of FLNP JINR is equipped with two irradiation channels of pneumatic transport system REGATA^[14] for NAA. Characteristics of two irradiation channels, one of which is cadmium screened for epithermal neutrons irradiation, are shown in Table 1.

Channels	Ch1(epithermal) (Cadmium-screened)			Ch2(thermal)		
Dimensions, mm	Diameter 28, length 260			Diameter 28, length 260		
Neutron type	Thermal	Resonance	Fast	Thermal	Resonance	Fast
Experimental fluxes, (s ⁻¹ cm ⁻²)	Cd- coated	3.6×10 ¹¹	5.5×10 ¹¹	1.5×10^{12}	1.8×10 ¹¹	2.7×10^{11}

Table 1 Neutron conditions of sample irradiation

Quality control. To provide quality control of the results obtained, several international standard reference materials (SRMs) were used (see Table 2). As follows from Table 2, the deviations for all elements are between -1% and +1%.

Samples preparation. After rinsing and drying for 24 hours at 40 $^{\circ}$ C, iron stick yam tuber was peeled by a pair of plastic tweezers to separate the peel and inner tissue which were placed with the peel pieces in a drying unit for 72 hours at 40 $^{\circ}$ C. Samples were homogenized by grinding into powder with agate ball mill, and about 0.3 g powder of each was packed in polyethylene bags for determination of short-lived isotopes and in aluminum cups for determination of long-lived isotopes. In total, 5 peel and 6 tuber tissue samples were prepared.

Element	Determined	Certified	Deviation	SRM		
Element	concentration	concentration	, %			
Na	299.5±9.9	298.8±4.8	0.2	NIST-1632c (trace elements in coal)		
Mg	4324±40	4320±80	0.1	NIST-1547 (peach leaves)		
Al	64434±710	64400 ± 800	0.05	NIST-2710 (montana soil)		
S	2400±700	2400±60	0	NIST-2710 (montana soil)		
Cl	579±25	579±23	0	NIST-1515 (apple leaves)		
Κ	24289 ± 1200	24300±300	-0.05	NIST-1547 (peach leaves)		
Ca	15637±550	15600±200	0.2	NIST-1547 (peach leaves)		
Sc	2.908±0.058	2.905±0.036	0.1	NIST-1632c (trace elements in coal)		
V	295.8±6.5	295.7±3.6	0.04	NIST-1633b (coal fly ash)		
Mn	132.0±3.4	131.8±1.7	0.2	NIST-1633b (coal fly ash)		
Fe	7339±499	7350±110	-0.1	NIST-1632c (trace elements in coal)		
Со	12.9±0.2	12.9±0.3	0	IAEA-433 (marine sediment)		
Cu	2952±730	2950±130	0.04	NIST-2710 (montana soil)		
Zn	100.9 ± 18.0	101±2	-0.1	IAEA-433 (marine sediment)		
As	18.92±0.42	18.9±0.5	0.1	IAEA-433 (marine sediment)		
Br	18.66±0.45	18.7±0.4	-0.2	NIST-1632c (trace elements in coal)		
Sr	301.6±12.0	302±6	-0.1	IAEA-433 (marine sediment)		
Rb	5.04 ± 1.10	5.05±0.11	-0.2	NIST-1632b (trace elements in coal)		
Zr	148±19	148±44	0	IAEA-433 (marine sediment)		
Sb	1.96±0.05	1.96±0.035	0	IAEA-433 (marine sediment)		
Ι	0.3014 ± 0.0430	0.30±0.09	0.5	NIST-1547 (peach leaves)		
Ba	67.6±10.4	67.5±2.1	0.1	NIST-1632b (trace elements in coal)		
Cs	0.594±0.017	0.594±0.010	0	NIST-1632c (trace elements in coal)		
La	27.79±1.10	27.8±1.0	-0.04	BCR-667 (estuarine sediment)		
Nd	24.9±2.3	25.0±1.4	-0.4	BCR-667 (estuarine sediment)		
Eu	0.997±0.110	1.00±0.01	-0.3	BCR-667 (estuarine sediment)		
Sm	1.082±0.036	1.078 ± 0.028	0.4	NIST-1632c (trace elements in coal)		
Au	0.01659 ± 0.00510	0.0166 ± 0.0012	-0.06	BCR-667 (estuarine sediment)		
Th	1.399±0.025	1.40±0.03	-0.06	NIST-1632c (trace elements in coal)		
U	0.5128±0.0150	0.513±0.012	-0.04	NIST-1632c (trace elements in coal)		

Table 2 NAA data and certified values of reference materials, mg/kg

Note: NIST is the national institute of standard and technology; IAEA is the international atomic energy agency; BCR is community bureau of reference, the former materials program of the European commission.

Irradiation and measurements. Three sub-samples of peel and three sub-samples of tissue were irradiated in cadmium-screened channel 1 for 2 days. To determine the long-lived isotopes gamma spectra were measured twice: for 30 minutes after 4~5 days of decay and for 1.5 hours after ~29 days of decay. To determine short-lived isotopes five sub-samples (two peel and three tissue sub-samples) were irradiated for 3 minutes in conventional Channel 2. After ~3 min of decay each irradiated sub-sample was measured for 15 min. Gamma-ray spectrometers based on high-resolution HPGe detector from Canberra with 50% relative efficiency and 1.9 keV resolution at 1.332 MeV for the line of ⁶⁰Co were used to measure gamma spectra of induced activity by means of Genie2000. A software package developed at the FLNP JINR [27] was used to calculate the concentrations of elements based on relative method using the certified reference materials as mentioned in Table 2. Descriptive statistics were applied to determine mean values and their standard deviations for each sample.

RESULTS AND DISCUSSION

The results of iron stick yam peel and tissue are shown in Table 3. They are compared with the relevant literature data [17].

	Pre	esent work (NAA	Ref. [8] (AAS+AES)			
-	iron-stick	iron-stick	Tissue/peel	Dioscorea bulbifera	Dioscorea bulbifera	Tissue/peel
	yann (peer)	yam (tissue)	ratio	(peel)	(tissue)	ratio
	(China)	(China)		(Nigeria)	(Nigeria)	
Na	1287±21	941±15	0.73	640	550	0.86
Mg	2840±71	1440±35	0.53	161	139	0.86
Al	194±3	12.0±0.4	0.056	-	-	-
Р	-	-	-	184	150	0.82
S	96±34	82±16	0.83	-	-	-
Cl	4255±221	2197±92	0.53	-	-	-
Κ	19867 ±2384	13800 ± 1656	0.69	920	440	0.49
Ca	6425±238	1496±51	0.23	316.31	205.60	0.65
Sc	0.036±0.003	-	-	-	-	-
V	1.29±0.05	-	-	-	-	-
Mn	30.1±1.0	5.76±0.23	0.19	18	4	0.22
Fe	106±10	-	-	17.35	5.90	0.34
Co	0.135 ± 0.008	-	-	-	-	-
Cu	14.0±3.8	6.9±1.7	0.48	8	5	0.63
Zn	37.9±0.8	15.8±0.4	0.42	4.12	1.52	0.37
As	0.117±0.007	-	-	-	-	-
Br	23.5±0.3	7.9±0.1	0.34	-	-	-
Sr	65.2±2.6	14.9±0.7	0.23	-	-	-
Rb	1.36±0.15	0.95±0.10	0.70	-	-	-
Zr	14.2±5.7	-	-	-	-	-
Sb	0.027 ± 0.003	0.050 ± 0.007	1.85	-	-	-
Ι	0.72±0.19	-	-	-	-	-
Ba	10.4±0.9	1.8±0.2	0.19	-	-	-
Cs	0.035 ± 0.003	0.007 ± 0.002	0.22	-	-	-
La	0.165 ± 0.011	-	-	-	-	-
Nd	8.34±0.46	2.84±0.16	0.34	-	-	-
Eu	0.22±0.05	0.14 ±0.02	0.63	-	-	-
Sm	-	0.0030±0.0003	-	-	-	-
Au	0.037 ± 0.007	0.0020±0.0004	0.054	-	-	-
	0.038±0.002	-	-	-	-	-
U	0.775 ± 0.015	0.0094±0.0007	0.015	-	-	_

Table 3 Element concentrations (mg/kg) of iron stick yam peel and tissue and Ref [8]

The tissue/peel ratios (column 4) shows that with except of Sb, concentrations of most of the elements in peel are much higher than those in tuber tissue. The same phenomenon was also observed in [8]. And the concentrations of Al, Au and U are extremely high in peer. As we all know, too much Al and U is harmful for human body. The main reason for these abnormally high concentrations perhaps is that different elements have different deposit rate in the peer of iron stick yam or soil particles remaining on the peel.

Table 4 Elemental concentrations (mg/kg) for different yams and Reference Plant(RP)							
	Present		(AAS)	(ICP-	(AAS)		
	work	(ICP-AES)	iron-	AES)	Dioscorea	(AAS)	D D [19]
	(NAA)	iron stick	stick	iron	dumetorum	Dioscorea	RP ^[18]
Element	iron stick	yam ^[2]	yam ^[3]	stick	(tissue) ^[10]	alata	
	yam(tissue)	(China)	(China)	yam [,] i	(Nigeria)	(India)	
	(China)		(ennu)	(China)	(i (igeila)		
Li	-	0.0198	-	-	-	-	0.2
Be	-	0.036	-	-	-	-	0.001
Na	941	280.6(Na ₂ O)	-	-	875	320	150
Mg	1440	1365(MgO)	580.7	370	675	5661	2000
Al	12	100.5(Al ₂ O ₃)	-	-	-	-	80
Р	-	1770	545	490	2735	1101	2000
S	82	-	-	-	-	-	3000
Cl	2197	-	-	-	_	-	2000
K	13800	14220(K ₂ O)	-	6470	7950	1550	19000
Ca	1496	897.6(CaO)	923.9	570	205.0	3381	10000
Ti	-	3.722	-	-	-	-	0.05
V	-	0.911	_	_	_	_	0.5
Cr	-	33.83	_	-	_	_	1.5
Mn	5.76	7.578	2.70	0.81	27.0	53.6	200
Fe	-	$368.2(Fe_2O_3)$	32.25	10.09	20.0	331	150
Co	-	0.6164	-	-	-	-	0.2
Ni	_	17.85	_	_	_	_	1.5
Cu	6.8	0.080	5.68	1.56	1.0	83	10
Zn	15.8	20.77	6.76	3.35	78.0	12.6	50
Ga	-	1.254	-	-	-	-	0.1
As	-	-	1.13	_	_	_	0.1
Se	-	-	0.29	0.01719	_	_	0.02
Br	7.9	-	-	-	_	_	4
$\frac{ST}{Sr}$	14.9	6.431	_	_	_	-	50
Rb	0.95	-	_	_	_	_	50
Y	-	0.0611	_	_	_	-	0.2
Zr	_	0.2223	_	_	_	_	0.1
Nb	_	0.9189	_	_	_	_	0.05
Sb	0.050	-	_	_	_	_	0.1
Ba	1.8	3.653	_	_	_	_	40
Cs	0.007	-	_	_	_	_	0.2
La	-	0.07991	_	_	_	_	0.2
Ce	-	1.277	_	_	_	_	0.5
<u>Nd</u>	2.84	-	_	_	_	_	0.2
Eu	0.14	_	_	_	_	_	0.008
<u>Da</u> Yb	-	0.03961	_	_	_	_	0.000
Sm	0.0030	-	_	_	_	_	0.02
<u>Au</u>	0.0020	-	_	_	_	_	0.001
Hg	-	_	0.039	_	_	_	0.1
Th	_	0.8075	-	_	_	_	0.005
U	0.0094	-	_	_	_	_	0.005
0	0.0074						0.01

Table 4 Elemental concentrations (mg/kg) for different yams and Reference Plant(RP)

In Tabe 4 are compared the present results with literature data in other yam species as well as with the Reference Plant by Markert [18]. Comparison with reference data shows that yams grown in different places demonstrate great variability of the elemental concentrations even between the same species. The main reason is probably due to different elemental content of soil in different areas. Moreover, different yam species perhaps exhibit various element accumulation mechanisms.

In our results, Na concentration in tissue is about 5 times higher than that in the Reference plant. This probably explains the medicinal effect of iron stick yam, as it is well-known that sodium is an essential element, which regulates blood volume, blood pressure, osmotic equilibrium and pH; the minimum physiological requirement for sodium is 500 milligrams per day. One may note that the concentration of Cl is almost the same as in the Reference plant.

Comparison with the Reference Plant [18] evidences that the concentrations of Na, Cl, Br, Nd, Eu and Au are much higher in iron stick yam tissue.

According to our results, Br concentration in dry iron stick yam tissue is 7.9 mg/kg that is about 2 times higher than in the Reference Plant. Bromine is also considered essential for mammals [19], producing positive effect on nerve system as a tranquilizer. Its recommended daily allowance (RDA) is 1.5-2.5 mg per day for adults [20, 21].

Abnormally high concentrations of rare earth elements (RREs), neodymium and europium, relatively to the Reference Plant were observed. The role of REEs in human body is under intense investigations [22]. At present there is no standard RDA for neodymium and europium. Nd has good magnetic property as a constituent of Nd2Fe14B magnet and may provide positive influence on blood and brain activity [23]. Meanwhile the toxic characters of lanthanides is still in studying process.

Gold is a trace element in human body and mainly distributed in lung, liver, and spleen [24]. Since the ancient times, pure gold is always used as the food decoration or additive and the constituent of drugs. Gold has the benefit for rheumatoid arthritis [25] and antitubercular [26].

In particular, the concentrations of Al, Au and U are extremely high in peer, and the concentrations of Nd and Eu are abnormally high compared to the Reference Plant. Further studies on element accumulation mechanism in iron stick yam and local soil elemental content will be conducted to clarify the reason of this phenomenon.

CONCLUSIONS

Concentrations of thirty elements in iron stick yam were determined by NAA. Among them, eleven elements (S, Cl, Br, Rb, Sb, Cs, Nd, Eu, Sm, Au and U) were reported for the first time in this kind of species. Determination of the elemental content provides the basis for explanation of the principle and treatment effect of Chinese traditional medicine.

REFERENCES

[1] T. U. Ferguson, Mineral and calorie content of yam tubers. Trinidad, Annual report 1968-1969, Faculty of Agr., Univ. West Indies, 1969.

[2] Hang Yueyu, Zhou Taiyan, Ding Zhizun, et al. Analysis and comparison of amino acids and trace elements of rhizome diosoreae. China Journal of Chinese Materia Medica, 1988, 07: 37-39, 63. (in Chinese)

[3] Huang Daoping, Mo Jianguang, Lao Yanwen, et al. Analysis of comparison of sixteen kinds of elements in Guangshanyao and Huaishanyao. Trace Elements Science, 2002, 02: 47-50. (in Chinese)

[4] Zhou Xinyong, Song Shuhui, Wang Wenqi, et al. Determination of the nutrient contents in the purple D. alata L. and the Dioscorea opposite Thumb. Journal of Anhui Agri, 2010, 38(35): 20005-20007. (in Chinese)

[5] Wu yanbing, Yan zhenmin, Han Weiyuan, et al. Determination of trace elements in Dioscorea opposite Thumb by ICP-AES. Chinese Journal of Spectrometry Laboratory, 2011, 28(2): 842-845. (in Chinese)

[6] Xu Hengjian, Li Cuixiang, Gong Xudong. Contents of mineral elements in different yam varieties. Crops, 2011, 6: 63-67. (in Chinese)

[7] Zhang Jingchao, Zhu Yanying, Ding Xifeng, et al. Study of Dioscorea opposite thumb from different producing areas with XRF and PXRD. Spectroscopy and Spectral Analysis, 2012, 32(7): 1972-1975. (in Chinese)

[8] Abara, A. E. Proximate and mineral elements composition of the tissue and peel of dioscorea bulbifera tuber. Pakistan Journal of Nutrition 2011, 10(6): 543-551.

[9] Akintayo E T, Adetunji A, Akintayo C O. Quality changes and mineral composition of African yam bean (sphenotilis sternocarpa) cooked in kaun (trona) solution. Food/Nahrung, 1999, 43(4): 270-273.

[10] I. Ogunlade, O. S. Owojuyigbe, and M. A. Azeez. Chemical composition and functional properties of four varieties of bitter yam (Dioscorea dumetorum). Bull. Pure Appl. Sci. C, 2006, 25: 7-12.

[11] S. Shanthakumari, V. R. Mohan, and John de Britto. Nutritional evaluation and elimination of toxic principles in wild yam (Dioscorea spp.). Tropical and Subtropical Agroecosystems, 2008, 8(3): 319-325.

[12] Shin Mee-Young, Young-Eun Cho, Chana Park, et al. The supplementation of yam powder products can give the nutritional benefits of the antioxidant mineral (Cu, Zn, Mn, Fe and Se) intakes. Preventive nutrition and food science, 2012, 17(4): 299-305.

[13] W. M. F. Dufie, I. Oduro, W. O. Ellis, et al. Potential health benefits of water yam (Dioscorea alata). Food & function, 2013, 4(10): 1496-1501.

[14] M. V. Frontasyeva, Neutron activation analysis in the life sciences. Physics of Particles and Nuclei, 2011, 42(2): 332-378.

[15] W. R. Marchkesbery, W. D. Ehmann, T. I. M. Hossain, et al. Instrumental neutron activation analysis of brain aluminum in Alzheimer disease and aging. Annals of neurology, 1981, 10(6): 511-516.

[16] T. Fei, L. Dehong, Z. Fengqun, et al. Determination of trace elements in Chinese medicinal plants by instrumental neutron activation analysis. Journal of radioanalytical and nuclear chemistry, 2010, 284(3), 507-511.

[17] P. Avino, G. Capannesi, A. Rosada. Ultra-trace nutritional and toxicological elements in Rome and Florence drinking waters determined by Instrumental Neutron Activation Analysis. Microchemical Journal, 2011, 97(2): 144-153.

[18] B. Markert. Establishing of 'Reference Plant' for inorganic characterization of different plant species by chemical finger printing. Water, Air, and Soil Pollution, 1992, 64(3-4): 533-538.

[19] A. S. McCall, C. F. Cummings, G. Bhave, et al. Bromine is an essential trace element for assembly of collagen IV scaffolds in tissue development and architecture. Cell, 2014, 157(6): 1380-1392.

[20] NRC, Recommended dietary allowances, national research council (US) subcommittee. Washington, DC: National Academy Press, 1989: 241. (PTWI)

[21] M. P. Patricelli, J. E. Patterson, D. L. Boger, et al. An endogenous sleep-inducing compound is a novel competitive inhibitor of fatty acid amide hydrolase. Bioorganic & medicinal chemistry letters, 1998, 8(6): 613-618.

[22] K. T. Rim, K. H. Koo, et al. Toxicological evaluations of rare earths and their health impacts to workers: a literature review. Safety and health at work, 2013, 4(1): 12-26.

[23] M. R. Hinman. Comparative effect of positive and negative static magnetic fields on heart rate and blood pressure in healthy adults. Clinical rehabilitation, 2002, 16(6): 669-674.

[24] M. Yukawa, K. Amano, M.S. Yasumoto, et al. Distribution of Trace Elements in the Human Body Determined by Neutron Activation Analysis. Archives of Environmental Health, 1980, 35(1): 36-44. Erratum, Archives of Environmental Health: An International Journal, 1980, 35(3): 191-191.

[25] P. Ellman, J. S. Lawrence, G. P. Thorold. Gold therapy in rheumatoid arthritis. The British medical journal, 1940, 2: 314.

[26] D. Hebert, The gold treatment of-tuberculosis. The British medical journal, 1926, 7: 158-160.

[27] S.S. Pavlov, A.Yu. Dmitriev, I.A. Chepurchenko, M.V. Frontasyeva. Automation system for measurement of gamma-ray spectra of induced activity for neutron activation analysis at the reactor IBRr-2 of Frank Laboratory of Neutron Physics at the Joint Institute for Nuclear Research. Physics of Elementary Particles and Niclei. 2014, 11(6): 737–742.