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Examination of distribution of trace elements in hair, fingernails and toenails as alternative biological materials. Application of chemometric methods

Research Article

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Abstract: The aim of this study was to find correlations between several studied elements and analyzed materials as well as the application and validation of an analytical method to determine trace elements in hair, fingernails and toenails of healthy volunteers (normal concentration). The method developed covers washing, mineralization and ICP- MS determination of 10 elements (Ca, Cd, Co, Cr, Cu, Fe, Mg, Ni, Pb and Zn) in hair and nails. Concentrations of the selected elements in hair, fingernails and toenails were measured for 24 women and 18 men. Furthermore, a chemometric approach (Principal Component Analysis, PCA) was employed to evaluate the correlations between concentrations of the elements in hair and nails and between these materials. Until now PCA has not been frequently applied in handling and interpretation of the results of analysis of biological materials. However, the results of the present investigation show the high potential of PCA in extraction of valuable information from analytical measurements. Additionally, PCA has become a useful tool for visualization of the obtained results. Moreover, the cluster analysis (CA) was used to group the samples according to gender, taking into account two different groups of elements: essential and toxic.

Keywords: *Metals • Hair • Nails • ICP-MS • Principal Component Analysis • Cluster Analysis*

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1. Introduction

The development of civilization, industry, urbanization and transport has caused many changes in the natural circulation of elements. Simultaneously, the elevated level of metals in the environment has led to many new clinical threats. As a consequence, direct exposure to poisons has increased for both people working in industry (mining and processing of metals, *etc.*) and for society as a whole through polluted air, soil, water and consumable goods [1-3]. Toxic metals can undoubtedly be described as both an occupational risk and environmental poison. Changes they may cause in a human body are mostly irreversible and may result in a variety of disorders, including DNA damage, lipid peroxidation and protein modifications [4,5]. Metals can be seen to influence cellular organelles and components towards apoptosis, inflammation or cancer [3,5-8]. Additionally, it has also been shown that essential metals may have an adverse effect on living organisms. Maintaining appropriate concentrations of an individual metal in the body is very important, however it is also significant to maintain the proper balance between them due to the synergistic and antagonistic relationships that exist between trace elements [9,10]. Deficiencies of some essential elements may increase toxicity of metals, while

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excessive concentrations of toxic metals can also affect metabolism of essential elements [11,12].

The description of the metabolic condition of the human body has become a topic of prime importance in recent years. Determination of macro- and microelements in humans can indicate susceptibility to certain diseases, support therapeutic interventions and explain disturbances associated with many pathological conditions [13]. Currently, the interest is focused on the choice of the most suitable biological material, which will allow assessment of these changes in the human body. Hair and nails have become excellent alternative materials which, in comparison to other body tissues, demonstrate many advantages. Hair and nails provide a picture of the concentrations of different elements in an organism. Furthermore, they are partially independent of the influence of metabolic processes and homeostatic mechanisms [14]. Additionally, hair-based measurements may provide results from longer exposure periods than the results based on blood (several days) or urine analysis (several weeks). It should also be noted that samples of hair and nails may be obtained in a non-invasive way [15].

Although increasing interest has been directed towards the choice of a suitable biological material, the role of an appropriate analytical method has become an equivalent problem. Modern instruments enable simultaneous determination of elements at parts per billion concentrations (ng g^{-1}) in a very short time and only consume a small quantity of biological material which, in terms of biological research, plays a considerable role. The development of inductively coupled plasma-mass spectrometry (ICP-MS) has revolutionized the analysis of trace elements [16] and has become a powerful technique in trace analysis [17,18]. Features which highlight ICP-MS as an outstanding technique in comparison with other methods of elemental analysis are: multi-elemental analysis, extremely low limits of detection (LODs), excellent linearity range, extensive analytical range, good precision and accuracy, and high throughput of samples. The most important advantage of the ICP-MS technique is the possibility to perform multi-elemental analysis; however, as a consequence vast numbers of results are obtained. In such cases, application of chemometric tools is a good solution in order to derive maximum relevant chemical information by analyzing the chemical data [19]. In this paper, the Principal Component Analysis (PCA) approach was employed to examine the correlations between the tested elements in hair and nails and also between these materials as alternative biological resources. Instead of simple correlations, we have decided to use PCA as a multivariate chemometric technique which allows us to find the relations in data of high dimension simultaneously. The aim of the study was optimization and application of a reliable and simple analytical method for determination of trace elements in the hair, fingernails and toenails of healthy volunteers.

2. Experimental procedure

2.1. Chemicals and materials

An ultrasonic bath Sonic-3 (Polsonic, Poland) vortex mixer (Labnet, USA) and mini-mill Pulverisette23 (Fritsch GmbH, Germany) were used for preparation of samples. A high pressure Mars 5X (CEM, USA microwave mineralizer) equipped with high-pressured XP-1500-type vessels, with the possibility of temperature and pressure control was employed for decomposition of samples. An Optima 2100 DV (Perkin-Elmer, USA) Inductively Coupled Plasma Optical Emission Spectrometer (ICP–OES) equipped with axially viewed plasma was used in the determination of Ca at 317.993 nm and all other measurements were carried out using an Elan DRC-e (Perkin-Elmer, USA) Inductively Coupled Plasma Mass Spectrometer (ICP-MS) in the standard mode. Argon (Linde, Poland) with a purity of 99.999% was utilized throughout the work.

All reagents were of analytical grade and deionized water was used throughout the work. The solutions were stored at room temperature. 1% (v/v) HNO_3 was prepared by diluting HNO_3 supra pure (Merck, Darmstadt, Germany) with deionized water. Methanol (Merck, Darmstadt, Germany) and a 1% solution of Triton X-100 (GR, Merck, Darmstadt, Germany) surfactant were used for washing the samples. The stock standard solution of Ca was prepared from Titrisol® (1000 mg L^{-1}) solution (Merck, Darmstadt, Germany) and 1% HNO_3 (v/v). Multi-element ICP-MS Calibration Std 3 (10 µg mL^{-1} in 5% HNO_3, Perkin Elmer Pure Plus, USA) and Multi-element Standard Solution VI (1000 mg L^{-1}, Merck, Darmstadt, Germany) were used for calibration and control of analytical processes. A daily test was performed with the use of Smart Tune Solution Std ELAN & DRC-e (Perkin-Elmer, USA).

2.2. Preparation of samples

The Certified Reference Material of Human Hair (GBW07601, GSH-1, China) was used for accuracy evaluation. A certified reference material of nails is not commercially available, therefore fingernails from healthy volunteers were collected in 5 g samples and prepared appropriately for analysis. These are described later in the text as Lab-Sample of Nails, or LSN. Natural samples of hair and nails were collected from 42 adult

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volunteers (healthy individuals from urban areas, totaling 24 women and 18 men). Hair samples were collected from the back of the head of each volunteer and nail samples were collected from fingers and toes.

Samples were cut into small pieces (4-5 mm long) with ceramic clippers. Nails were stored in plastic vials whilst hair was stored in envelopes, both at room temperature. The preparation process included washing, mixing and grinding samples in a mini-mill. The samples were subsequently washed with 2 mL of solvent with the use of a vortex mixer. The procedure was as follows: water (twice), Triton X-100 (once), water (several times until bubbles disappeared), methanol (once) and finally methanol in an ultrasonic bath for 15 min. After the washing process, the samples were dried at 80°C overnight. The samples were then stored in desiccators. Samples which had been stored for a period longer than one month were dried again for 30 min at 80°C before mineralization. The hair reference material was also dried before the mineralization process. An accuracy improvement of 15% was noted with the inclusion of a drying process.

Preparation of samples was carried out using a 12-position microwave system MARS X (CEM, USA) with an internal control system of pressure (ESP-1500 Plus) and temperature (RTP-300 Plus). The mineralization process was performed in high pressure Teflon vessels (type XP-1500) in one step, which has been described in Table 1. A blank sample was processed in the same way. After digestion the vessels were cooled down to room temperature. The gases from the above mentioned digested samples were removed using a nitrogen or air stream.

In the case of nail samples, 5 mL of concentrated HNO_3 was added into each Teflon digestion vessel containing a sample. They were then left for 20 min before the digestion process took place. In the case of hair samples, the procedure was similar, except that the samples were soaked in acid overnight at room temperature. In both cases the digested samples solutions were transferred into 10 mL volumetric flasks and diluted with water. If needed, the liquid-phase was decanted before analysis according to Schramm guidelines [19]. Sample solutions were stored in vials in a refrigerator at 4°C. The digests were analyzed after appropriate dilution to meet the optimal working concentration range.

2.3. Instrumentation conditions

Determination of elements was performed using ICP methods. The procedure included two steps that depended on the content of elements in the biological materials. In the case of elements which are present in the human body at low concentrations, the solutions were diluted twofold (^{52}Cr, ^{59}Co, ^{63}Ni, ^{63}Pb, ^{111}Cd). The Multi-element ICP-MS Calibration Std 3 was used for standard solution preparation at a concentration of 20 µg L^{-1} and the ICP Multi-element Std. VI Merck was used as a control solution at a concentration of 10 µg L^{-1}.

Elements present in higher concentrations were diluted twentyfold (^{65}Cu, ^{57}Fe, ^{24}Mg, ^{66}Zn, ^{63}Pt). The Multi-element ICP-MS Calibration Std 3 was used for standard solution preparation at concentrations of 20 µg L^{-1} and 100 µg L^{-1} and the ICP Multi-element Std. VI Merck was used as a control solution at a concentration of 50 µg L^{-1}. For the same purpose, Std Calcium at a concentration of 10 mg L^{-1} was employed for the ICP-OES method. The determination of Ca was carried out using calibration solutions with concentrations of 1, 10 and 20 µg L^{-1}. The accuracy of the measurements was calculated in comparison to the reference material. These results are shown in Table 2. Furthermore, additional validation parameters including limit of detection, limit of quantification as well as precision were calculated. The limit of detection (LOD) and the limit of quantification (LOQ) were estimated based on the analysis of blank samples (1% nitric acid). To calculate LOD and LOQ, the following criteria were used: LOD = 3•S, LOQ = 10•S (S - standard deviation of the blank signal). In order to estimate the standard deviations, 10 measurements of blank samples were performed. The interassay precision of a single measurement was evaluated using the variation coefficient (CV) of three replicated measurements of hair reference material (GBW07601). Intra-assay precision was estimated using the variation coefficient (CV) of three replicated measurements of hair reference material (GBW07601) on different days. Results are shown in Table 3. The limit of detection (LOD) ranged from 0.002 µg g^{-1} for Co to 0.016 mg g^{-1} for Ca, while the limit of quantification ranged from 0.008 µg g^{-1} for Mg to 0.054 mg g^{-1} for Ca, respectively. The interassay and intra-assay precision measured were below 10%, with the exception of chromium, which was 15.79%. The results obtained indicate the high accuracy of the method, with the exception of Fe and Cr. It is possible that different procedures for determination of these elements are needed. Better results for Cr may be obtained through the use of the Dynamic Reaction Chamber (DRC-e) in ICP-MS measurements.

2.4. Chemometric analysis

The main aim of the chemometric analysis was to reveal and visualize the correlation between elements in different alternative biological materials. The Principal

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Table 1. Mineralization procedures for hair and nails samples.

Samples	Max Power (W)	Power (%)	Ramp (min)	Psi	Max temperature (°C)	Hold (min)	Awaiting time (min)
Nails	600	100	15	800	180	15	20
Hair	600	100	15	800	200	15	20

Table 2. Accuracy of ICP methods (Certified Reference Material of Human Hair (GBW07601)).

Elements	Certificate value ± SD [$\mu g\ g^{-1}$]	Found value ± SD [$\mu g\ g^{-1}$] (n=5)	RE [%]
Ca	2.9±0.2*	2.91±0.19*	0.25
Fe	54.00±6.00	55.42±3.52	2.63
Mg	360.00±30.00	360.38±6.07	0.11
Cu	10.60±0.70	10.97±0.48	3.53
Zn	190.00±5.00	190.57±27.21	0.30
Co	0.07±0.008	0.07±0.01	6.00
Ni	0.83±0.15	0.83±0.06	0.50
Cd	0.11±0.020	0.11±0.012	3.56
Cr	0.37±0.050	0.50±0.10	35.11
Pb	8.80±0.90	8.96±0.73	1.82

** - mg g^{-1}*
n - number of series of analytical measurements
RE-relative systematic error

Table 3. Validation parameters of the analytical procedure.

Element	LOD [$\mu g\ g^{-1}$]	LOQ [$\mu g\ g^{-1}$]	Precision	
			Interassay variation coefficient (CV %)	Intra-assay variation coefficient (CV %)
Ca	0.016*	0.054*	0.90	8.50
Mg	0.002*	0.009*	0.36	4.05
Fe	1.555	5.185	3.30	4.40
Zn	0.279	0.931	4.97	4.38
Cu	0.009	0.031	7.30	3.92
Mn	0.032	0.109	6.58	2.44
Pb	0.006	0.022	6.67	0.82
Cd	0.004	0.016	6.45	6.77
Co	0.002	0.008	9.62	5.81
Cr	0.012	0.041	1.99	15.79

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Component Analysis (PCA) was employed because in this method the new orthogonal variables (principal components – PCs) are created on the basis of the maximum variance criterion [21]. As a result, the first PC explains most of the total variance in the data set and the following PCs successively less. Because concentrations of the tested elements differ significantly, the concentrations in the raw data matrix (**X**) cannot be compared directly. Therefore, each data set was subsequently autoscaled [21]:

$$z_{ij} = (x_{ij} - \bar{x}_j) / s_j$$

where z_{ij} is the autoscaled value of x_{ij}, x_{ij} is the concentration of *jth* element in sample *i*, $\bar{x}_j$ is the mean value of variable x_j (calculated from the data in column j of the matrix **X**) and s_j is the standard deviation of variable x_j (calculated from the data in column j of the matrix **X**). The data matrix (**X**) contained 42 objects (24 women and 18 men) and 27 variables (concentrations of Ca, Cd, Co, Cu, Fe, Mg, Ni, Pb and Zn in hair, fingernails and toenails). It was necessary to exclude some objects or variables for further analysis due to lack of the concentration values resulting from measurements below the LOD. Thus in every presented cases there is a different number of objects or variables which were examined in the PCA.

3. Results and discussion

Analysis of alternative biological materials for determination of metals has been carried out for many years [19]. In most studies hair is used as an alternative material to blood and urine. Information about the level of essential and toxic metals in nails is rare. Hair and nails present the crucial advantage of being collected in a non-invasive manner. However, there is some controversy relating to the credibility of the results of determination of metals in these materials [21].

In this investigation, the concentrations of ten elements were measured in a group of healthy volunteers but only 7 were analyzed. The elements were divided into two groups. The first one – essential elements: Ca, Cu, Fe, Mg, Zn, and the second one – elements interesting from a toxicological point of view: Cd, Cr, Co, Ni, Pb. Although, chromium, cobalt and nickel have some physiological importance, high levels are often also toxic in humans. These elements were determined in the hair, fingernails and toenails of 24 women and 18 men.

The ICP-MS method was optimized and validated before each analysis. In the first step, the method of washing (Triton, water, methanol) and drying (80°C, 6 h) was developed. The mineralization process was performed in a microwave oven in the optimized conditions presented in Table 1.

The applied ICP-MS method enabled determination of the selected element on the certified levels with satisfactory accuracy (Table 2).

Concentrations of calcium and magnesium in hair (H), toenails (T), fingernails (F) were compared and presented in Fig. 1 as a projection on the PC1 *vs*. PC2 plane. In this case the data set included 16 objects (samples from 8 men and 8 women) and 6 variables (concentrations of calcium in hair, toenails, fingernails and concentrations of magnesium in hair, toenails, fingernails). As can be seen in Fig. 1, the first two PCs explain about 75.4% of the total variance in the data set, which enables qualitative interpretation of the data. The variables are divided into three distinct groups which correspond to different alternative materials. The concentrations of magnesium and calcium are highly correlated within the types of alternative materials - hair (H), toenails (T) and fingernails (F). On the other hand, as can be seen in Fig. 1, there is no correlation between groups H and F, whereas groups H and T are weakly correlated. Furthermore, negative correlation between groups F and T is also observed in the examined data set.

Subsequently, zinc and copper were compared. The results obtained from PCA are shown in Fig. 2. In this case, the three first PCs amounted to 89.65% of the total variance in the data. This time the data matrix included 17 objects (samples from 9 men and 8 women) and 6 variables (concentrations of copper and zinc in hair (H), toenails (T) and fingernails (F)). Three groups of variables can be seen in Fig. 2. The concentrations of zinc and copper in fingernails or toenails are strongly correlated; weaker but still significant correlation is observed within the hair group. The relationship between the materials demonstrates the correlation between toenails and fingernails.

Finally, the data set for nickel, chromium, and cadmium was analyzed by the PCA method. The projection of the variables onto the first two PCs is presented in the Fig. 3. The data matrix was constructed out of 15 objects (samples from 9 men and 5 women) and 6 variables (concentrations of nickel, chromium, cadmium in hair (H) and fingernails (F)). 81.35% of the total variance in the data set is explained by the first two PCs. The variables are grouped in two clusters according to the type of materials and they are strongly correlated. Correlation has not been observed between clusters.

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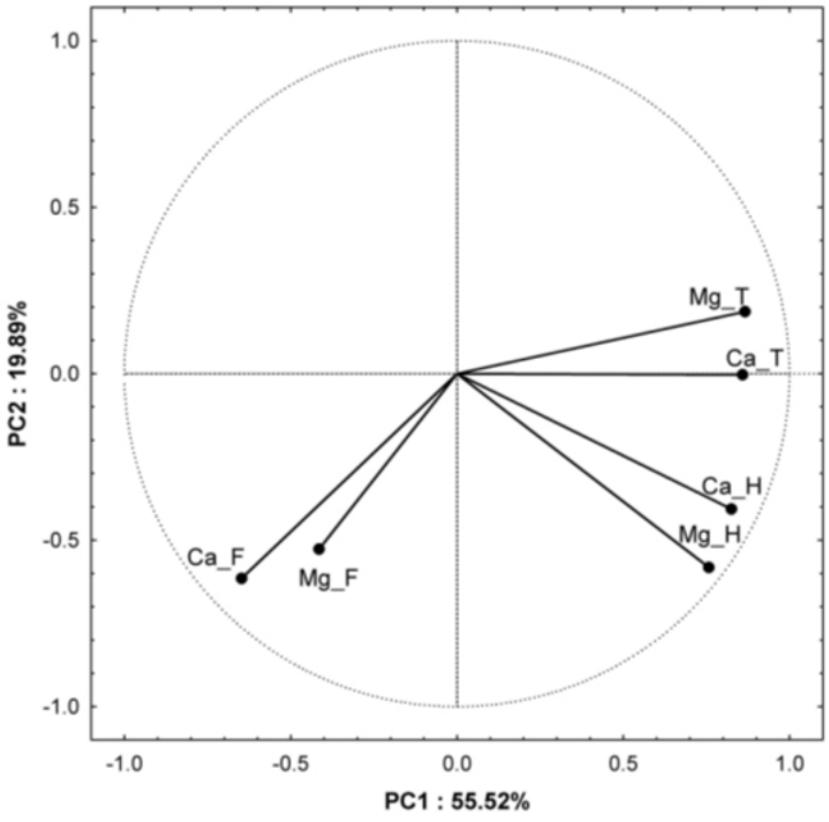

Figure 1. Projection of variables (Ca and Mg) on the plane of PC1 (55.52%) and PC2 (19.89%) principal components.

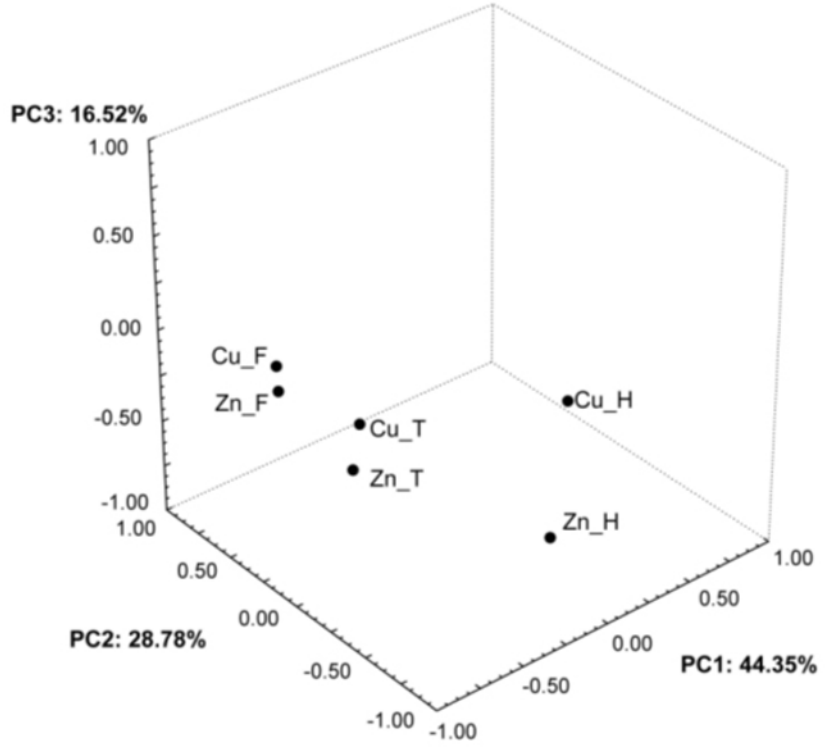

Figure 2. Projection of variables (Cu and Zn) on the space of PC1 (44.35%), PC2 (28.76%) and PC3 (16.52%) principal components.

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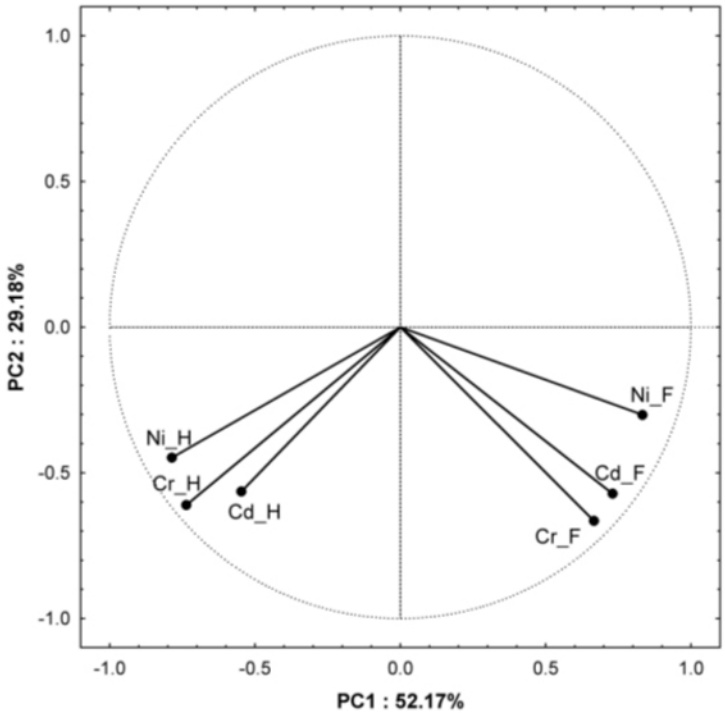

Figure 3. Projection of variables (Cr, Ni, Cd) on the plane of PC1 (52.17%) and PC2 (29.18%) principal components.

Table 4. Mean concentration of essential metals in hair and nails of healthy volunteers (24 women; 18 men).

	Material	Concentration±SD [ng g^{-1}] Element				
		Calcium*	Copper	Iron	Magnesium	Zinc
Women	Hair	1.57±0.84	18.4±3.8	38.8±12.5	83.4±33.6	246.5±87.7
	Fingernails	0.71±0.34^{b}	7.6±4.6^{b}	53.7±31.1^{b}	94.2±36.2	138.5±57.7^{b}
	Toenails	1.08±0.30^{c,d}	5.3±1.0^{c,d}	43.7±21.4	159.5±28.4^{c,d}	123.1±26.7^{c}
Man	Hair	0.73±0.78^{a}	15.9±3.1^{a}	40.2±13.4	46.2±20.1^{a}	222.1±85.9^{a}
	Fingernails	0.63±0.32	8.9±3.8^{b}	66.0±21.7^{b}	101.0±23.5^{b}	145.0±24.3^{b}
	Toenails	1.00±0.40^{d}	4.3±1.5^{a,c,d}	42.0±23.6^{d}	155.1±37.1^{c,d}	119.7±34.5^{c,d}

** - Calcium concentration µg g^{-1}*
a – women vs. man $p<0.05$
b – hair vs. fingernails $p<0.05$
c – hair vs. toenails $p<0.05$
d – finger vs. toenails $p<0.05$

3.1. Relationship between gender and concentration of the selected metals in hair and nails

Differences in the concentration of metals in hair between women and men may be caused by faster growth of hair in women [23]. Our results obtained for the essential elements seem to support this hypothesis. In women's hair the concentration of Ca, Cu, Mg and Zn was lower than in the hair of men. For calcium and magnesium the decrease was twofold. It was also observed that the concentration of essential metals in fingernails and toenails was similar in women and men. These results have been proved by Cluster Analysis (CA), where the distance between objects was defined as 1-r, where r is the correlation coefficient between objects (the paper concerning the methodology of applying the correlation coefficient as a measure of similarity between objects is under preparation). Ward's method [24] was chosen as the agglomerative method. The outcome is illustrated on a dendrogram which was made on the basis of 16 objects 8 women (K) and 8 men (M)) and 12 variables - concentrations of Ca, Mg, Cu and

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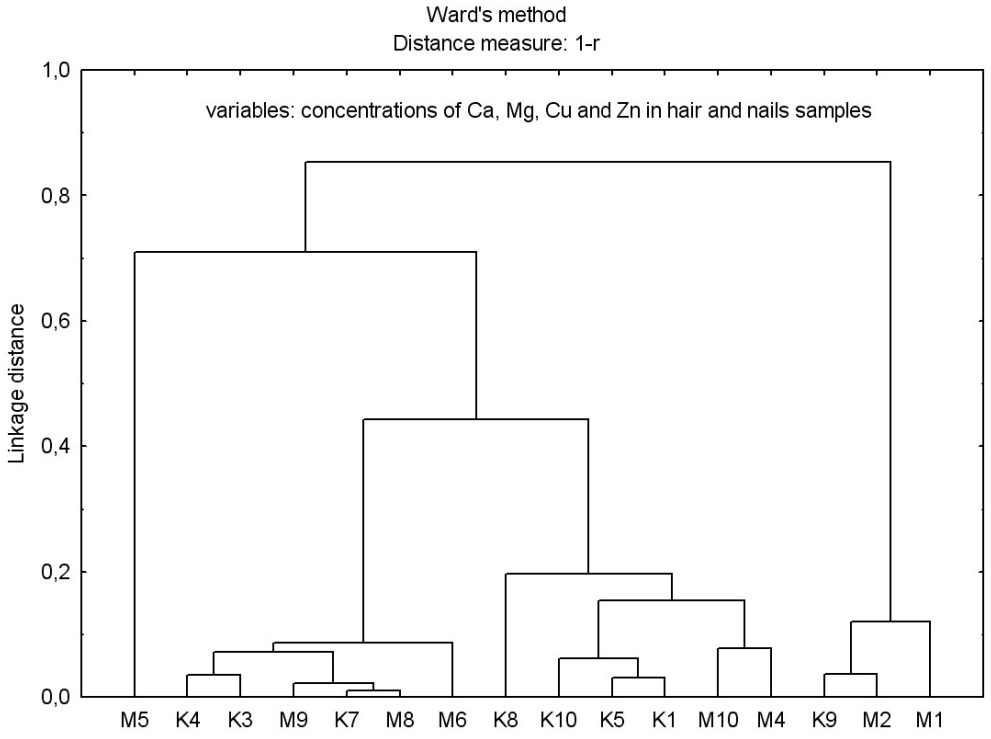

Figure 4. Dendrogram of cluster analysis made on the basis of Ward's method and 1-r distance for the essential elements.

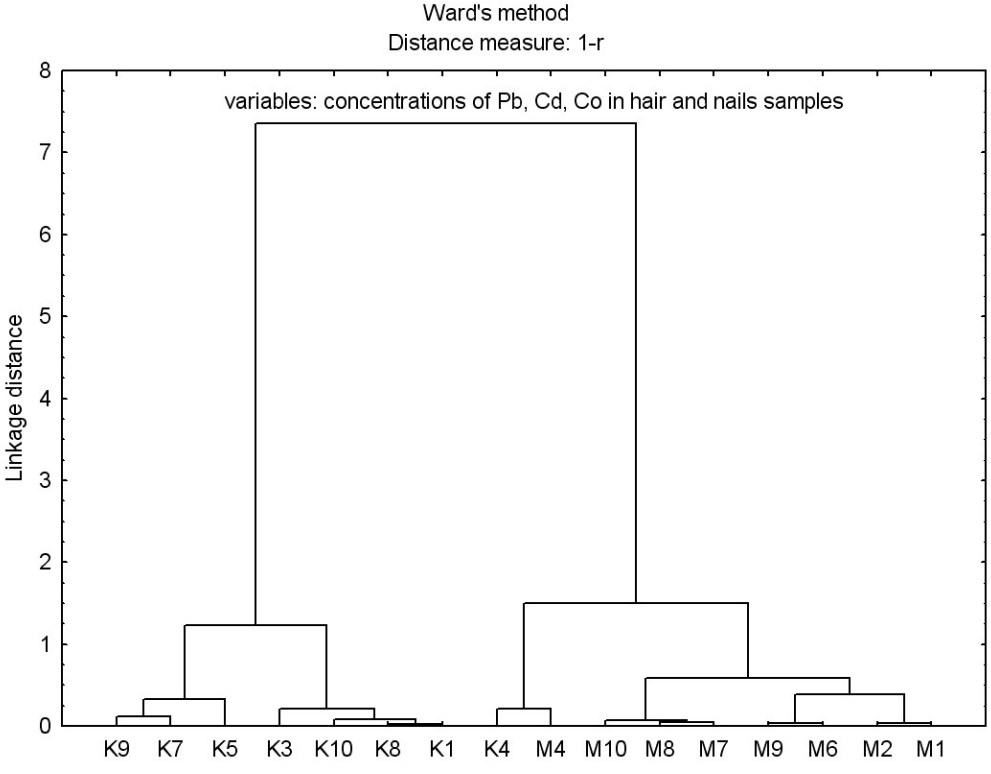

Figure 5. Dendrogram of cluster analysis made on the basis of Ward's method and 1-r distance for the toxic elements.

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Table 5. Mean concentration of metals interested from toxicological point of view in hair and nails of healthy volunteers (24 women; 18 men).

	Material	Concentration ± SD [ng g^{-1}] Element				
		Cadmium	Chromium	Cobalt	Lead	Nickel
Women	Hair	0.16±0.21	1.25±1.52	0.150±0.15	1.36±1.24	1.25±1.46
	Fingernails	0.25±0.65	1.81±1.64	0.034±0.03[b]	1.18±1.12	2.88±1.81[b]
	Toenails	0.14±0.15	1.77±1.60	0.047±0.06[c]	1.15±0.78	3.25±1.60[c]
Man	Hair	1.81±1.70[a]	2.71±2.03	0.052±0.03[a]	0.17±0.18[a]	1.62±1.33
	Fingernails	0.16±0.15[b]	3.11±1.60[a]	0.056±0.05	0.16±0.15[a]	3.12±2.03[b]
	Toenails	0.59±0.41[a,c,d]	3.11±1.88[a]	0.027±0.01	0.17±0.14[a]	2.20±1.24

a – women vs. man $p<0.05$
b – hair vs. fingernails $p<0.05$
c – hair vs. toenails $p<0.05$
d – finger vs. toenails $p<0.05$

Zn in hair and nails samples (Fig. 4). Similar qualitative results were obtained when squared Euclidean distance and Ward's method were used. A similar result was obtained when hair and nail samples were taken into account separately.

In relation to toxic elements the situation is not so clear. The hair of women showed higher concentrations of cobalt and nickel than in men's hair, but at the same time it showed lower concentrations of cadmium (Table 5). Differences in toxic metal concentration in fingernails and toenails were similar for both sexes. The concentration of chromium was twofold lower in women's nails than in men's nails and the concentration of lead was sevenfold higher in women's nails than in men's nails. In the clustering analysis (CA), concentrations of three toxic metals Pb, Cd and Co in hair and nails samples obtained from 8 women and 8 men (16 objects) were taken into account. The corresponding dendrogram is presented in Fig. 5, where grouping on the basis of the gender is clearly visible (apart from a single case of sample K4 which was incorrectly matched to the men's cluster). These results are difficult to explain and are not supported in literature [25].

3.2. Relationship between concentration of the studied elements in hair, fingernails and toenails

The aim of comparing the concentration of metals in the studied materials was to confirm whether hair, fingernails and toenails can be used as alternative materials for determination of metals.

The concentration of metals in hair and nails can be influenced by genetic and environmental factors. To avoid the influence of environmental factors, healthy volunteers - non smokers, social drinkers, living in the same area (Krakow) and of a similar age - were recruited for the study. The determinations performed showed that the concentration of toxic elements was different in the fingernails and toenails of men and women (Table 5). This behavior was observed only for toxic elements. In the case of essential elements, their concentration in fingernails and toenails was similar (except for copper) and was not gender dependent (Table 4).

4. Conclusions

On the basis of our own examinations, along with previously published studies, it may be concluded that it is of prime importance to perform analysis of samples collected from volunteers prior to conducting tests on patients. This is related to differences in the elemental content of the environment and region of habitation of the examined persons, even among persons of similar age and sex [16,25-30].

The results of this preliminary study showed that hair, fingernails and toenails are good materials for essential and toxic metals determination. The possibility of using them as alternatives to blood does however require further studies with a larger population of volunteers. The results revealed that individual nail and hair samples showed differences in concentration of toxic elements dependent on the sex of the volunteer. Higher concentrations of Co and Pb were observed in women's hair, as well as higher concentrations of Pb and Cd in fingernails. The concentrations of Cd and Cr were

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higher in men's hair and toenails. The concentrations of the essential elements (Cu, Fe, Mg, Zn, Ca) in nails were similar for both sexes.

Application of the Principal Component Analysis (PCA) is not popular in toxicological studies. However, this type of chemometric analysis turns out to be very helpful in searching for relationships between elements. The approach applied enabled examination of the degree of correlation of the selected elements within and between the alternative materials. The advantage of application of the results in assessment of the exposure to metals requires further research on a group diversified in terms of the kind of exposure. In conclusion, the results of this study suggest that hair and nails may be used as interchangeable material for assessment of exposure to toxic metals and disturbance of physiological metal homeostasis only with high caution. Thus, various kinds of alternative samples should be collected and analyzed together to reveal a clearer image of homeostasis in the body.

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