Elemental Composition of Head Hair and Fingernails of Some Nigerian Subjects

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ABSTRACT

In this article, we present the elemental concentrations determined by INAA for 30 elements measured in some or all head hair samples of 100 Nigerian subjects and 20 elements in the fingernails of some of the same subjects. Measurements of the skewness of the distribution of each element in both tissues confirm previous reports that many tend toward a log-normal distribution. Thus, their concentrations in the tissues may not be under any homeostatic control. The ranges of elemental concentrations together with the medians, and the arithmetic and geometric means, with their respective standard deviations are presented and compared with literature values for other populations. Correlations between elements detected in hair are also sought.

Index Entries: Elemental baseline levels; head hair and nails neutron activation analysis; Nigerian subjects.

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INTRODUCTION

The use of the metabolically inactive tissues, hair, and nails in biomonitoring has become well established, especially in investigating the levels and changes of many trace elements accumulated in the body over long periods of time. The ease of sample collection, transport, storage, and preparation, coupled with the usually elevated levels of several trace elements in these tissues have compelled further research even in the face of the well-known shortcomings of these tissues as biomonitors. Such shortcomings include problems with exogeneous contaminants and interpretation of the results. At the present time, hair is being used to study human trace element metabolism *(1,2)* assessing environmental pollution and occupational exposures *(3–5)*, in practical interpretation of the elemental distributions of immediate "human" environment (water supply, cosmetics, smoking habits, and so forth) *(6,7)*, and generally in epidemiological studies *(8,9)*.

The use of nails in biomonitoring is not as widespread as hair, but it is increasing in recent times. The applicability of nails to some of the uses mentioned above has been reviewed by Jenkins *(10)* and also Berlin *(5)*, whereas the possibility of substituting or complementing hair with nails has been investigated by Oluwole and coworkers *(11,12)*.

Before these tissues could be reliably used in any of the applications highlighted above, the baseline levels of the trace elements of interest in "normal" subjects within the same geographical and socioeconomic environment had to be established first. In this article, we have determined the baseline levels of the 30 elements, Ag, Al, Au,* Ba, Br,* Ca, Ce,* Cl, Co,* Cr,* Cs, Cu,* Eu,* Fe,* Hg,* I, La,* Mg, Mn, Na,* S, Sb,* Sc,* Se,* Sm,* Tb, Ti, V, Zn,* and Zr, from a population comprising 100 normal Nigerian subjects, using instrumental neutron activation analysis (INAA). The 16 asterisked elements together with K, Th, Hf, and Rb were also determined in the toenails of some of the same subjects, predominantly the children (age < 15; $n = 21$). The distribution pattern of each element, as well as correlations between the different elements in hair were also investigated. Corresponding values in nails have been reported elsewhere *(12,13)*. The baseline levels recorded in this work for both head hair and fingernails are compared with available data from other regions of the world *(14–17)*.

MATERIALS AND METHODS

Population and Sampling

Scalp hair samples were collected from 100 volunteers (45 males, 55 females), whereas fingernail samples were also collected from 21 of the pedriatric subjects. The ages of the subjects ranged from 3–60 yr. Hair samples were obtained consistently from the left side of the nape, 3–5 mm from the scalp. Nails were obtained from the fingers using a pair of nail clippers. Our procedure for washing of hair samples is similar to the one described previously by Othman and Spyrou *(18)*. It comprised repeated washing and decantation for about 2 h in an ultrasonic bath using only deionized water. A few of the hair samples were viewed under a Scanning Electron Microscope to assess the extent of external contamination. A similar protocol was observed for the nails, except that the nail surfaces were first scraped clean of any exogeneous material using a plastic toothbrush, before the washing.

Analysis

Irradiations were carried out both at the Washington State University (WSU) TRIGA III-fueled research reactor (thermal neutron flux ≈6 × 10^{12} neutrons/cm^2/s) and at the Imperial College Reactor Centre (ICRC) (thermal neutron flux ≈2 × 10^{12} $n/cm^2/s$ for short irradiations and ≈1 × 10^{12} $n/cm^2/s$ for long irradiations). The samples were analyzed as three sets. Set A, comprising 21 pediatric subjects, and Set B, comprising 52 adults, were analyzed for both "intermediate" and "long-lived" elements at WSU, whereas Set C, comprising 27 individuals, was analyzed at the ICRC using both short and long irradiation.

At the WSU, the intermediate-lived isotopes ^{198}Au, ^{47}Ca, ^{152m}Eu, and ^{24}Na were determined by irradiating the samples for 1 h and counting for 1800 s each after allowing initial decay of about 3 d. The long-lived isotopes ^{131}Ba, ^{141}Ce, ^{60}Co, ^{51}Cr, ^{134}Cs, ^{152}Eu, ^{59}Fe, ^{75}Se, ^{160}Tb, ^{65}Zn, and ^{95}Zr were determined by counting for 5000 s after about 2 wk of decay following an 8-h irradiation. NBS fly-ash was used both as neutron flux monitor and a comparator standard.

At the ICRC, the relatively short-lived isotopes ^{24}Na, ^{27}Mg, ^{37}S, ^{38}Cl, ^{49}Ca, ^{51}Ti, ^{52}V, ^{56}Mn, ^{66}Cu, ^{80}Br, ^{85m}Sr, and ^{128}I were determined by irradiating the samples for 360 s, followed by a waiting time of 60 s and a counting time of 360 s. For the intermediate and long-lived isotopes ^{46}Sc, ^{60}Co, ^{59}Fe, ^{82}Br, ^{110m}Ag, ^{153}Sm, ^{131}Ba, ^{203}Hg, ^{140}La, and ^{198}Au, about 30 h of irradiation were carried out, followed first by 5 d of initial decay and 3600 s of counting, as well as a further 1 wk of decay and 5000 s of counting. Bowen's Kale and single-element standards deposited on a filter paper (for Ti, Cu, I, Hg, Sc, Cs, Co, Ag, Cr, Sb, and Au) were used as comparator standards, whereas pure thin zirconium wires were used as flux monitors, thus allowing us the possibility of carrying out "absolute" analysis, at a later stage.

RESULTS AND DISCUSSION

The arithmetic mean, geometric mean, and their respective standard deviations together with the median, range, and skewness of elemental distribution, γ_1, of the concentrations of each element in hair is shown are Table 1, whereas the levels of the elements in fingernails in pediatric subjects are shown in Table 2, which also compares the levels with those

Table 1
Concentrations (μg/g) of Elements in Head Hair of Nigerian Subjects

Element	No.*	Arith Mean (±SD)	Geom Mean (x+GSD)	Median	Range	γ_1
Ag	6	1.79 (0.94)	1.533 (1.810)	1.735	0.45-2.80	0.18
Al	27	93.7 (58.7)	71.6 (2.2)	69.17	9.48-210.0	0.51
Au	75	0.047 (0.105)	0.012 (25.6)	0.017	0.006-0.88	2.00
Ba	6	24.5 (6.8)	23.3 (1.3)	21.2	15.6-36.3	0.22
Br	63	16.8 (36.7)	2.73 (6.14)	33.73	0.16-282.2	2.71
Ca	27	2659.7 (1252.8)	2295.1 (1.8)	2534.0	487.4-5543.0	0.41
Ce	27	1.44 (1.51)	0.81 (3.00)	1.17	0.25-6.87	1.77
Cl	27	654.3 (573.9	430.8 (2.5)	446.6	68.39-2724.2	1.65
Co	77	0.399 (0.273)	0.309 (2.039)	0.437	0.06-2.009	1.77
Cr	66	2.594 (2.373)	1.909 (2.435)	3.54	0.31-14.42	1.25
Cs	36	0.221 (0.133)	0.178 (1.922)	0.184	0.034-0.604	1.03
Cu	23	29.95 (18.94)	22.97 (1.99)	22.8	2.12-64.77	0.62
Eu	50	0.051 (0.037)	0.040 (1.98)	0.042	0.01-0.145	1.40
Fe	77	202.6 (133.1)	176.8 (42.8)	213.0	26.7-559.9	0.63
Hg	9	0.17 (0.09)	0.30 (0.01)	0.13	0.09 0.33	1.04
I	27	5.565 (6.482)	3.109 (2.777)	2.30	0.45-37.62	2.97
La	55	0.900 (1.280)	0.180 (4.460)	0.370	0.015-6.109	2.02
Mg	22	269.1 (150.7)	239.3 (1.635)	276.6	79.16-599.0	0.75
Mn	26	8.62 (4.74)	7.44 (1.71)	8.08	2.72-21.93	1.09
Na	60	165.9 (165.9)	89.34 (3.66)	96.3	4.38-216.0	0.10
S	27	26700 (6570)	25800 (1)	26500	3180-40000	- 0.62
Sb	74	0.397 (0.586)	0.202 (3.225)	0.690	0.003-3.94	1.22
Sc	75	0.058 (0.047)	0.040 (32.561)	0.059	0.004-0.25	0.34
Se	23	0.559 (0.438)	0.419 (2.113)	1.156	0.10-1.863	- 0.28
Sm	53	0.013 (0.012)	0.010 (2.223)	0.013	0.001-0.016	1.73
Tb	39	0.084 (0.110)	0.050 (2.624)	0.047	0.006-0.608	3.12
Ti	19	25.89 (22.32)	18.564 (25.891)	20.92	2.64-84.35	1.27
V	27	0.323 (0.244)	0.257 (1.966)	0.21	0.08-0.99	1.19
Zn	77	124.8 (79.0)	129.4 (1.7)	178.5	8.89-550.5	1.86
Zr	15	92.79 (50.76)	72.2 (1.9)	95.6	21.2-220.3	0.53

*No. is the no. of samples in which element is detected. Extraneous values are not included in means, but included in median.

obtained elsewhere. Our results were compared with elemental levels in hair obtained from Japanese *(14)*, Bulgarian *(15)*, and Chinese *(16)* subjects, as well as the averages of worldwide mean values compiled by Iyengar et al. (*17*). It has been suggested by Liebscher and Smith *(19)* and also Othman and Spyrou *(18)* that the distribution of elemental concentrations in tissues could be used to determine whether or not those elements are essential in body metabolism. Also Evans and Jervis *(20)* have shown that the distribution should determine the way that the results obtained should be interpreted. Usually, the distribution is determined by plotting for each element, a frequency distribution diagram, and then guessing the function that fits the shape *(18,21)*. Since several elements have been shown to have log-normal distribution in hair and nails, another approach has been to transform the concentrations measured logarithmically and see how good the fit is to a straight line on a log-linear sheet *(14)*. All these could be tedious, in addition to their not being truly quantitative. In this work, we have determined the skewness of the distribution of each element γ_1, using a formula proposed by Pearson *(22)*. γ_1, was obtained first by transforming the individual concentrations X into a z-score ($\approx[X - \bar{X}]/\sigma$, where $\bar{X}$ is the mean and s the standard deviation of the distribution). Cubing the z-scores and then finding their means yields γ_1, as shown below:

$$\gamma_1 = \sum_{i=1}^{N} z_i^3/N \quad (1)$$

The various values for γ_1 shown in Table 1 can be better appreciated by considering the transformations given by Glass and Hopkins *(22)* for a given normal distribution X (γ_1 = 0.0), which when transformed into the distributions of X^2, X^3, $1/X$, $\sqrt{X}$, and log X, respectively, have the skewness parameters $\gamma_1 = 1.2$, $\gamma_1 = 2.1$, $\gamma_1 = -0.3$, and $\gamma_1 = -0.7$.

Values obtained in this work agree well with the distribution diagrams of Qureshi et al. *(21)* for the elements Au, Co, Cr, Cu, Fe, Hg, Mn, and Sb, and also with results plotted by Othman and Spyrou *(18)* for Ca, Mg, and V. However, whereas the shapes for the distribution of Zn by Qureshi and Cu, Hg, Mn, and Zn by Othman and Spyrou agree with our values, the degrees of skewness (magnitudes) do not agree well. There is outright disagreement in Qureshi's distribution of Ag and ours, but ours has been obtained from only six individuals, which is not large enough to determine a distribution reliably.

The Nigerian subjects in this work have comparable levels of trace elements in their hair relative to subjects from other countries. In comparing these values, allowance should be made for differences in sample preparation, especially washing, which could introduce significant differences. For the Bulgarian subjects *(15)* for which results for different washing techniques were available, we have chosen the results obtained under conditions closest to ours.

In general, the elements Ag, Br, Ca, Co, Cr, Cu, I, Mn, Na, Sb, and V have higher mean values relative to the literature data (Mn is lower than Kenyan values, *[18]*), but the ranges are in good agreement. In sum, the differences in mean values are not statistically significant, since they

Table 2
Trace Elements in Fingernails of Nigerian Pediatric Subjects (in μg/g)[a]

Elt	THIS WORK (NIGERIA)				BANGLADESH (PIXE)			Other Available References
	No.	Range	Arith. Mean (±std dev)	Geom. Mean (x+std dev)	Range	Arith Mean	Geom Mean	
Sm	19	0.021-0.413	0.148 (0.098)	0.118 (1.732)	-	-	-	-
Au[b]	19	8.05 - 38.89	20.57 (8.58)	18.65 (1.47)	-	-	-	-
La	19	0.169-3.297	1.114 (0.750)	0.896 (1.733)	-	-	-	-
K	19	732.4-3657	2043.9 (858.7)	1842.2 (1.5)	25 - 241	91.1 ± 41.0	82.4 (1.56)	357-2800[*,23]
Ce	15	0.446-8.729	3.223 (1.971)	2.650 (1.704)	-	-	-	-
Th	15	0.064-1.58	0.402 (0.371)	0.291 (1.934)	-	-	-	-
Hf	8	0.139-1.731	0.626 (0.491)	0.458 (2.208)	-	-	-	-
Eu	19	0.072-0.701	0.274 (0.174)	0.227 (1.734)	-	-	-	-
Cr	19	2.233-20.38	9.651 (5.393)	8.031 (1.848)	-	-	-	-
Sc[b]	18	56.74-614	270.58 (140.88)	233.4 (1.6)	-	-	-	-
Fe	17	411.4-2434	1276.7 (570.1)	1150.3 (1.5)	15.6-360.0	77.8 (67.2)	64.4 (1.89)	27-347[*,23]
Zn	19	104.0-261.6	162.6 (40.6)	157.7 (1.2)	72.0-171.0	113 (20)	112 (1.19)	73-304[*,23]; 83-200[*,13]; 129[†,13]
Co	19	0.189-3.388	1.016 (0.684)	0.841 (1.685)	-	-	-	-
Sb	18	0.3-6.0	1.497 (1.441)	0.992 (2.337)	-	-	-	-
Cu	18	26.97-104	54.9 (22.3)	50.565 (1.439)	1.67 - 27.2	6.85 (4.40)	5.26 (1.65)	31[†,14]; 7.5[†,15]; 3-18.6[*,15];
Br	19	5.21-36.7	15.15 (8.42)	13.06 (1.62)	0.68 - 4.03	1.65 (0.71)	1.52 (1.50)	-
Na	18	835.2-3261	1640.9 (610.0)	1537.7 (1.35)	-	-	-	152[†,14]
Se	10	0.634-3.536	1.482 (0.763)	1.333 (1.425)	0.41-2.00	1.28 (0.34)	1.24 (1.36)	-
Hg[b]	4	99.56-972.4	375.2 (348.0)	258.3 (2.4)	-	-	-	-
Rb	5	4.381-9.357	7.31 (1.66)	7.09 (1.28)	0.54 - 2.68	1.41 (0.54)	1.29 (1.54)	-

*Range
†Arithmetic Mean.
[a]If not otherwise stated.
[b]μg/g.

can be accounted for by the standard deviations. On the other hand, the elements Zn, Se, Cs, and S, although also agreeing in the ranges, have mean values lower than those found in the literature. Mean values for La in Nigerian subjects are comparable to those in the literature, but a few high values extend the high limit far beyond literature values. In all cases, however, the mean values are within the range of average mean values compiled by Iyengar et al. *(17)*. Good agreement between both means and ranges of levels in Nigerian subjects and literature was observed for Au, Cl, and Mg. However, Al, Ce, Ti, Eu, and Fe are much elevated in Nigerian subjects. Other elements, including Eu, Ba, and Zr, could not be compared because of unavailability of literature data.

Intercomparison of the nail data is difficult also because of unavailability of literature data. The few available references usually involve just a few elements. The only available baseline measurements on nails was on a Bangladeshi population *(23)* with the analysis carried out by PIXE. In general, the values obtained in the nails of Nigerian subjects for K, Fe, Br, and Rb are higher than the Bangladeshi one by about an order of magnitude. Na was compared with values for Kenyan subjects *(18)*, whereas Cu was compared with both Kenyan *(18)* and German *(24)* data. For both elements, values in Nigerian subjects are higher. K, Zn, Se, and As levels are, however, similar in Nigerian results and the literature data. It should be noted that whereas the Bangladeshi population considered here comprised adults only, the Nigerian subjects were pediatric subjects from low-income parents whose fingernails are prone to considerable contamination through occupational exposure, as has been observed in a previous IAEA report *(25)*. Moreover, for most elements where other references are available, levels in the Bangladeshi population were found to be much lower.

Correlations between elements in nails have been previously reported by us *(12,13)*. In hair, correlations were sought between elements detected in the three sets of subjects used in this work. However, correlations between elements that are log-normally distributed might be better reflected by considering rather the logarithmic concentrations of the elements *(14,24)*. We have also done this (Table 3).

Strong correlations were observed within the rare earth elements Sm, Eu, and La, and the transition elements Fe, Sc, Co, and Sb; among the halogens Br, Cl, and I together with Cu and Na; and also among other elements, such as Mg, S, Ca, V, Mn, and Al. Many of these interelemental correlations coincide well with correlations of elements found in Japanese hair *(14)*. In the Japanese, the elements K, Mn, V, Al, Cl, Br, and I also clustered together and were found to have medians that decrease gradually with increasing age, whereas another group comprising Cu, Mg, Ca, Zn, and S has medians that increase gradually with increasing age. These correlation patterns could also suggest the form of the compound in which most of the elements are stored. For instance, considering the table, Na would be complexed mostly with Cl (NaCl) and to a smaller extent with Br, whereas most of I would be complexed in hair with Cu.

Table 3
Statistically Significant ($p < 0.05$) Elemental Correlations in Hair Using (a) Concentrations and (b) Logarithm of Concentrations in Hair

Elt	Correlating Elements (using concentrations)	Correlating Elements (Log concentrations)
Al	V*, Mn*	Mn***, V*
As	Sc, Fe, Zn, Au*	Co
Au	Sc, Zn, As**	La**, Sc, Fe, Zn, Sm, Co**
Br	Co, Eu, La, Na, Sc**, Cl***	Ti, Co*, Eu*, Fe***
Ca	S*, Mg***	Mg***
Co	Br, Cr*, Sc**, Sm**, La***, Sb***, Eu†, Fe†, Zn†	Sb, As*, Br*, Sm***, Au***, La***, Sc***, Fe†, Zn†, Eu†, Sb*
Cl	Br***, Na†	S*, Cu**, Na***
Cu	Zn*, Na†, I†	I*, Mg*, Cl**
Cr	Zn*	Sb*
Eu	Br, Sm**, La***, Sc***, Fe†, Co†	Br*, La*, Sm*, Sb*, Sc*, Fe***, Co†
Fe	Sm†, Eu†, La†, Sc†, Zn†, Co†, Sb†	Au, Sb*, Br***, Eu***, Co†, Sc†, Sm†, La†, Sc†
I	Cu†	Cu*
La	Br, Co***, Eu***, Fe†, Sc†	Sb, Eu*, Au**, Co***, Sc†, Fe†, Sm†
Mg	S*, Ca***	S, Cu*, Ca***
Mn	Al*, V***	V**, Al***
Na	Br, Eu**, Cu†, Cl†	V, Cl***
S	Mg*, Ca*	Mg, Cl*
Sb	Fe†, Zn†	La, Co*, Cr*, Fe*, Eu*
Sc	Ag, Au, Br**, Co**, Eu***, Sm†, La†	Au, Eu*, Co**, Sb***, Fe†, Sm†, La†
Sm	Fe, Co**, Eu**, La†,Sc†, Fe†	Au, Eu*, Co***, La†, Sc†, Fe†
Ti	-	Br
V	Al*, Mn**	Na, Mn**, Al†
Zn	Au, Cr, Cu*, Fe†, Co†, Sb†	Au, Sc, Co*

*Implies $p < 0.025$, **implies $p < 0.01$; ***implies $p < 0.005$; †implies $p < 0.0005$.

It is interesting to note that although most patterns are retained, a few changes are seen in the correlation patterns when the logarithms of the concentrations are correlated together. This agrees with the observed fact that the correlation between elements could be destroyed when the distribution is distorted, as for example in permanent hair wave treatment. Perhaps extensive sample washing, especially with chemicals, will produce the same effect.

SUMMARY

Baseline for 30 elements in the head hair and 20 elements in the fingernails of some Nigerian subjects has been presented and compared with similar results from other countries. There is no evidence of any major deficiency or excess accumulation of elements in our Nigerian subjects relative to these other results. The skewness of the elemental distributions has also been quantitatively measured and compared with available data. Elemental correlations found between elements in hair were noted. For some elements, it might be more appropriate in seeking correlations to transform first the concentration values appropriately to reflect their distribution in hair.

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