

Nuclear Methods in Environmental Science Section

TRACE ELEMENT CONCENTRATION IN HEAD HAIR OF THE INHABITANS OF THE RAWALPINDI-ISLAMABAD AREA

I. H. QURESHI, M. S. CHAUDHARY, S. AHMAD

*Nuclear Chemistry Division, Pakistan Institute of Nuclear Science and Technology,
P. O. Nilore, Rawalpindi (Pakistan)*

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Instrumental neutron activation analysis technique has been used to determine the concentration levels of 12 trace elements in human head hair samples collected from 105 individuals living in various areas of Rawalpindi-Islamabad. The data show that the average concentrations of Mn, Co, Ag and Au are higher in the female group as compared to the male group. Four individuals were found to have elevated levels of Se due to the use of anti-dandruff shampoos, whereas two individuals had elevated levels of Hg.

Introduction

The ever-increasing release of toxic trace elements and chemicals in the environment from agricultural and industrial activities of man tends to contaminate the biosphere with foreign chemicals.^{1,2} Pollution of the biosphere is likely to contaminate man as these chemicals may find their way to human organism through the environment and food chain.³⁻⁵ The higher concentrations of these elements in the human body may adversely affect human health.^{2,6} Therefore, it is important to determine the concentrations of the trace elements in various human organs so as to determine base line levels and to indicate contamination. Biological monitoring of trace elements in man is a complex problem as it involves a number of factors.^{2,7,8} Further it is very difficult to obtain samples in a standard and quantified manner from a living person to determine trace element distribution and composition in the whole body. Therefore, a suitable tissue or substrate may be used as an indicator of human contamination. Head hair, which can be easily obtained from a living person, can be used as a preliminary indicator for monitoring the levels of trace elements in human body.⁹⁻¹³ Trace element concentrations of head hair may reflect short or long term variations in the corresponding blood-

levels.^{1,4} Since hair is a metabolically dead tissue, it may store a record of past concentrations of trace elements in the body.^{2,8} Further, the concentrations of trace elements in head hair are generally higher than those in other tissues which facilitate the analysis. The elemental analysis of hair may provide useful preliminary information on the trace element levels of the body which can then be supplemented by the analysis of other tissues.

The present study was undertaken to determine the prevailing concentration levels of twelve trace elements in head hair samples of people living in various areas of Rawalpindi-Islamabad. The samples were analyzed using Instrumental Neutron Activation Analysis technique.

Experimental

Sample collection

Head hair samples were collected from 105 persons including 45 female and 60 male donors. The donors belong to different social and occupational groups and their ages range from 4 to 55 years. The samples were obtained by clipping hair strands with pre-cleaned stainless steel scissors from four to five different places close to the scalp. These samples were assigned code numbers and stored in small paper envelopes. The particulars of the donors were also obtained and recorded.

Prior to analysis, the greasy material and adhering dust was removed by washing the sample successively with 25 ml portions of analytical grade alcohol, twice with deionized water and finally with alcohol. After final washing the samples were air-dried at room temperature in a dust-free area.

Irradiation and radioassay

About 50 to 100 mg of the samples were sealed in pre-cleaned polyethylene vials for short irradiations. Three samples together with two standards were packed in another container and irradiated for a period ranging from 30 s to one hour at a thermal neutron flux of $2 \cdot 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ in the pneumatic tube facilities of PINSTECH research reactor PARR-I. For longer irradiations the samples were sealed in quartz vials then packed in aluminium containers and irradiated in the core of the reactor.

After appropriate cooling, the irradiated samples and standards were carefully transferred to other vials and reweighed. The gamma-ray spectrometry measurements were made with a co-axial 30 cm^3 Ge(Li) detector (ORTEC Model 8011) coupled to a charge sensitive preamplifier (ORTEC Model 120-4) and a spectroscopic amplifier (ORTEC Model 2010), which incorporates a pole zero cancellation system.

The pulses from the amplifier were analyzed by a semi-computerized Nuclear Data Multichannel Analyzer (ND-4410) having an 8 K memory. The spectrum was stored in 3072 channels. The system has an energy resolution (FWHM) of 2.1 keV for 1332.5 keV gamma-rays of ^{60}Co and a peak to compton ratio of 40 : 1.

Results and discussion

Optimum conditions for obtaining interference-free photopeaks of the desired elements were determined by varying irradiation and cooling times and studying the gamma-ray spectra. It was observed that Mn, Cu, As and Au can be determined using short irradiation times, whereas Zn, Fe, Co, Cr, Ag, Sb, Se and Hg require longer irradiation. The optimum irradiation and cooling times along with the relevant nuclear data of these elements are listed in Table 1. The photopeaks of ^{203}Hg at 279 keV and that of ^{75}Se at 280 keV cannot be resolved. Therefore, the contribution of ^{75}Se to this unresolved peak was calculated and the necessary correction was applied to determine the amount of Hg from this peak. Similar correction was applied for the contribution of ^{24}Na in the 511 keV peak of ^{64}Cu .

In order to check the accuracy of our method a US NBS Standard Reference Material No. 1571 (Orchard leaves) was analyzed and compared with the certified values in Table 2 which shows fairly good agreement. This method was then used for the determination of 12 elements in the hair samples. All the samples were analyzed in triplicate and the average values were calculated.

The arithmetic mean and standard deviation, the geometric mean and geometric standard deviations, the median and the range of concentration of all the elements analyzed were computed. The results are summarized in Tables 3 and 4 for male and female groups, respectively, whereas the results of all the samples are presented in Table 5. The population distributions of these elements are plotted as histograms of concentration in linear co-ordinates in Fig. 1.

The comparison of the data for male and female groups does not show any significant differences except for Mn, Co, Ag and Au. The concentrations of these elements are higher in the female group. It is rather difficult to find a possible explanation for higher concentrations of Mn and Co in the female group. However, the higher concentration of Ag and Au in the female group may possibly be due to the extensive use of silver and gold jewelry in our society.

The arithmetic mean, geometric mean and median values for Zn and Se show good agreement and comparatively lower relative standard deviations, which indicate a low scatter in the data. The frequency histograms also indicate approximately gaussian distribution for these elements. The other elements studied show

Table 1
Nuclear data for the elements^{1 5}

Nuclide	Abundance, %	Cross-section, b	Radionuclide used (Half-life)	γ -Ray used, keV	Irradiation time	Cooling time
⁵⁵ Mn	100.0	13.3	⁵⁶ Mn (2.56 h)	847	2 m	2 h
⁶³ Cu	69.1	4.5	⁶⁴ Cu (12.7 h)	511 (1345)	1 h	12 h
¹⁹⁷ Au	100.0	98.8	¹⁹⁸ Au (2.695 h)	411.8	1 h	2 d
⁷⁵ As	100.0	4.5	⁷⁶ As (26.4 h)	559 (657)	1 h	2 d
⁶⁴ Zn	48.9	0.78	⁶⁵ Zn (244 d)	1115.5	48 h	2 w
⁵⁸ Fe	0.3	1.1	⁵⁹ Fe (45.6 d)	1099 (1292)	48 h	2 w
⁵⁹ Co	100.0	19.0	⁶⁰ Co (5.2 y)	1173 (1332)	48 h	4 w
⁵⁰ Cr	4.3	17.0	⁵¹ Cr (27.8 d)	320	48 h	4 w
¹⁰⁹ Ag	48.17	4.5	^{110m} Ag (250.4 d)	763 (884, 937)	48 h	4 w
¹²¹ Sb	57.2	6.0	¹²² Sb (60.6 d)	1691	48 h	4 w
⁷⁴ Se	0.87	30.0	⁷⁵ Se (120.4 d)	264 (136, 279.5)	48 h	4 w
²⁰² Hg	29.8	4.0	²⁰³ Hg (46 d)	279	48 h	4 w

Table 2
Analysis of NBS SRM-1571 (Orchard leaves)

Element	Certified value, ppm	Our value,* ppm
Cu	12 ± 1	13.5 ± 1.5
Mn	91 ± 4	94.8 ± 4
Zn	25 ± 3	27.3 ± 2.1
Fe	300 ± 20	296 ± 8
Co	(0.2)**	0.22 ± 0.03
Cr	2.6 ± 0.3	2.8 ± 0.2
Au	N. A.	0.001 ± 0.0005
Sb	2.90 ± 0.3	2.72 ± 0.2
As	10 ± 2	12.7 ± 2
Se	0.08 ± 0.01	0.09 ± 0.01
Hg	0.155 ± 0.015	0.168 ± 0.01

*Average of 3 determinations. The error quoted is the standard deviation of these measurements.

**Uncertified value.

N. A. – Not reported by NBS.

Table 3
Trace element concentration in male hair samples (ppm)

Element	Range	A. M.	G. M.	Median	S. D.	G. S. D.
Cu	3.9 – 23.1	9.3	8.3	8.3	4.7	1.60
Mn	0.49– 12.60	3.26	2.21	2.11	3.1	2.4
Zn	128.5 –480.0	254.4	245.8	245.8	69.2	1.3
Fe	11.3 –136.1	46.5	37.4	42.3	30.3	1.97
Co	0.04– 1.40	0.21	0.13	0.13	0.29	2.5
Cr	0.26– 6.34	1.44	1.04	0.88	1.35	2.15
Au	0.01– 1.26	0.17	0.09	0.09	0.23	3.18
Ag	0.02– 1.78	0.31	0.18	0.16	0.40	2.67
Sb	0.04– 0.70	0.14	0.11	0.11	0.13	1.92
As	0.04– 1.41	0.30	0.18	0.13	0.32	2.72
Se	0.57– 1.91	1.05	1.01	1.00	0.28	1.29
Hg	0.20– 3.78	1.42	1.19	1.02	1.01	2.07

A. M. – Arithmetic mean.

G. M. – Geometric mean.

S. D. – Standard deviation.

G. S. D. – Geometric standard deviation.

Table 4
Trace element concentration in female hair samples (ppm)

Element	Range	A. M.	G. M.	Median	S. D.	G. S. D.
Cu	2.1 – 24.6	10.2	9.1	9.3	4.9	1.65
Mn	1.0 – 16.15	5.9	4.6	4.8	3.7	2.20
Zn	130.5 –471.5	256.2	242.5	245.9	87.4	1.39
Fe	14.8 –156.4	58.9	49.2	45.5	36.3	1.84
Co	0.04– 1.7	0.62	0.33	0.28	0.77	3.01
Cr	0.19– 5.07	1.39	0.97	0.90	1.18	2.38
Au	0.03– 3.01	0.55	0.25	0.15	0.74	3.54
Ag	0.01– 3.93	0.71	0.31	0.36	0.94	4.18
Sb	0.03– 0.57	0.16	0.13	0.15	0.11	1.96
As	0.04– 0.84	0.20	0.15	0.14	0.17	2.13
Se	0.42– 1.72	0.98	0.93	0.92	0.30	1.37
Hg	0.17– 8.80	2.28	1.5	1.52	2.34	2.53

A. M. – Arithmetic mean.

G. M. – Geometric mean.

S. D. – Standard deviation.

G. S. D. – Geometric standard deviation.

Table 5
Trace element concentration in human head hair samples (ppm)

Element	Range	A. M.	G. M.	Median	S. D.	G. S. D.
Cu	2.1 – 24.6	9.6	8.6	8.4	4.82	1.62
Mn	0.49– 16.15	4.27	2.92	3.13	3.60	2.50
Zn	128.5 –480.0	255.1	244.9	245.8	76.5	1.33
Fe	11.3 –156.4	51.1	41.4	44.8	33.2	1.94
Co	0.04– 1.70	0.33	0.18	0.17	0.40	2.96
Cr	0.19– 6.34	1.42	1.01	0.89	1.29	2.24
Au	0.01– 3.01	0.31	0.13	0.11	0.52	3.63
Ag	0.01– 3.93	0.47	0.23	0.18	0.68	3.30
Sb	0.03– 0.70	0.15	0.12	0.11	0.13	1.94
As	0.04– 1.41	0.26	0.17	0.14	0.28	2.51
Se	0.42– 1.91	1.03	0.99	0.97	0.29	1.32
Hg	0.17– 8.80	1.73	1.23	1.21	1.68	2.27

A. M. – Arithmetic mean.

G. M. – Geometric mean.

S. D. – Standard deviation.

G. S. D. – Geometric standard deviation.

considerably higher relative standard deviations, indicating a wider scatter in the data. The geometric standard deviations for these elements indicate that concentrations of these elements differ by one or more than one order of magnitude in the samples studied. The data indicate that the concentrations of these elements do not follow a gaussian distribution.

Of the 105 samples analyzed, four samples (2 males and 2 females) show abnormally high amount of Se (33, 40, 47 and 72 ppm) whereas two samples (one male and one female) show higher amounts of Hg (23 and 27 ppm). The higher amount of Se in the four samples was found to be due to the use of anti-dandruff shampoos. The shampoos used by these persons were analysed and were found to contain 0.8 to 1.4% Se. These persons were advised to discontinue the use of the shampoo and the hair samples from one person were collected every week after the use of the shampoo was discontinued. The analysis of these samples showed an exponential decrease in the concentration of Se with time. The concentrations were found to be 21, 11, 8 and 6 ppm after 1, 2, 3 and 4 weeks, respectively, as compared to the initial value of 72 ppm. This experiment indicates that the elevated level of Se in the hair was due to adsorption of Se from the shampoo which can be removed by washing.

The cause for the elevated levels of mercury could not be explained with the available information. However, studies were made to estimate the time of maxi-

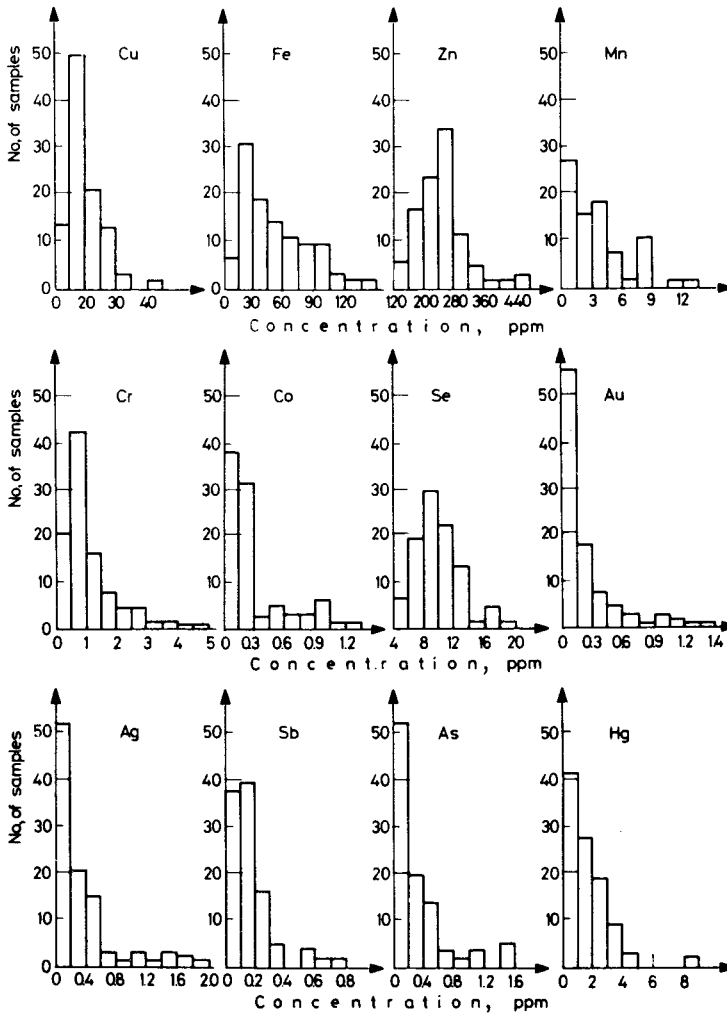


Fig. 1. Distribution histograms for the concentration of trace elements in head hair (higher values not included).

imum exposure of the person to mercury. The female hair sample which had an average concentration of 27 ppm was cut into 8 portions of 3 cm each and analyzed for Hg. The concentrations of Hg along the length of the hair strands from the root end were found to be 19, 21, 24, 28, 30, 33, 31 and 24 ppm. Assuming

an average growth rate of about 1 cm per month, the time of maximum exposure to Hg is estimated to be approximately 18 months from the date of collection of the sample.

Conclusion

In this study human head hair samples were analysed by instrumental activation analysis technique to determine the prevailing concentration levels of 12 trace elements and to reveal individuals having elevated levels of toxic trace elements in their hair. The screening of the data shows that four persons were exposed to higher levels of Se and two to Hg. The exposure to Se was from an external source, whereas the source of Hg could not be ascertained. The data further indicate that the average concentrations of Mn, Co, Ag and Au are higher in female than male samples. The comparison of our data with those of other countries² in Table 6 shows that our values of Fe, Mn, Se and Sb are similar to those of India. The values of Zn, Cr, Co and As are higher and that of Au, Ag and Cu are lower than the Indian values. These values however, are similar to the values of certain other countries. Our values of Hg are comparable with that of Iraq and Italy but lower than those from many other countries.

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Table 6
Intercomparison of trace elements data of human head hair

Elements	Countries							
	Pakistan	India	Iraq	Japan	USA	Canada	England	
Cu	A.M.	9.6±4.82	16.2±6.2	N.A.	13.1±9.9	N.A.	N.A.	23.1
	G.M.	8.6 \bar{x} ±1.62	15.3 \bar{x} ±1.56		11.4 \bar{x} ±1.6	15 \bar{x} ±1.4		20.6 \bar{x} ±1.61
	M	8.4	16.3		10.7	15		19.1
Mn	A.M.	4.27±3.60	3.36±3.43	N.A.	1.1 ±3.8	N.A.	N.A.	N.A.
	G.M.	2.92 \bar{x} ±2.50	2.51 \bar{x} ±2.66		0.49 \bar{x} ±2.6	0.14 \bar{x} ±1.7		1.33 \bar{x} ±2.6
	M	3.13	2.97		0.42	0.14		1.2
Zn	A.M.	255.1±76.5	138±44	180±70	183±59	N.A.	N.A.	N.A.
	G.M.	244.9 \bar{x} ±1.33	128 \bar{x} ±1.5	165 \bar{x} ±1.6	179 \bar{x} ±1.30	164 \bar{x} ±1.4	N.A.	261 \bar{x} ±1.4
	M	245.8	138	175	170	160	190	260
Fe	A.M.	51.1±33.2	60±38	122±115	N.A.	N.A.	N.A.	N.A.
	G.M.	41.4 \bar{x} ±1.94	50 \bar{x} ±1.72	106 \bar{x} ±2.5	N.A.	30 \bar{x} ±1.7	N.A.	
	M	44.8	59	93	10	31	41	

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Table 6 (cont.)

Elements	Countries							
	Pakistan	India	Iraq	Japan	USA	Canada	England	
Co	A.M.	0.33±0.40	0.07±0.10	0.28±0.28	0.084±0.22	N.A.	N.A.	N.A.
	G.M.	0.18 \times 2.96	0.05 \times 2.16	0.22 \times 2.2	0.041 \times 2.5	0.03 \times 1.6	N.A.	
	M	0.17	0.08	0.19	0.036	0.03	0.48	
C	A.M.	1.42±1.29	0.46±0.39	4.1±4.3	N.A.	N.A.	N.A.	N.A.
	G.M.	1.01 \times 2.24	0.34 \times 2.34	2.6 \times 3.0	N.A.	1.5 \times 2.7		
	M	0.89	0.42	2.6	0.2	1.7		
Au	A.M.	0.31±0.52	0.66±0.87	0.059±0.082	0.035±0.122	N.A.	N.A.	N.A.
	G.M.	0.13 \times 3.63	N.A.	0.029 \times 3.4	0.01 \times 3.7	N.A.		0.047 \times 2.8
	M	0.11	0.53	0.028	0.009	0.1		0.05
Ag	A.M.	0.47±0.68	0.68±0.11	0.60±1.32	0.39±0.43	N.A.	N.A.	N.A.
	G.M.	0.23 \times 3.30	0.39 \times 2.58	0.35 \times 2.5	0.28 \times 2.1	N.A.		
	M	0.18	0.62	N.A.	0.26	N.A.		
Sb	A.M.	0.15±0.13	0.12±0.15	2.7±3.8	N.A.	N.A.	N.A.	0.69
	G.M.	0.12 \times 1.94	0.09 \times 2.16	1.2 \times 3.8	N.A.	0.166 \times 2.1	N.A.	0.41 \times 2.59
	M	0.11	0.13	1.2	0.031	0.200	9.7	0.34
As	A.M.	0.26±0.28	0.083±0.14	0.27±0.30	N.A.	N.A.	N.A.	0.65
	G.M.	0.17 \times 2.51	0.07 \times 5.31	0.26 \times 2.0	N.A.	0.13 \times 4.6	N.A.	0.46 \times 2.28
	M	0.14	0.073	0.19	0.058	0.12	0.75	0.46
Se	A.M.	1.03±0.29	1.28±0.84	1.4 ±1.6	1.18±4.2	N.A.	N.A.	N.A.
	G.M.	0.99 \times 1.32	1.32 \times 2.46	0.92 \times 2.6	0.70 \times 1.89	1.15 \times 4.7	N.A.	
	M	0.97	1.23	0.96	0.69	0.58	1.9	
Hg	A.M.	1.73±1.68	N.A.	1.4 ±2.1	4.2±1.95	N.A.	N.A.	5.52
	G.M.	1.23 \times 2.27		0.73 \times 3.0	3.8 \times 1.59	1.8 \times 1.5	N.A.	3.51 \times 3.03
	M	1.21		0.73	3.9	1.7	2.0	4.2

A.M. — Arithmetic mean.

G.M. — Geometric mean.

M — Median.

N.A. — Not available.

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