

NEUTRON ACTIVATION ANALYSIS OF Ca, Cl, I, K, Mg, Mn, Na, and Sr CONTENTS IN THE SCALP HAIR OF HEALTH HUMANS

S. Zaichick¹, V. Zaichick²

¹*Northwestern University, Chicago, IL, 60611, USA*

²*Medical Radiological Research Centre of RAMS,
Koroleva str., 4, Obninsk, 249020, Russia,
e-mail: vezai@obninsk.com*

Introduction

During the past five decades, the determination of chemical element contents in human scalp hair has been a subject of continual interest in the environmental, clinical, occupational and forensic medicine. Hair has been increasingly used as a monitor for many elements and has been proposed for assessing environmental exposure, nutritional status, and for diagnosis of disease.¹⁻⁵ Hair has many advantages for assessment over the more traditional kinds of medical objects such as blood and urine because of ease of collection, transport and storage. Also, trace element contents in hair samples represent an integrated response over time compared with blood and urine levels, which can rapidly fluctuate in response to variations of nutritional and environmental conditions. The fact that contents of many chemical elements in hair are relatively high also facilitates the analysis.

Before hair analysis can be applied to monitoring environmental exposure, evaluating systematic intoxication, assessing nutritional status, or diagnosing diseases, it is necessary to establish normal values related to gender, age, inhabitancy and some other factors. The chemical elements that are essential for normal human metabolism are homeostatically regulated. Consequently, their contents in hair as well as in other biological tissues are expected to fluctuate within relatively narrow limits under conditions of normal human metabolism. Unfortunately, the literature abounds with a diverse array of frequently contradictory normal values for the levels of the chemical elements in human hair.

The objectives of this study were to determine the normal levels and age-related changes of chemical element contents in the scalp hair of healthy women and men – residents of an uncontaminated area in the Central European Part of Russia.

Experimental

Samples of scalp hair were obtained at postmortems from intact cadavers (32 females and 22 males, with ages from 15 to 58 years) within 24 hours of death. Each death had resulted from automobile accidents, falls, shootings, stabbing, hanging, acute alcohol poisoning, or hypothermia. A hair bunch of ≤ 5 cm length was taken from proximal end of hair by the titanium scalpel. The washing procedure was according to the IAEA recommendation: washing once in acetone, twice in double deionized water and once more in acetone, for ten

minutes in each case.⁶ After air drying over night at room temperature, hair samples were packaged in pre-cleaned polyethylene envelopes and then kept in desiccators until analysis. For instrumental neutron activation analysis (INAA) the hair samples weighing about 50-100 mg were sealed in thin polyethylene films previously washed with acetone and rectified alcohol. The sealed samples were then placed in labeled polyethylene ampoules.

To determine contents of the elements by comparison with a known standard, biological synthetic standards (BSS) prepared from phenol-formaldehyde resins were used.⁷ Corrected certified values of BSS element contents were reported by us before.⁸ In addition to SSB, aliquots of commercial, chemically pure compounds were also used as standards. Seven certified reference material IAEA HH-1 (Human Hair)⁹ and Japan NIES No13 (Human Hair) sub-samples weighing about 50-100 mg, were analyzed in the same conditions that scalp hair samples to estimate the precision and accuracy of results.

The content of Ca, Cl, I, K, Mg, Mn, Na, and Sr were determined by INAA using a horizontal channel equipped with the pneumatic rabbit system of the WWR-c research nuclear reactor. The neutron flux in the channel was $1.7 \cdot 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. Ampoules with hair samples, SSB, intralaboratory-made standards, and certified reference materials were put into polyethylene rabbits and then irradiated separately for 180 s. Copper foils were used to assess neutron flux.

The measurement of each sample was made twice, 1 min and 120 min after irradiation. The duration of the first and second measurements was 10 min and 20 min, respectively. A coaxial 98 cm³ Ge (Li) detector and a spectrometric unit (NUC 8100), including a PC-coupled multichannel analyzer, were used for measurements. The spectrometric unit provided 2.9 keV resolution at the ⁶⁰Co 1332 keV line.

A dedicated computer program of INAA mode optimization was used.¹⁰ Using standard programs, the summary of statistics, arithmetic mean, standard deviation, standard error of mean, minimum and maximum values, median, percentiles with 0,025 and 0,975 levels were calculated for chemical element contents. The reliability of difference in the results between two age groups and between females and males was evaluated by Student's *t*-test.

Results

Radionuclides and some of their characteristics used for INAA of Ca, Cl, I, K, Mg, Mn, Na, and Sr contents in scalp hair and reference material samples are given in Table 1.

Table 2 depicts our data for chemical elements in seven sub-samples of IAEA HH-1 Human Hair and Japan NIES No13 Human Hair reference material and the certified values of this material.

Table 3 represents certain statistical parameters (arithmetic mean, standard deviation, standard error of mean, minimal and maximal values, median, percentiles with 0.025 and 0.975 levels) of chemical element contents in hair of females and males separately and of both females and males taken together.

Fig. 1 shows the individual data for Ca, Cl, I, K, Mg, Mn, Na, and Sr mass fraction in scalp hair for all samples (female and male), and lines of trend with age.

The comparison of our results with published data for chemical element contents in the scalp hair of women and men is shown in Table 4.

To estimate the effect of age on the Ca, Cl, I, K, Mg, Mn, Na, and Sr content we examined two age groups: one comprised a younger group with ages from 15 to 35 years and the other comprised older people with ages ranging from 36 to 58 years (Table 5).

We used the entire dataset for both females and males taken separately, seeking to detect the presence of gender-related differences (see Table 6).

Table 1. Radionuclides, some of their characteristics and conditions used for INAA of scalp hair samples and sub-samples of certified reference materials

Element	Radionuclide	Half-life	Gamma-energy used (keV)	Conditions of analysis*
Ca	⁴⁹ Ca	8.75 m	3085	A
Cl	³⁸ Cl	37.29 m	1642, 2167	A
I	¹²⁸ I	54.99 m	443	A
K	⁴² K	12.4 h	1524	B
Mg	²⁷ Mg	9.46 m	844	A
Mn	⁵⁶ Mn	2.58 h	847	B
Na	²⁴ Na	14.96 h	1369, 2754	B
Sr	^{87m} Sr	2.83 h	389	B

* Time of irradiation, decay, and measurement:

(A) 180 s, 60 s, 10 m; sample-detector distance - 10 cm; shielding - 5 cm lead.

(B) 180 s, 120 m, 20 m; sample-detector distance - 0 cm; shielding - 5 cm lead.

Table 2. INAA data of chemical element contents in certified reference material (Human Hair) IAEA HH-1 and Japan NIES No13 (mg/kg, dry weight basis)

Element	IAEA HH-1	This work results	NIES No13 Japan	This work results
	Mean±SD	Mean±SD	Mean	Mean±SD
Ca	522±160	522±42	820*	550±126
Cl	2270±478	2210±340	-	553±37
I	20.3±8.9	19.1±6.2	-	1.71±0.65
K	9.2±5.2	10.7±4.0	-	65.3±64.6
Mg	62.0±9.6	64.7±18.6	160*	261±99
Mn	0.85±0.25	0.93±0.16	3.9*	4.13±0.47
Na	12.6±4.8	14.0±2.7	61*	89.1±12.0
Sr	0.82±0.16	1.24±0.57	-	7.89±2.72

Mean –arithmetical mean; SD – standard deviation; * non-certified values.

Table 3. Some statistical parameters of chemical element contents in the scalp hair of healthy humans (mg/kg, dry weight basis)

Gender		Age	Ca	Cl	I	K	Mg	Mn	Na	Sr
Female (n=32)	M	36.6	2215	924	3.76	156	208	2.32	291	56.0
	SD	11.8	1449	812	3.25	116	139	2.59	273	45.6
	SEM	1.92	265	143	0.58	21.0	24.9	0.47	49.0	8.20
	min	16	428	75	0.29	15.8	23.0	0.08	9.9	0.20
	max	55	6677	3226	13.8	486	652	13.9	1302	189
	Med	37.5	2045	667	2.73	130	176	1.45	209	43.0
	Per0.025	16.9	457	85.1	0.38	19.7	23.7	0.50	28.7	3.05
	Per0.975	55.0	5703	2680	10.6	425	568	9.06	977	159
Male (n=22)	M	36.2	996	1712	11.8	129	96.1	2.25	438	18.0
	SD	11.4	401	1034	9.79	71	53.0	1.37	293	9.80
	SEM	1.69	87.4	220	2.14	16.0	11.6	0.31	62	2.09
	min	15	218	449	0.83	29.0	26.2	0.50	55	7.70
	max	58	1866	4094	37.9	278	217	5.05	1030	45.2
	Med	37	934	1482	9.80	129	83.5	1.92	341	14.2
	Per0.025	17.1	303	453	1.03	30.0	29.7	0.68	84	8.07
	Per0.975	55.0	1699	3821	35.2	270	204	4.97	992	40.1
Female and Male (n=54)	M	36.4	1713	1245	6.93	146	163	2.29	352	40.2
	SD	11.5	1284	981	7.67	101	125	2.18	288	40.0
	SEM	1.25	180	133	1.05	14.2	17.3	0.30	39.5	5.49
	min	15	218	75	0.29	15.8	23.0	0.08	9.9	0.20
	max	58	6677	4094	37.9	486	652	13.9	1302	189
	Med	37	1430	920	3.30	130	128	1.68	301	25.8
	Per0.025	17.0	397	106	0.41	23.0	24.5	0.54	41	4.76
	Per0.975	55.0	5300	3462	28.5	379	499	6.84	1008	141

n – number of samples; M – mean; SD – standard deviation; SEM – standard error of mean; min – minimal value; max – maximal value; Med – median; Per0.025 – percentile with 0.025 level; Per0.975 – percentile with 0.975 level.

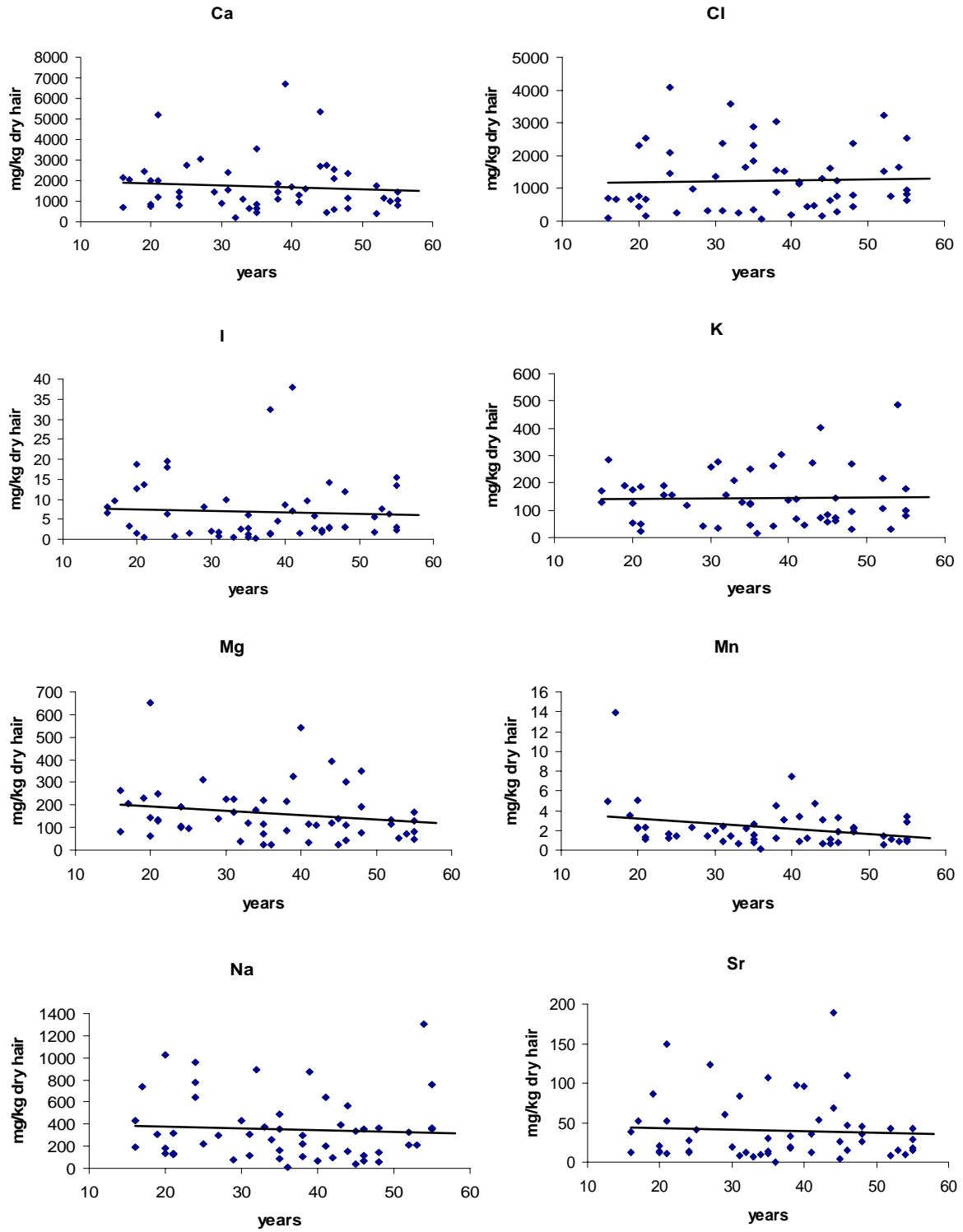


Fig. 1. Individual data of the Ca, Cl, I, K, Mg, Mn, Na, and Sr contents in human scalp hair and lines of trend with age.

Table 4. Comparison of our results with the reference data of chemical element contents in human hair (mg/kg, dry weight basis)

Element	USA Range of Norms ¹¹	USA Range of Norms ¹²	Whole world Range of means ^{13,14}	Whole world Range of means ^{15,16}	Whole world Min-max ⁶	England Bulgaria New Zealand Min-max ¹⁷	Whole world Min-max ¹⁸	∑ Whole world Reference data Min-max	This work results Min-max
Ca	204-860	200-600	150-3200	146-3190	7-10887	150-1900	113-7600	7-10887	218-6677
Cl	-	-	1000-20000	-	<3.6-14000	110-2340	9-27000	<3.6-27000	75-4094
I	0.63-0.85	-	0.1-15	0.4-1.0	<0.045->70	0.18-7.9	0.03-33	0.03->70	0.29-37.9
K	8-430	75-180	150-660	150-663	0.94-2370	4.5-77.6	4-1100	0.94-2370	15.8-486
Mg	29-137	25-75	19-160	19-163	9.8-1412	25-149	1.5-1040	1.5-1412	23.0-652
Mn	0.26-1.97	1.0-10	0.25-5.7	0.5-1.5	0.075-81.5	0.2-4.3	0.03-50	0.03-81.5	0.08-13.9
Na	18-1080	150-350	18-1700	18-1720	0.04-3500	45-465	0.04-2100	0.04-3500	9.9-1302
Sr	0.5-7.6	-	0.05-0.9	0.046-15	0.01-0.04	0.055-0.35	0.14-860	0.01-860	0.20-189

Table 5. Effect of age on mean values (M±SEM) of chemical element contents in the hair of female and male (mg/kg, dry weight basis)

Gender	Age years	n	Ca	Cl	I	K	Mg	Mn	Na	Sr
Female	16-35	15	2152±315	716±162	3.6±1.0	139±23	224±35	2.57±0.90	247±44	57.4±11.3
	36-55	17	2277±436	1107±224	3.9±0.6	172±35	194±36	2.11±0.45	333±86	54.7±12.2
	p(t-test)		N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
Male	16-35	11	928±116	2210±333	10.3±2.1	157±18	103±15	2.43±0.45	576±91	15.0±2.1
	36-55	11	1071±134	1215±210	13.1±3.7	102±23	89±17	2.08±0.43	300±66	21.0±3.5
	p(t-test)		N.S.	≤0.05	N.S.	N.S.	N.S.	N.S.	≤0.05	N.S.

M - arithmetic mean, SEM – standard error of mean, N.S. - not significant

Table 6. Effect of gender on mean values (M±SEM) of chemical element contents in scalp hair of healthy humans (mg/kg, dry weight basis)

Element	Females n=32	Males n=22	<i>p</i> t-test
Ca	2215±265	996±87	≤0.001
Cl	924±143	1712±220	≤0.01
I	3.76±0.58	11.8±2.1	≤0.001
K	156±21	129±16	N.S.
Mg	208±25	96.1±11.6	≤0.001
Mn	2.32±0.47	2.25±0.31	N.S.
Na	291±49	438±62	N.S.
Sr	56.0±8.2	18.0±2.1	≤0.001

M - arithmetic mean, SEM – standard error of mean,
N.S. - not significant

Discussion

Good agreement with the data of IAEA HH-1 certified reference material indicates an acceptable accuracy of the results obtained in the study of chemical element contents in the scalp human hair presented in Tables 3-6.

The obtained means Ca, Cl, I, K, Mg, Mn, Na, and Sr, as shown in Table 4, are inside of ranges cited by other researches for the human scalp hair.^{6,11-18}

No statistically significant changes of Ca, Cl, I, K, Mg, Mn, Na, and Sr content in female scalp hair with age were found. The mass fractions of Cl and Na in male hair decrease with age (Table 5). The literature is very contradictory on the effect of age of the donor and the chemical element content of hair.¹⁹

It was shown that higher Ca, Mg and Sr mass fractions as well as lower Cl and I content were typical of female scalp hair as compared to those in male hair (Table 6). Data from other sources, referring to the impact of gender on values of Ca and Mg agrees well with our results. In some reports, mean hair calcium and magnesium contents for females were found to be twice the values found for the males.²⁰⁻²³ IAEA reported difference in 50% of Ca and 10% of Mg only.⁶ Lower Cl and I content in female scalp hair as compared to those in male hair were marked in the IAEA report too.

High level Ca and Mg in the hair of women compared with men can be attributed to physiological characteristics of the female body related to reproduction. A high content of Sr in the hair of women is likely due to differences in the ratio of nutrition foods of animal and plant origin. Usually, women consume more plant foods, which is the main supplier of Sr in the human body.

All the deceased were citizens of Obninsk, a small city of non-industrial region 105km south-west from Moscow. None of those who died a sudden death had suffered from any systematic or chronic disorders before. Thus, our data for Ca, Cl, I, K, Mg, Mn, Na, and Sr mass fractions in scalp human hair may serve as indicative normal values for residents of the Central European Part of Russia.

References

1. A. AL-HASHIMI, S.S. KRISHNAN, R.E. JERVIS, *J Radioanal Nucl Chem, Articles*, 161 (1992) 171.
2. O.A. AKANLE, J. HO, K. MUHIDDIN, L. ADMANS, N.M. CROFT, N.M. SPYROU, *J Radioanal Nucl Chem*, 259 (2004) 355.
3. C.K. BASKETT, V.L. SPATE, M.M. MASON, T.A. NICHOLS, A. WILLIAMS, D. DUBMAN, A. GUDINO, J. DENISON, J.S. MORRIS, *J Radioanal Nucl Chem*, 249 (2001) 429.
4. A.O. CAVDAR, F. SOYLEMEZ, B. CENGIZ, F. AYDEMIR, *J Trace Elements Exp Med*, 16 (2003) 175.
5. Z.F. CHAI, Q.F. QIAN, X.Q. FENG, P.Q. ZHANG, N.Q. LIU, W.Y. FENG, M.X. KUANG, H.Y. WANG, Y.Z. ZHANG, *J Radioanal Nucl Chem*, 259 (2004) 153.
6. INTERNATIONAL ATOMIC ENERGY AGENCY, *Activation Analysis of Hair as an Indicator of Contamination of Man by the Environmental Trace Element Pollutants*. IAEA, Report IAEA/RL/50, Vienna, 1978.
7. L. M. MOSULISHVILI, M. A. KOLOMI'TSEV, V. Yu. DUNDUA, N. I. SHONIA, O. A. DANILOVA, *J Radioanal Chem*, 26 (1975) 175.
8. V. ZAICHICK, *Fresenius J Anal Chem*, 352 (1995) 219.
9. S.B. M'BAKU, R. PARR, *J Radioanal Chem*, 69 (1982) 171.
10. A. M. KORELO, V. ZAICHICK, in: *Activation Analysis in Environment Protection*, JINR, Dubna, 1993, p.326.
11. DOCTOR'S DATA, INC., *Mineral Analysis Report*. Post Office Box 111, West Chicago, IL 60185, USA, 1991.
12. MINERALAB, INC., 22455 Maple Court, Hayward, CA 94541, USA.
13. H.J.M. BOWEN, D. GIBBONS, *Radioactivation Analysis*. Clarendon Press, Oxford, 1963.
14. H.J.M. BOWEN, *Environmental Chemistry of the Elements*. Academic Press, London, 1979.
15. G.V. IYENGAR, W.E. KOLLMER, H.J.M. BOWEN, *The Elemental Composition of Human Tissues and Body Fluids. A Compilation of Values for Adults*. Verlag Chemie, Weinheim, 1978.
16. G.V. IYENGAR, *Radiat. Phys. Chem.*, 51 (1998) 545.
17. N.I.WARD, N.M. SPYROU, A.A. DAMYANOVA, in: *Modern Trends in Activation Analysis (23-27 June 1986, Copenhagen)*. Risø National Laboratory, Roskilde, Denmark, 1986, Vol.2, p.1087.
18. I. RODUSHKIN, M.D. AXELSSON, *Sci. Total Environ.*, 262 (2000) 21.
19. A. CHATT, S.A. KATZ, *Hair analysis – applications in the biomedical and environmental sciences*. VCH, New York, 1988.
20. H.A. SCHROEDER, A.P. NASON, *J Invest Dermatol*, 53 (1969) 71.
21. A. IMAHORI, J. FUKUSHIMA, S. SHIOBARA, Y. JANAGIDA, K. TOMURA, *J. Radioanal Chem*, 52 (1979) 167.
22. W. WIESENER, W. GORNER, S. NIESE, K. BALDAUF, W. GRUND, M. HENNING, T. MENDE, *Isotopenpraxis*, 17 (1981) 278.
23. W. WIESENER, U. SCHAEFER, *Zentralbl Pharm, Pharmakother Laboratoriumsdiagn*, 121 (1982) 459.