

Sains Malaysiana 46(4)(2017): 605–613
<http://dx.doi.org/10.17576/jsm-2017-4604-13>

Neutron Activation Analysis and Assessment of Trace Elements in Fingernail from Residents of Tokyo, Japan

(Analisis Pengaktifan Neutron dan Penilaian Unsur Surih dalam Kuku Penduduk di Tokyo, Jepun)

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ABSTRACT

We report herewith the study of fingernail clippings obtained from the residents of Tokyo, Japan. A total of 18 participants with no health problems and occupational exposure to metals were recruited to provide fingernails samples for this study. Through the use of instrumental neutron activation analysis (INAA), 18 elements (Ag, Al, As, Ca, Cl, Co, Cu, Fe, Hg, K, Mg, Mn, Na, S, Sb, Se, V, and Zn) were determined. The results showed that the toxic elements in the fingernails are in the lower range when compared to literature values. There were no chronic exposures to toxic elements such as As and Hg found. The level of Hg found is lower than that reported 20 years ago, possibly due to the strict regulation control in Japan on the release of Hg to the environment. The elements Se and Zn are found to be rather uniformly distributed among participants and are in agreement with results from other countries. There were no significant differences in elemental concentrations due to genders and smoking habits. The overall data from this study showed similar concentrations to those of healthy participants from other countries. Thus, the current data could represent the background level of elemental concentrations in fingernails of residents in Tokyo, which could serve as reference values for future study.

Keywords: Fingernail; neutron activation analysis; trace elements

ABSTRAK

Kajian ini melaporkan mengenai keratan kuku yang diperoleh daripada penduduk Tokyo, Jepun. Seramai 18 orang subjek yang tidak mempunyai masalah kesihatan dan pendedahan kepada logam telah direkrut bagi menyediakan sampel kuku dalam kajian ini. Melalui penggunaan instrumental analisis pengaktifan neutron (INAA), 18 unsur-unsur (Ag, Al, As, Ca, Cl, Co, Cu, Fe, Hg, K, Mg, Mn, Na, S, Sb, Se, V dan Zn) telah ditentukan. Hasil kajian menunjukkan bahawa unsur toksik dalam kuku berada dalam keadaan yang lebih rendah apabila dibandingkan dengan nilai daripada sumber rujukan. Tiada pendedahan kronik kepada unsur toksik seperti As dan Hg telah dijumpai. Didapati bahawa tahap Hg adalah lebih rendah daripada yang dilaporkan 20 tahun yang lalu, berkemungkinan disebabkan oleh kawalan peraturan yang ketat di Jepun dalam membebaskan Hg ke alam sekitar. Penyebaran unsur Se dan Zn juga didapati agak seragam dalam kalangan peserta dan keputusan ini juga sama seperti negara-negara lain. Tiada perbezaan yang signifikan dalam kepekatan unsur yang disebabkan oleh faktor jantina dan tabiat merokok. Keseluruhan data kajian ini telah menunjukkan kepekatan yang sama dengan subjek sihat dari negara lain. Oleh itu, data semasa dapat mewakili tahap latar belakang kepekatan unsur dalam kuku penduduk di Tokyo, yang boleh dijadikan sebagai nilai rujukan untuk kajian pada masa hadapan.

Kata kunci: Analisis pengaktifan neutron; keratan kuku; unsur surih

INTRODUCTION

Biological tissues such as nails have been utilized as biomonitors for evaluating the environmental pollution level through the studies of trace element composition. Thus, individuals exposed to environmental pollution could be diagnosed through the abnormality of trace element concentrations in nail samples. The reason for using fingernails as diagnostic material is that trace elements accumulated in the nails can reflect the long term exposure to environmental pollution (Menezes et al. 2004). It is known that chemical composition of nail is stable after its formation and will not be affected by blood chemistry or chemical exposure (Daniel III et al. 2004). Besides those, nails can be easily collected and

stored at normal room temperature prior to analysis and small amounts of samples (about 10 mg) are sufficient for chemical analysis.

The chemical compositions of nails may be related to gender, nutrition, occupation, age, disease and season. Hayashi et al. (1993) showed that Cd and Pb in nails of males are higher than those of females. They argue that higher Cd and Pb in males are attributed to outdoor activities or higher dietary intake. Arsenic concentration anomalies (mean of 7.24 µg/g) in nails have been used as an indicator for arsenic poisoning in residents of West Bengal, India, which is caused by consumption of water polluted with arsenic (Samanta et al. 2004). The high concentrations of Cl, Cr, K and

Na in nails can be used as the indicators for person with cystic fibrosis disease (Aguilar & Saiki 2001). On the other hand, patients infected with *Schistosoma mansoni* showed increased level of Al, Cl, I and Br in fingernails compared to healthy individuals (El-Khatib et al. 1995). Thus, elemental concentrations in nails can be a useful indicator for disease diagnosis. Besides, individuals from different regions exhibit variable pattern of trace element concentrations as reported by Takagi et al. (1988) in an international comparison study of nail samples collected from Japan, India, U.S.A, Canada and Poland. Takagi et al. (1988) suggested that dietary intake and living habits of individuals from different regions may affect the trace element concentrations in nails.

There are many analytical techniques usable for the determinations of element concentrations in nails such as atomic absorption spectrometry (Hayashi et al. 1993) and inductively coupled plasma mass spectrometry (Samanta et al. 2004). In this study, instrumental neutron activation analysis (INAA) was selected for the analysis of fingernail samples because of its simple sample preparation and multi-element analysis capability. By using different irradiation and counting schemes, many elements with variable half-lives could be determined reliably. Several studies utilizing INAA for multi-elemental analysis of nail samples have been reported (Aguilar & Saiki 2001; Chaudhary et al. 1995; Cheng et al. 1995; El-Khatib et al. 1995; Menezes et al. 2004; Morris et al. 2006).

In this study, the individuals recruited were university students and staff who stay around the area of Minami-Osawa, Tokyo. Their dietary habits are typical Japanese food consisted of rice, fish, meat and vegetables. They eat at school restaurant during lunch and dinner and drink green tea after each meal. Among the individuals, five were habitual smokers whereas the remaining were non-smokers. To the best of our knowledge, there is no published data on the study of trace elements in fingernails from the residents of Tokyo. Furthermore, multi-elemental analyses of fingernail samples of Japanese are scarcely reported. Thus, this study aims to present the results of trace element concentrations in fingernails obtained from healthy individuals residing in suburban area of Tokyo. In addition, the results from this study were compared to data from literatures reporting elemental concentrations in nail samples.

MATERIALS AND METHODS

SAMPLE COLLECTION AND PREPARATION

The participants of this study are healthy and non-exposed individuals who stay in suburban Tokyo and its vicinity. A total of 18 individuals (11 males, 7 females) participated in this study with an average age of 27.7 years old. Fingernail samples (from 10 fingers) were collected from the participants using a clipper and kept in polyethylene bags. The samples were then transferred

to clean beakers and washed with acetone for 20 min in ultrasonic bath. Then, the nail samples were washed twice with deionized water (MilliQ) for 20 min. Finally, the samples were washed again with acetone for 20 min and dried on a clean bench overnight. After drying, the samples were kept in acid-cleaned glass bottles.

SAMPLE IRRADIATIONS AND DATA ANALYSES

About 10 - 40 mg of fingernail was double-sealed in acid-cleaned polyethylene bags prior to irradiation. The NIST 1566b (Oyster Tissue) was used as a reference standard for the quantification of elemental concentrations, while the NIES No. 5 (Human Hair) and NIST 1577a (Bovine Liver) were analyzed as quality control materials. These control samples were properly dried (at 85°C for 4 h) prior to irradiation. The moisture contents of NIES No. 5 (Human Hair) and NIST 1577a (Bovine Liver) were 7.4 and 3.8%, respectively. Several 10s mg of reference and control materials were used for irradiation. The neutron-irradiation was performed at the research reactor of Japanese Atomic Energy Agency with a thermal neutron flux of about 10^{13} n/cm²/s. All the samples, reference standard and quality control materials were firstly subjected to 2 min irradiations and measured for γ -rays emitted by short-lived radionuclides for 5 min. Then, the samples were secondly irradiated for 20 min and their γ -rays were measured 2 to 3 times with different decay intervals in order to detect radionuclides of variable half-lives. The radionuclides used for determination of elemental concentrations are listed in Table 1. Relative method was used for the quantification of elemental concentrations in the fingernail samples and the quality control materials. All results were presented as dry weight basis.

The results obtained in this study were analyzed using *t*-test to evaluate the difference in terms of gender and smoking habit. When a probability value (*P*) is smaller than 0.05, the difference was considered to be significant. In addition, the compositional relationships among elements in fingernails are evaluated by using correlation matrix.

RESULTS AND DISCUSSION

ANALYTICAL QUALITY CONTROL

The NIES No. 5 (Human Hair) and NIST 1577a (Bovine Liver) were analyzed as analytical quality control samples using INAA technique. These two reference materials were used because many trace elements are certified and suitable as analytical quality controls for fingernail analysis. Their results could be cross-referenced to ensure the reliability of the procedure. The results obtained were presented in Table 2 and compared with literature values. The Hg value for NIES No. 5 (Human Hair) was found to be significantly lower than a certified value. This could be due to vitalization of Hg during irradiation. This could suggest

TABLE 1. Radionuclides (arranged in increasing half-life) used for the determination of elemental concentrations in fingernails

Element	Radionuclide	Half-life	γ -ray energy (keV)*
Al	²⁸ Al	2.24 m	1778.7
V	⁵² V	3.76 m	1434.1
S	³⁷ S	5.06 m	3104
Cu	⁶⁶ Cu	5.10 m	1039.2
Ca	⁴⁹ Ca	8.72 m	3084.4
Mg	²⁷ Mg	9.46 m	1014.4
Cl	³⁸ Cl	37.3 m	1642.2
Mn	⁵⁶ Mn	2.58 h	1810.7
K	⁴² K	12.36 h	1524.6
Na	²⁴ Na	15.02 h	1368.5
As	⁷⁶ As	26.3 h	559.1
Sb	¹²² Sb	2.7 d	564.4
Fe	⁵⁹ Fe	44.5 d	1292
Hg	²⁰³ Hg	46.8 d	279.2
Se	⁷⁵ Se	118.5 d	264
Zn	⁶⁵ Zn	224.1 d	1115
Ag	^{110m} Ag	252 d	657.7
Co	⁶⁰ Co	5.27 y	1332.5

* The γ -ray energies used for quantifications of elemental concentrations

that Hg in hair is bonded less strongly than Hg in bovine liver tissues. Except for Hg, our values are in agreement with certified and literature values within $\pm 15\%$ for most of the elements determined. Therefore, data obtained for fingernails in this study can be acceptable for further discussions.

ELEMENTAL CONCENTRATIONS IN FINGERNAILS

Data of 18 elements in fingernail samples determined using INAA are compiled in Table 3. Among these elements, S is the most abundant with a mean value of 33600 $\mu\text{g/g}$. Mean concentrations of Ca, Cl, Mg and Zn range from 77 to 464 $\mu\text{g/g}$, while those of Ag, As, Co, Hg, Mn, Sb, Se and V are below 1 $\mu\text{g/g}$. Mean concentrations of Al, Cu, Fe, K and Na are between 5 and 17 $\mu\text{g/g}$. In Table 3, the minimum and maximum values are indicated. It is noted that all elements except S, Se and Zn showed large differences in their concentration values. The uniformity of S concentrations in fingernails clearly reflects the fact that S is a major constituent element in nails. The S data from this study are compared with several literature data in Table 4; our data are found to be similar to those of Rodushkin and Axelsson (2000), while the values reported by Cheng et al. (1995) and Olabanji et al. (2005) are about 4 times lower than our data and S values of Jervis et al. (1977) (43 to 360 $\mu\text{g/g}$) are anomalously low. Recently, Dittmar et al. (2008) reported that S contents in nails of healthy Germans ($n = 225$) are about 2.4 to 4.3% with an average value of 3.3%.

Arsenic concentrations in fingernails determined in this study are low (mean of 0.099 $\mu\text{g/g}$), which implies

no chronic environmental exposure for the participants. Apparently, the low As content in the drinking-water in Tokyo (As: < 0.001 to 0.008 mg/L; Suzuki et al. 2004) is reflected in their fingernails. In comparison, As concentration in drinking water in West Bengal, India, was reported to be in the range of 0.1 to 0.23 mg/L (Mandal et al. 1998) and seem to be reflected in fingernails of West Bengali whose mean As concentration is 7.24 $\mu\text{g/g}$ (Samanta et al. 2004), approximately 73 times the mean of this study (As: 0.099 $\mu\text{g/g}$). The ratio of As concentrations of drinking water between the two countries (about 100) is comparable to that of their fingernails. This clearly indicates that drinking-water can be a main source of As in fingernails.

Mercury is widely studied because of its toxicity to humans. Dietary intake is the main source of Hg in humans. Mercury abundances in fingernails obtained in this study (Table 3) were found to be about 8 times lower than those reported 20 years ago by Takagi et al. (1988) for Japanese residents (0.91 $\mu\text{g/g}$). As shown in Table 4, Hg concentrations in fingernails vary among countries but are mostly below 1 $\mu\text{g/g}$. Apparently, the participants of this study were not exposed to high level of Hg through dietary intake compared with those reported by Takagi et al. (1988). Rice is a staple food for Japanese, but it only contributes about 1% of total Hg intake because of low concentration of Hg (below 1 ng/g, Nakagawa & Yumita 1998). According to Nakagawa et al. (1997), major Hg intakes of Japanese people are from fish and shellfish, which contribute about 97% of the total Hg intake from all foods.

TABLE 2. Results for reference materials and comparison with literature values. All values are in $\mu\text{g/g}$ (dry mass basis)

Element	NIES No. 5 Human hair											
	This work			Saiki et al. (1998)			Abugassa et al. (1999)			Certified		
Na	35.8	\pm	3.6	24	\pm	4	27.1	\pm	0.1	26	\pm	1
Mg	235	\pm	59	308	\pm	36	32.4	\pm	0.9	208	\pm	10
Al	259	\pm	21	295	\pm	45	4.60	\pm	0.06			240
S	45100	\pm	2030				209	\pm	4			
Cl	250	\pm	3	252	\pm	10	154	\pm	1	34	250	3
K	35.1	\pm	2.4	30	\pm	3	1.40	\pm	0.02	728	\pm	30
Ca	620	\pm	34	820	\pm	44	0.093	\pm	0.001			
V	0.549	\pm	0.078	0.55	\pm	0.07	3.90	\pm	0.04	5.2	\pm	0.3
Mn	5.12	\pm	0.30	5.00	\pm	0.02				225	\pm	9
Fe	223	\pm	13	197	\pm	19						\pm
Co	0.103	\pm	0.014	0.108	\pm	0.002					0.100	
Cu	15.5	\pm	3.7	13.4	\pm	1.9				16.3	\pm	1.2
Zn	160	\pm	5	162	\pm	5				169	\pm	10
As	0.083	\pm	0.020	0.088	\pm	0.001						
Se	1.27	\pm	0.06	1.47	\pm	0.16					1.40	
Ag	0.104	\pm	0.045									
Sb	0.060	\pm	0.015	0.066	\pm	0.003					0.070	
Hg	1.04	\pm	0.06	4.25	\pm	0.24				4.4	\pm	0.4

Element	NIST 1577a Bovine Liver											
	This work			Andrási et al. (1993)			Wasim et al. (2002)			Certified		
Na	2390	\pm	200	2030	\pm	100	2500	\pm	144	2430	\pm	130
Mg	601	\pm	47	650	\pm	30	614	\pm	19	600	\pm	15
Al												2
S	7610	\pm	267	7160	\pm	200				7800	\pm	100
Cl	2790	\pm	210				2780	\pm	87	2800	\pm	100
K	9400	\pm	520	9540	\pm	180	9840	\pm	75	9960	\pm	70
Ca	121	\pm	5							120	\pm	7
V	0.108	\pm	0.005							0.099	\pm	0.008
Mn	9.49	\pm	0.54	8.9	\pm	1.4	9.8	\pm	0.7	9.9	\pm	0.8
Fe	174	\pm	10	172	\pm	20	195	\pm	22	194	\pm	20
Co	0.240	\pm	0.012							0.21	\pm	0.05
Cu	157	\pm	6	148	\pm	6				158	\pm	7
Zn	113	\pm	3	113	\pm	7	124	\pm	8	123	\pm	8
As	0.051	\pm	0.031				0.052	\pm	0.005	0.047	\pm	0.006
Se	0.788	\pm	0.062							0.71	\pm	0.07
Ag	0.056	\pm	0.030							0.04	\pm	0.01
Sb	0.005	\pm	0.002								0.003	
Hg	0.006	\pm	0.002							0.004	\pm	0.002

COMPARISONS OF ELEMENTAL CONCENTRATIONS IN
FINGERNAILS WITH DIETARY INTAKES
AND REFERENCE MAN

Dietary intake of chemical elements plays an essential role in human nutrition and health. In recent years, collaborative studies joined by many countries have been conducted to determine the reference values for daily dietary intake of chemical elements. In Figure 1, elemental concentrations in nail samples are compared with elemental dietary intakes and elemental compositions of reference man. In this figure, mean values from this work and literatures for nail samples were plotted by arranging the elements in increasing atomic numbers. All values plotted are assumed for healthy individuals representing individual countries. Based on their contents,

elements determined can be divided into two groups: Na, Mg, Al, S, Cl, K, Ca, Fe and Zn vs. V, Mn, Co, Cu, As, Se, Ag, Sb and Hg. Our data showed lower values for elements Na, Al, K, V, Sb and Hg than the literature values. It is noticeable that the data for Japanese reported by Takagi et al. (1988) have higher concentrations of Na, Al, K, V, Sb and Hg than the data of this study. This may be due to lower dietary intake of these elements for the individuals of this study.

From Table 4, it is found that the transition elements V, Mn, Fe, Co, Cu and Zn show an interesting distribution in nails, being different from those for the other elements plotted in Figure 1. When their concentrations are compared among those of dietary intake, reference man (except for V; Iyengar 1998) and literature values,

TABLE 3. Elemental concentrations ($\mu\text{g/g}$ dry mass) in fingernail samples ($n = 18$)

Element	Geometric Mean	Standard deviation (1σ)	RSD (%)	Min.	Max.	Max/Min
Na	16.8	31.6	188	1.79	114	63.7
Mg	77.6	35.1	45.2	28.4	174	6.13
Al	8.62	11.3	131	0.78	49.6	63.6
S	33600	5340	15.9	26600	48900	1.84
Cl	98.9	128	129	29.6	502	17.0
K	11.9	32.4	272	2.65	144	54.3
Ca	464	281	60.6	116	1040	8.97
V	0.0176	0.0197	112	0.0035	0.082	23.4
Mn	0.482	0.475	98.5	0.117	1.76	15.0
Fe	17.7	10.3	58.2	10.2	41.2	4.04
Co	0.0191	0.0312	1.63	0.0052	0.135	26.0
Cu	5.18	1.72	33.2	2.96	10.4	3.51
Zn	104	21	20.2	80.4	159	1.60
As	0.0993	0.0391	38.5	0.051	0.182	3.57
Se	0.998	0.150	15.0	0.801	1.26	1.57
Ag	0.184	0.109	98.2	0.033	7.57	229
Sb	0.0073	0.0069	79.0	0.0019	0.0332	17.5
Hg	0.112	0.047	50.7	0.068	0.224	3.29

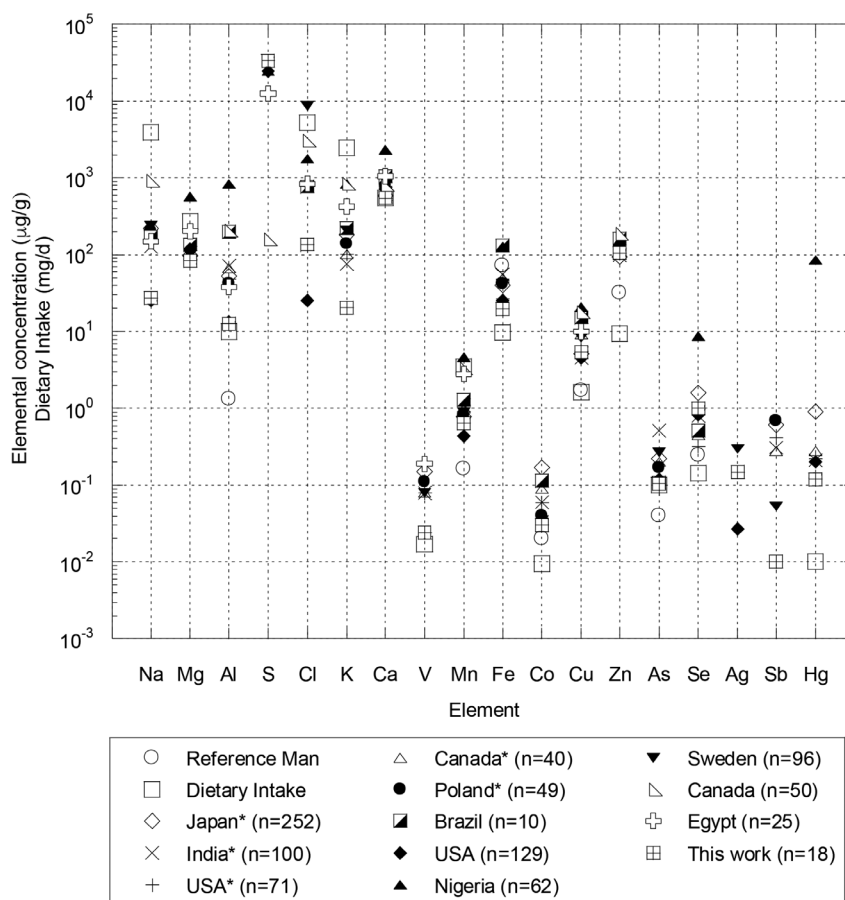


FIGURE 1. Comparisons of mean elemental concentrations of this study with those of literatures, dietary intake (Iyengar 1998; Parr et al. 2006; Shiraishi 2005) and reference man (Iyengar 1998). Elements are arranged according to atomic numbers. The numbers in parentheses indicate sample numbers. The data for countries indicated with asterisks were from Takagi et al. (1988). The values for elemental concentrations and dietary intakes are sharing the same y-axis

TABLE 4. Element concentrations ($\mu\text{g/g}$) in fingernails from this work and literature values

Elements	This work	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Na	1.79 – 114	37 – 960	1.31 – 258		78.9 – 479	375 – 2110	99.4 – 196			3.1
Mg	28.4 – 174	23 – 110	9.4 – 696	129 – 3520	51 – 298	110 – 730	197 – 234			
Al	0.78 – 49.6	12 – 137	1.5 – 59.4	285 – 1940	79 – 354	49 – 940	20.1 – 52.3			
S	26600 – 48900	23400 – 43500	5180 – 36500	5778 – 47460		43 – 360	10630 – 14020			
Cl	29.6 – 502	2020 – 22600	3.9 – 840	188 – 5330	361 – 1510	350 – 7350	675 – 945			332 – 3010
K	2.65 – 144	17 – 1080		121 – 3600	25 – 1960	122 – 1970	331 – 488			368 – 3070
Ca	116 – 1040	345 – 1160	155 – 1620	420 – 5980	343 – 1930	290 – 2130	861 – 1220			
V	0.0035 – 0.082	0.018 – 0.476	0.0026 – 0.17				0.18 – 0.22			
Mn	0.117 – 1.76	0.19 – 3.30	0.043 – 3.6	1.5 – 13	0.503 – 2.95	0.2 – 7.8	2.4 – 3.1	3.51 – 91.3		
Fe	10.2 – 41.2	12 – 189	8.2 – 207	30.1 – 266	50.7 – 246			39.8 – 1970	23 – 72	
Co	0.0052 – 0.135	0.006 – 0.120	0.0076 – 0.19		0.066 – 1.08				0.032 – 0.400	
Cu	2.96 – 10.4	4.2 – 17	1.71 – 34.8	3.89 – 107	3.1 – 55.0	1.6 – 36	14.2 – 18.2	4.60 – 28.8		
Zn	80.4 – 159	80 – 191	60.8 – 290	48.2 – 380	99 – 566	88 – 420		72.8 – 130	88.5 – 495	73 – 304
As	0.051 – 0.182	0.065 – 1.09	0.022 – 0.89	5.9 – 12.5	0.044 – 1.34			0.74 – 36.6	0.210 – 0.637	0.362 – 1.97
Se	0.801 – 1.26	0.62 – 1.53	0.54 – 2.82	10.3 – 33.2	0.359 – 0.809			0.24 – 1.5	0.35 – 0.60	0.0011 – 0.08
Ag	0.033 – 7.57	0.019 – 1.76	0.003 – 0.24						0.004 – 0.075	0.003 – 1.40
Sb	0.0019 – 0.0332	0.014 – 0.128								0.0011 – 0.08
Hg	0.068 – 0.224	0.028 – 0.311	0.027 – 0.77	12 – 312				0.18 – 1.32	0.024 – 0.955	0.357 – 2.80

Data sources:

(1) Sweden: Rodushkin and Axelsson (2000), fingernails, $n = 96$, double focusing SF-ICP-MS method.(2) U.S.A.: Cheng et al. (1995), toenails, $n = 129$, INAA and GFAAS methods.(3) Nigeria: Olabanji et al. (2005), fingernails, $n = 62$, PIXE method.(4) Brazil: Aguiar and Saiki (2001), fingernails, $n = 10$, INAA method.(5) Canada: Jervis et al. (1977), fingernails, $n = 50$, INAA method.(6) Egypt: El-Khatib et al. (1995), fingernails, $n = 25$, INAA method.(7) India: Samanta et al. (2004), fingernails, $n = 33$, ICP-MS method.(8) Italy: Pietra et al. (1985), fingernails, $n = 4$, RNAA method.

(9) Iyengar et al. (1978), compilation of nail values.

TABLE 5. Correlation matrix for elemental concentrations in fingernail samples. The number in bold indicates that a correlation is significant at $P = 0.05$

	Na	Mg	Al	S	Cl	K	Ca	V	Mn	Fe	Co	Cu	Zn	As	Se	Ag	Sb	Hg
Na	1																	
Mg	0.359	1																
Al	-0.081	0.084	1															
S	0.083	0.282	-0.204	1														
Cl	0.174	-0.179	-0.065	0.259	1													
K	0.859	0.025	-0.060	-0.052	0.109	1												
Ca	-0.281	-0.024	0.053	0.239	-0.207	-0.080	1											
V	-0.028	0.090	0.633	0.072	-0.135	-0.033	-0.072	1										
Mn	0.015	0.152	0.748	-0.428	-0.214	0.054	0.211	0.400	1									
Fe	-0.096	-0.007	0.358	-0.468	-0.312	0.357	-0.311	0.034	0.695	1								
Co	-0.147	0.089	0.863	-0.254	-0.054	-0.071	0.102	0.267	0.679	0.319	1							
Cu	-0.119	0.122	0.135	0.477	0.061	-0.070	0.396	0.374	0.204	-0.351	0.073	1						
Zn	-0.335	-0.252	-0.223	0.022	-0.141	-0.204	0.301	0.015	-0.104	-0.508	-0.329	0.292	1					
As	-0.069	-0.030	-0.221	0.250	0.106	-0.035	0.107	0.084	-0.342	-0.115	-0.337	0.294	0.371	1				
Se	-0.388	-0.248	-0.119	0.241	-0.075	-0.313	-0.247	0.215	-0.302	-0.072	-0.199	0.067	0.328	0.288	1			
Ag	-0.165	-0.067	0.024	-0.279	-0.286	-0.111	-0.085	-0.130	0.245	0.586	0.255	0.242	-0.349	-0.157	-0.348	1		
Sb	0.045	0.285	0.787	0.048	0.074	0.033	0.049	0.484	0.584	0.073	0.810	0.393	-0.145	-0.028	0.069	-0.033	1	
Hg	0.133	0.327	0.039	0.098	-0.074	-0.143	-0.205	-0.028	0.062	0.641	0.004	0.161	-0.151	0.355	0.030	0.135	0.205	1

these elements behave in the same order, implying the mutual relationship between dietary intake and elemental accumulation in nails. From the present observation, it seems likely that dietary intake exerts a greater influence to the presence of V, Mn, Fe, Co, Cu and Zn in human bodies than other factors such as environment, living habits, genders and geography. Similar elemental patterns of nails, dietary intake and reference man lead to an understanding that the absorption of these elements is counterbalanced by their excretions in human body. In addition, Iyengar (1998) pointed out that elements not physiologically controlled in blood are expected to show variations similar to constituents in the food. For the other elements in Figure 1, different population groups showed variable concentrations in nails, meaning that these elements are more susceptible to changes due to body physiological control, environment, living habits and other factors. Thus, nail serve as a good biomonitor for chemical elements present in human body.

CORRELATIONS BETWEEN ELEMENT CONCENTRATIONS IN FINGERNAILS

Correlation coefficients showed potential relationships or interactions between two elements in nail samples and examples have been reported by Chaudhary et al. (1995), Cheng et al. (1995), Samanta et al. (2004) and Slotnick et al. (2005). Correlation coefficients of this study are shown as correlation matrix in Table 5. Through the use of *t*-test, significant correlations at the level $P = 0.05$ for the elements were identified in bold in Table 5. The elements Na and K showed the highest correlation coefficients ($r = 0.859$, $P < 0.001$) among all the other pairs of the elements. There are also significant correlations between Na with Mg ($r = 0.359$) and between Na and Se ($r = -0.388$). The elements K, Na and Mg are abundant in biological tissues and may behave coherently. The element Al correlates significantly ($P < 0.001$) with Co, Mn, Sb and V, which may reflect exposures to different sources because dietary intakes of these elements are very little (below 10 mg/d). Cheng et al. (1995) reported that Al correlate with Mn and V in toenails. It is said that excessive dietary intake of Zn can cause Cu deficiency (Fraga 2005). Considering no negative correlation between Zn and Cu in this study, it is implied that both elements are in good balance in participating people. For elements As and Hg, a significant correlation was observed in this study. Because this study involves healthy and uncontaminated individuals, the correlation of As and Hg suggested that there is minimal exposure to As and Hg from dietary intakes. The element Ag is found to correlate positively with Fe and negatively with Zn and Se. The element Cl has no significant correlation with other elements determined in this study. Further study on the inter-element interactions is needed to explain the correlations of chemical elements observed in nails.

CONCLUSION

In this study, fingernails from 18 healthy individuals have been collected and analyzed. The use of INAA has been

successfully performed for the elemental determination of nail samples and results are verified with quality control materials. The Hg level found in this study is lower than that reported 20 years ago, highly due to strict environmental control in Japan. The elemental concentrations of Co, Cu, Fe, Mn, V and Zn in fingernails were found to reflect the dietary intakes. These elements showed similar patterns to those for dietary intakes and reference man. This finding appeals the effectiveness of nails as a biomonitor. A correlation matrix displayed a complex relationship among elements in nails. Significant correlations were found between Na and K and Na and Mg. The results of this study could represent the current background level for the people of Tokyo, Japan.

ACKNOWLEDGEMENTS

The authors would like to thank the participants of this study for providing their fingernail samples. One of the authors (B.S.W.) greatly appreciates the Ministry of Education, Culture, Science and Technology of Japan (MEXT) for funding. Neutron irradiation was made possible through the inter-university program for the cooperative use of the JAEA reactors supported by University of Tokyo and MEXT.

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Received: 28 June 2016

Accepted: 18 September 2016