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New Method of Spectral Analysis of Human Hair

Vladimir Otmakhov^{1, a)}, Irina Kuskova^{1, b)}, Elena Petrova^{1, c)}, Evgeniy Rabchevich^{1, d)}, Nadegda Kataeva^{3, e)}, Inessa Shilova^{1,2, f)}

¹Tomsk State University, 36 Lenina Avenue, Tomsk 634050 Russian Federation

²Goldberg Research Institute of Pharmacology and Regenerative Medicine, 3 Lenina Avenue, Tomsk 634028 Russian Federation

³Siberian State Medical University, 2 Moskovsky Trakt, Tomsk 634050 Russian Federation

^{a)}corresponding author: otmahov2004@mail.ru

^{b)}kuskova.i@mail.ru

^{c)}elena1207@sibmail.com

^{d)}evgenia882-a@mail.ru

^{e)}nadi-51@yandex.ru

^{f)}inessashilova@gmail.com

Abstract A new optimal method of preparing one of the human biosubstrates (hair) to an arc atomic emission spectral analysis is proposed on the basis of complex physical and chemical studies. A new method of determining the content of macro- and micro-elements is developed. Following the developed technique we performed analysis of hairs in group of patients in order to diagnose diseases additionally, assess the habitat, and restore the element balance in the body. Comparing the content of elements in the human hair with reference values, it is possible to assess the degree of element imbalance in the body. This technique has passed metrological certification. Obtained by this method results of analysis of hair were used to identify clinical and laboratory correlations, to determine the elemental human status, and to diagnose various diseases.

INTRODUCTION

Stability of chemical composition of a human body is one of the conditions for its normal functioning. The change in the content of chemical elements due to biological, geographical climatic and other factors can cause pathological deviations in human health [1–6]. Modern practice of diagnosis the macro- and microelements in the human body have methods for their determination in whole blood, urine, hair, saliva, tooth dentin and bone tissue. Hair as an object of research, are more preferable among other biological substrates [7, 8]. Their chemical composition is more stable due to outer keratin shell, which prevents both loss of internal components and penetration of external contaminants. The advantages also are the possibility of obtaining information about the content of elements in the body for a long enough period of time due to their accumulation, unlimited storing the samples without special equipment, non-invasivity in their selection, as well as ease of removing external contamination.

Regulated minimum content of elements in hair samples is generally greater than 0.1 microgram/g, therefore for the analysis it is advisable to use the method of arc atomic emission spectroscopy (AES) with a multichannel analyzer of emission spectra (MAES) [9–12]. MAES is an advanced detector based on photodiode array. It allows to automate numerous procedures for spectral analysis, reduce the limit of detection for a number of elements, and to improve significantly the analysis of metrological characteristics. At present there are no certified metrological techniques for analysis using arc AES with MAES. This depresses significantly its application at accredited laboratories.

Methods of AES and mass spectrometry (MS) with inductively coupled plasma (ICP) have lower detection limits, but this advantage is not significant for current laboratory tests. Moreover, high requirements are imposed on pH (<5%), and the total salt content (<0.1%) of the analyzed solutions, as well as on the purity of the reagents used. MS-ICP has interference problems when detecting the light elements.

The aim of this work is to develop a new spectral method with a multichannel analyzer of emission spectra for element analysis of hair of patients.

MATERIALS AND METHODS

Development of techniques and previous studies were performed on the real samples of patients aged from 18 to 90 years (n=500). The basal part of the hair (3–4 cm from the root) was analyzed. The hairs were cut in the back of the head, neck, and other parts of the head. This part of the hair contains the most important information about the condition of the body over the past few months [13]. Cleaning of hair from external contamination included degreasing with acetone, and washing with bidistilled water.

Weighed portions of completely dry test samples (1.0000–5.0000 g) were ashed in a muffle furnace at a temperature of 400–450 °C for 2–3 hours to grayish-white ash residues. After weighing the hairs were homogenized and then were diluted with high-purity graphite powder by 10 and 100 times, or were used to prepare solutions. Heat mineralization removes organic component from samples, and gives the concentrate, convenient for the method of arc AES with MAES.

Quantitative determination of the macro- and microelements in the concentrates of hair samples was performed by MAES method using "Grand" equipment complex consisting of spectral analytical generator "Vesuvius-3", polychromator "Rowland" and MAES itself ("Optoelektronika", Russia). To analyze the element content of base and micro-impurities we used different dilution of hair ash residues with graphite powder: 1 : 100 and 1 : 10, respectively. Weighed portions of test samples and standard samples of the composition of graphite collector of micro-impurities (0.015 g) [14] were evaporated from the channel of the anode electrode (depth and the diameter of crater were 0.004 and 0.0045 m, respectively). Graphite electrode sharpened conically was used as cathode. To stabilize the conditions of spectra excitation, half-alcoholic solution of NaCl (5 wt% of sodium) was added by microdoser to electrodes with test samples and standard samples in doses of 20 microliters. Conditions for registration of spectra: direct current 13 A; electrode spacing 0.003 m; gap width $3.0 \cdot 10^{-5}$ m; aperture 0.005 m; number of accumulations 160; duration of accumulations 125 ms; total exposure 20 s.

To determine the alkali elements by flame AES, to carry out matching tests by mass spectrometry with inductively coupled plasma (MS-ICP), by atomic absorption spectrometry (AAS), and spectrophotometry (SF) – the ash residues of hair were dissolved in 0.15 ml of concentrated nitric acid at a slight heating, followed by dilution to 2 ml with bidistilled water. The obtained solutions were filtered in a 25 ml flask and filled with water up to the mark.

In order to study the composition of the hair ash residues at the stage of sample preparation, and to carry out matching tests – the following methods were used: MS-ICP (Agilent 7500cx, Agilent Technologies, USA), AAS (Solaar S series, Thermoelectron, USA), SF (PE-5400UF, Russia), IR spectroscopy with Fourier spectrometer "Nicolet 6700" (Termo Scientific, USA), XRD with diffractometer "Rigaku MiniFlex 600" (USA), and scanning electron microscope TM-3000 (Hitachi, Japan). The work performed at an accredited Tomsk Regional Center of collective use, National Research Tomsk State University (Accreditation certificate No. POCC RU.0001.517686).

RESULTS AND DISCUSSION

Determination of Basic Elements and Their Forms in Hair Ash

To carry out reliably a spectral analysis of impurities content in the hair ash residue, it is necessary firstly to define the contents of the main elements in them. Table 1 shows the content of predominant elements in the hair ash residue, detected in mixture of ash residue with graphite powder (1:100) by arc AES with MAES.

TABLE 1. Contents of the main elements in ash residue hair, microgram/g (P = 0.95, n = 10)

Element	Method of analysis				
	arc AES	MS-ICP	AAS	flame AES	SF
Ca	$(2.0 \pm 0.2) \cdot 10^3$	$(2.2 \pm 0.2) \cdot 10^3$	–	–	–
K	$(9.0 \pm 1.0) \cdot 10^3$	–	–	$(8.7 \pm 0.8) \cdot 10^3$	–
Mg	$(2.9 \pm 0.3) \cdot 10^4$	$(3.0 \pm 0.3) \cdot 10^4$	–	–	–
Na	–	–	–	$(5.4 \pm 0.5) \cdot 10^3$	–
P	500 ± 50	–	–	–	480 ± 30
Zn	$(1.7 \pm 0.2) \cdot 10^4$	$(1.8 \pm 0.2) \cdot 10^4$	$(1.9 \pm 0.2) \cdot 10^4$	–	–

At the same time these elements were checked in solution of hair ash residue by MS-ICP (Ca, Mg, P, Zn, K), AAS (Zn), flame AES (Na, K), and SF (P). The performed analysis showed that hair ash residue consists mainly of the following elements (in decreasing order): Ca > Mg > Zn > K > Na > P. Moreover, the calcium content exceeds the content of the other elements by 10 times and more.

Anionic composition of the hair ash residue was defined by IR spectroscopy (Fig. 1).

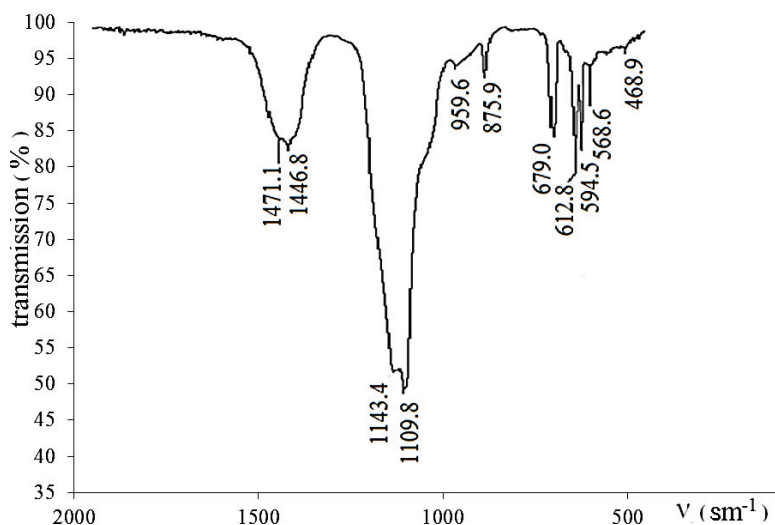


FIGURE 1. IR absorption spectrum of hair ash in the range 2000–450 cm^{-1}

The main absorption band lies in the range 1250–000 cm^{-1} belongs to the sulfate ions SO_4^{2-} . They also cause absorption bands 679 cm^{-1} и 612 cm^{-1} . A small bend in 1100–1000 cm^{-1} is caused by ions PO_4^{3-} [15]. We can conclude that the dominant anions in hair ash residue are (in decreasing order): $\text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{PO}_4^{3-}$.

XRD showed (Fig. 2), that hair ash residue is represented mainly by two crystalline phases: CaSO_4 (75%) and CaCO_3 (25%). The most complete picture of the elemental composition is shown in Figure 3. The analysis was performed by scanning electron microscope and confirms the specified anion-cation composition of the ash.

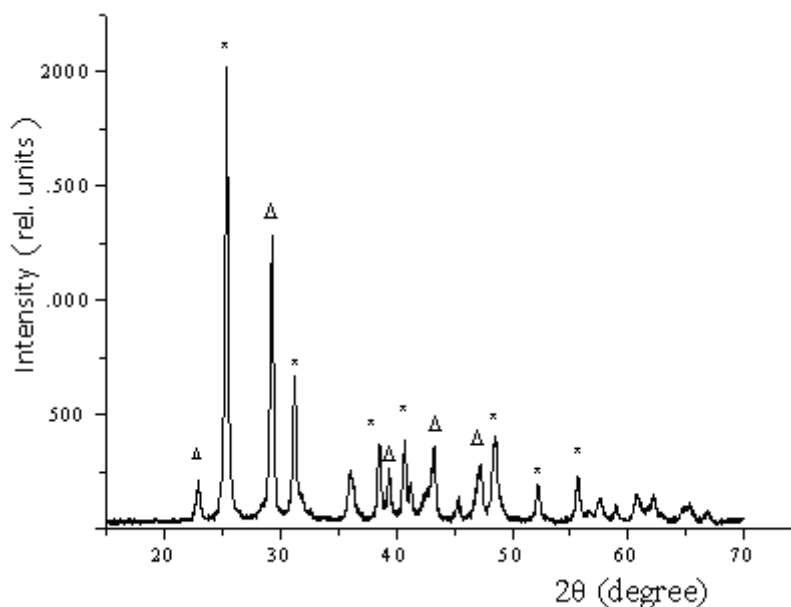


FIGURE 2. XRD analysis of hair ash residue: * – calcium sulfate (CaSO_4); Δ – calcium carbonate (CaCO_3)

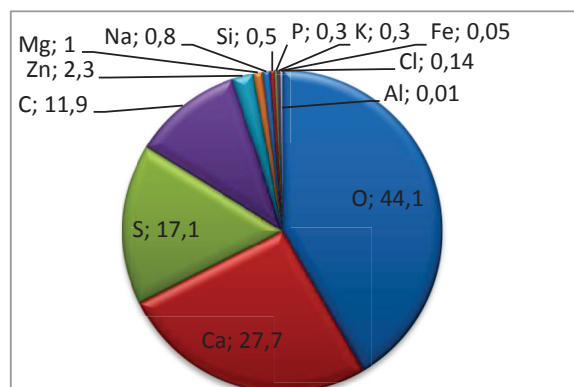


FIGURE 3. Analysis of the elements in the hair ash residue obtained with SEM, wt%

Influence of Macro Components on the Results of Analysis

The main components of the hair ash residue ($\text{CaCO}_3 : \text{CaSO}_4 = 1 : 3$) may affect the processes of evaporation and excitation of microelements in an arc discharge, distorting the results of their quantitative determination by arc AES with MAES (matrix effect). This effect can be reduced significantly by diluting the hair ash residue with graphite powder. But more than 10-fold dilution of is inappropriate, because the content of a number of microelements will be below out of detection limit by this method. However, this dilution does not fully eliminate the influence of macro components of the sample. This is evident from the data in Table 2, which shows the results of an analysis of two model samples, obtained by introducing into standard samples [10] 2% calcium in the form of $\text{CaCO}_3 : \text{CaSO}_4 (1 : 3)$, which corresponds to a real sample diluted by 10 times.

TABLE 2. Spectral determination of microelements in standard samples at the level (1–10 microgram/g) in the presence of 2% Ca in the form of $\text{CaCO}_3 + \text{CaSO}_4 = 1 : 3$, ($P = 0.95$, $n = 5$)

Elements	Standard sample, containing 10 microgram/g of an element		Standard sample, containing 1 microgram/g of an element	
	Found in the presence of 2% Ca ($\text{CaCO}_3 : \text{CaSO}_4 = 1 : 3$), microgram/g	k	Found in the presence of 2% Ca ($\text{CaCO}_3 : \text{CaSO}_4 = 1 : 3$), microgram/g	k
Ag	10.0 ± 0.5	1.0	0.77 ± 0.03	1.3
Al	10.0 ± 0.5	1.0	1.10 ± 0.1	0.9
Cd	8.7 ± 0.4	1.2	0.71 ± 0.03	1.4
Co	12.2 ± 0.6	0.8	0.61 ± 0.06	1.6
Cr	9.4 ± 0.5	1.1	0.88 ± 0.04	1.1
Cu	10.4 ± 0.5	1.0	1.60 ± 0.20	0.6
Fe	8.7 ± 0.4	1.2	0.95 ± 0.06	1.0
Mn	11.2 ± 0.6	0.9	1.10 ± 0.10	0.9
Mo	12.5 ± 0.7	0.8	1.60 ± 0.20	0.6
Ni	8.7 ± 0.9	1.2	0.67 ± 0.06	1.5
Pb	$8.4 \pm 0,8$	1.2	0.64 ± 0.06	1.6
Sn	9.5 ± 0.6	1.1	0.85 ± 0.09	1.2
Ti	9.5 ± 0.5	1.1	0.87 ± 0.05	1.2
V	8.4 ± 0.4	1.2	0.59 ± 0.06	1.7
Zr	8.5 ± 0.6	1.2	0.68 ± 0.07	1.5

Influence of calcium salts on the results of analysis is increased with decreasing the content of the elements in a sample (greater deviation from unity of the correction coefficient k , calculated as the ratio of certified content of an element to the obtained one). This influence is expressed both as a gain ($k < 1$) and the weakening ($k > 1$) of analytical signals from impurities due to their individual properties. To obtain reliable results, the correction factor k must be taken into account for calculation using the formula:

$$c_x = \eta \frac{(c_{\text{sample}} - c_{\text{blank}})q}{Q} k,$$

where

C_x – is the mass fraction of the element in the analyzed sample, microgram/g; η – is the dilution rate of hair ash with graphite powder; C_{sample} – is the measured mass fraction of the element in the concentrate of the analyzed sample, microgram/g; C_{blank} – is the measured mass fraction of the element in the concentrate of the blank sample, microgram/g; Q – is the mass of the original hair samples, g; q – is the mass of hair ash, g; k – is a correction factor that takes into account the influence of the base.

Two other alternative methods of taking into account influence of the base components (introduction of corrective graphite additives into standard sample, and decrease of accuracy) are worse than the method of correction factors.

Metrological Certification of Atomic Emission Techniques for Hair Analysis

TABLE 3. Measuring ranges, the relative values of the indicators of accuracy, repeatability and within-laboratory precision of atomic-emission method of hair analysis with an arc excitation source ($P = 0.95$)

Elements	Range of measurements, microgram/g	Defined indicators		
		Repeatability σ_r , %	Within-laboratory precision σ_R , %	Accuracy (error limits) δ , %
Ca	200–5000	1.7	5.1	9.9
Mg	10–500	1.6	5.2	10
P	10–500	1.8	5.4	11
Si	10–500	1.3	4.6	9.0
Zn	10–500	4.2	5.0	9.8
Al	1–10	7.6	8.0	16
Mn	1–10	2.4	6.3	12
Ti	1–10	3.6	9.6	19
V	1–10	5.2	7.4	14
Fe	2–20	1.8	6.9	14
Cu	2–20	5.6	5.5	11
As	0.1–1	9.8	12	24
Pb	0.1–1	7.5	10	20
Cd	0.1–1	7.7	9.5	19
Co	0.1–1	3.6	7.3	14
Cr	0.1–1	6.0	7.7	15
Sn	0.1–1	4.2	7.7	15
Mo	0.1–1	3.2	6.6	13
Ni	0.1–1	8.5	9.6	19
Zr	0.1–1	5.3	9.0	18
Ag	0.1–1	1.9	7.7	15

TABLE 4. Results of element analysis of hair ($P = 0.95$, $n = 5$)

Elements	Content of elements (microgram/g), defined with different methods		
	arc AES	MS-ICP	Other methods
Al	12.5 ± 0.6	13.8 ± 0.7	–
Ca	5590 ± 280	5260 ± 350	–
Cu	23.5 ± 1.2	22 ± 2	–
Fe	37 ± 2	38 ± 3	34 ± 4 (AAS)
Mg	798 ± 40	835 ± 45	–
Mn	4.6 ± 0.2	4.1 ± 0.5	4.5 ± 0.4 (AAS)
Ni	4.8 ± 0.7	5.5 ± 0.2	–
P	16.3 ± 0.9	–	15.7 ± 0.6 (SF)
Pb	0.31 ± 0.03	0.24 ± 0.07	–
Si	280 ± 14	–	–
Sn	2.6 ± 0.3	2.9 ± 0.3	–
Sr	33 ± 4	29 ± 3	–
Ti	2.5 ± 0.5	3.0 ± 0.5	–
Zn	470 ± 68	–	537 ± 35 (AAS)
Zr	79 ± 4	71 ± 8	–
Na	–	–	150 ± 20 (FP)
K	–	–	213 ± 25 (FP)

Taking into account the proposed method of sample preparation, the procedure for quantification of macro- and microelements of hairs was developed [16–20]. This technique has passed metrological certification (the results are presented in Table 3) (Certificate for procedure (method) of measurement No. 08-47/380.01.00143-2013.2016 from 02.02.2016).

Table 4 presents the results of analysis of hair samples by the developed technique in comparison with the results of independent analysis. The difference between the results obtained by different methods is insignificant against the background of random dispersion.

Following the developed technique we performed analysis of hairs in group of patients in order to diagnose diseases additionally, assess the habitat, and restore the element balance in the body (Table 5 and Table 6).

TABLE 5. Content of chemical elements in the hair of men in Siberia (P=0.95, n=10).

Mc – median; q25 – bottom quartile; q75 – top quartile

Elements	Age of 20–30, Mc (q25–q75)	Age of 50–60, Mc (q25–q75)	Age of 80–90, Mc (q25–q75)
Ca	663 (289–1474)	393 (312–3081)	300 (294–306)
Mg	54 (32–76)	50 (30–337)	36 (33–38)
P	128 (89–311)	100 (84–221)	182 (117–248)
Si	44 (33–324)	167 (52–393)	185 (72–297)
Zn	173 (97–336)	129 (109–214)	172 (118–225)
Al	8 (5–12)	4.5 (4.1–21)	3.1 (0.40–5.8)
Fe	13.4 (10–19)	11 (6.1–20)	7.3 (4.9–9.7)
Cu	6.2 (2.8–12)	4.7 (3.9–7,8)	4.3 (2.4–6.2)
Mn	1.03 (0.6–1.5)	0.64 (0.47–3)	0.45 (0.39–0.50)
Pb	0.52 (0.3–1.1)	0.37 (0.22–0.96)	0.68 (0.050–1.3)
Ti	2.24 (1.5–5.2)	2.3(1.5–3.2)	1.4 (0.90–1.9)
B	0.06 (0.025–0.1)	0.14 (0.02–0.26)	0.006 (0.002–0.01)
Bi	0.05 (0.002–0.090)	0.1 (0.03–0.86)	0.019 (0.010–0.027)
Cd	0.05 (0.01–0.10)	–	0.006 (0.002–0.009)
Co	0.05 (0.01–0.1)	0.01 (0.006–0.08)	0.013 (0.008–0.017)
Cr	0.17 (0.1–0.6)	0.11 (0.08–0.35)	0.085 (0.040–0.13)
Sn	0.19 (0.1–0.4)	0.11 (0.07–0.13)	0.031 (0.018–0,044)
Mo	0.01 (0.003–0.035)	0.05 (0.01–0.20)	0.82 (0.070–1.8)
Ni	0.11 (0.05–0.13)	0.05 (0.01–0.18)	0.067 (0.034–0.10)
Zr	0.08 (0.015–0,20)	0.05 (0.02–0.18)	0.015 (0.0004–0.030)
Ag	0.25 (0.1–0.70)	0.10 (0.08–0.22)	0.030 (0.010–0.050)

TABLE 6. Content of chemical elements in the hair of women in Siberia (P=0.95, n=10).

Mc – median; q25 – bottom quartile; q75 – top quartile

Elements	Age of 20–30, Mc (q25–q75)	Age of 50–60, Mc (q25–q75)	Age of 80–90, Mc (q25–q75)
Ca	4468 (3093–5251)	3110 (572–4747)	996 (694–1606)
Mg	252 (131–326)	302 (153–639)	61 (59–252)
P	122 (100–176)	123 (118–125)	81 (39–97)
Si	240 (122–397)	123 (10–187)	459 (43–465)
Zn	268 (156–476)	767 (130–1337)	80 (43–141)
Al	15 (4.3–21)	6 (4.6–12)	6.2 (6.0–7.1)
Fe	10.6 (5.3–24)	17.7 (11–156)	14 (4.2–28)
Cu	7.7 (5.9–17)	7.7 (5,1–14)	3.0 (2.6–3.2)
Mn	4.6 (2.5–7.7)	4.3 (0.9–24)	3.3 (1.4–5.0)
Pb	0.5 (0.30–0.72)	0.12 (0.05–0.16)	0.19 (0.05–0.86)
Ti	1.9 (1.0–6.1)	2.8 (0.14–3.0)	0.58 (0.43–3.5)
B	0.03 (0.004–0.01)	0.06 (0.01–0.29)	0.01 (0.008–0.02)
Bi	0.1 (0.01–0.20)	–	0.15 (0.05–0.58)
Cd	0.5 (0.1–1.0)	–	–
Co	0.5 (0.01–0.1)	–	–
Cr	0.19 (0.10–0.32)	0.059 (0.029–0.21)	0.01 (0.09–0.20)
Sn	0.77 (0.50–12)	0.46 (0.14–2.2)	0.12 (0.04–0.26)
Mo	0.30 (0.12–0.49)	0.14 (0.12–0.17)	–
Ni	0.19 (0.12–0.31)	0.56 (0.28–0.76)	0.32 (0.02–3.2)
Zr	0.61 (0.10–9.4)	0.32 (0.13–1.0)	0.06 (0.02–0.08)
Ag	0.13 (0.06–20)	0.23 (0.02–0.73)	0.050.02–0.11)

Comparing the content of elements in the human hair with reference values [21, 22], it is possible to assess the degree of element imbalance in the body. The tables 5 and 6 show that about 80% of patients have a more or less pronounced imbalance (deviation from the norm) of trace elements. There are reasons more than enough for this imbalance: stress, inadequate intake of micronutrients from food, radiation (increased solar activity, ozone holes, etc.), attacks of toxic substances (increased concentration of exhaust gas in the air of large cities), and other reasons. All this leads to an imbalance of essential chemical elements in the body of modern man. Chronic imbalance of trace elements leads to serious changes in the body's functions (deviation in metabolism of proteins, fats, carbohydrates, vitamins, and the production of enzymes; weakening immunity; disorders in the endocrine and nervous systems). It also causes neuropsychiatric disorders, cancer, inflammatory lesions of organs and tissues.

CONCLUSION

Microelement correction is a new step in the development of modern medicine. A new technique using arc AES analysis with MAES allows to determine rapidly the chemical composition of hairs with high accuracy. It also allows to compare the obtained data with reference values for different gender and age as well as to identify significant deviations. This makes it possible to develop the most optimal and exclusive individual scheme of correction of deviations and preventive measures.

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