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Original Research

X-Ray Fluorescence Spectrometry in Multielemental Analysis of Hair and Teeth

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Abstract

During our study a procedure of hair (62 samples) and teeth (38 samples) preparation for the XRF analysis was worked out. The samples were collected from the inhabitants of Katowice, Gliwice, Pyskowice and Tychy (Silesia, Poland). In hair samples S, Ca, Na, Mg, P, K, Mn, Fe, Cu, Zn, Sr, Pb content was determined and in teeth samples Ca, P, Na, Mg, Al, S, K, Fe, Ni, Cu, Zn, Sr, Pb content was determined. Conformity between the XRF and ICP results was obtained. Several correlations between the concentration of some elements and personal features (sex, age, smoking related) and environmental contamination were indicated. There were differences in the content of Al, Pb and Fe in women's teeth and men's teeth. A positive correlation between age and Mg, Fe, Cu, Sr and Pb content in teeth samples was noticed. Zn, S and Pb content depended on the level of pollution in the environment the samples came from. There were high levels of Zn and Pb concentration in teeth samples from smokers.

In hair, positive correlations between the content of Ca, Fe and P and age were observed. Differences in Na, K and S content between women's and men's hair were noticed. Ca and Pb levels were different in samples obtained from different cities in Silesia. No correlation for Ba, Zn, Cu, Mn, Si was observed.

Keywords: XRF, multielemental analysis, hair, teeth.

Introduction

Human hair and teeth analysis has been carried out in many different studies on the influence of environmental pollution on the human body. There have been many investigations concerning hair analysis [1-6, 10-12, 14-19, 26], while teeth samples have rarely been analyzed [7-9, 13, 20-25, 27], which might be caused by poor access to the material. In most analyses heavy metals, usually Pb and Cd, are examined. The most popular methods are AAS [1-9], ICP [6-13] and NAA [14]. The X-ray techniques are not often used in such analyses. Prior to our research the ED XRF [1, 13,15-19] technique was used for hair analysis and for teeth, PIXE [20-25] and SR XRF [22,24,26,27]. Thin layers of teeth were used in the SR XRF analysis and powdered teeth were used in the XRF analysis. XRF has not been used previously in studies on the correlation between sex, age or pollution and metals content in teeth. XRF and ICP have not been compared in studies, either. Biological samples (teeth and hair) from various polluted cities of Silesia are the subject of this research. The use of the X-ray technique allows us to determine heavy metals as well as macro elements in the examined samples and enables us to point out proper correlations.

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Materials and Methods

62 samples of hair and 38 samples of teeth were collected from the inhabitants of Katowice, Gliwice, Pyskowice and Tychy (Silesia, Poland). Katowice and Gliwice

are highly industrial and polluted cities with numerous factories (steelworks and mines). This area has been among the most polluted regions in Europe for many years. Tychy and Pyskowice are much less polluted because of the agricultural character of the surrounding lands, as well as favourable winds (Fig.1.). All samples were divided into four groups according to the sex, age, place of residence of the volunteers, types of teeth and smoking habits.

In this work, X-ray fluorescence spectrometry with the dispersal of wave length was used for the qualitative and quantitative analysis of human hair and teeth. Thirteen elements in teeth and twelve elements in hair were analyzed simultaneously.

Experimental Procedure

Hair Samples Preparation

For the purpose of the study natural hair (no dye, no bleach) was taken exclusively, without distinguishing the part of the head they came from. 62 samples of hair were analyzed.

Samples of hair, about 2-3 g (length: 1-3 centimeters), were washed in 4 stages, 15 minutes each. The hairs were treated in several turns: in 20 ml of acetone, twice in 40 ml of twice distilled water, and then again in 20 ml of acetone. After washing, they were dried at 80ºC. The samples were ground in a vibratory grinder (*Willy Bleuler Apparatebau Zollikon* model "*1/4 PS*") for 2 minutes. Then 500 µl of ethanol was added (to prevent samples from dusting) and grinding was continued for another 2 minutes.

Fig. 1. Situation schema.

The ground hair (0.5 g) and boric acid (0.1 g) were weighed, the mixture was pastilled by means of a hydraulic press, under the pressure of 20 tons for 2 minutes. The tablets were analyzed by XRF immediately after their preparation.

Teeth Samples Preparation

38 samples of teeth were rinsed with water, cleaned mechanically with a hard brush and then left in 10% solution of H_2O_2 for 24 h. The teeth were rinsed again, brushed, put in a 10% H_2O_2 solution for another 24 h, rinsed and dried in 120ºC. The teeth were ground in a vibratory grinder for 1 minute. The size of grains was smaller than 0.12 mm .

The preparation of teeth tablets was identical to that of the hair samples described above .

Standards Preparation

The standards for the analysis of hair samples were prepared from certified reference material (CRM) for human hair – GBW07601 (GSH-1) – China.

To increase the concentration of the elements in standards, suitable quantities of KCl, $CuSO_4$, $ZnSO_4$, $Pb(CH_3COO)_2$ (concentration 0.1 mg/ml) solutions were added to 0.5g of CRM for hair. The samples were dried, and mixed to homogeneity. To dilute the CRM for hair, suitable quantities of boric acid were added.

All samples were pressed with 0.1 g of H_3BO_3 before analysis.

The standards for teeth analysis were prepared on the basis of certified reference material- apatite CTA-AC-1 (Institute of Chemistry and Nuclear Technology – Poland) as well as on the basis of dibasic phosphate of calcium pro analysis. To increase the concentration of some elements in standards, suitable solutions of $PbCl_2$, $ZnCl_2$, $MgCl_2$ and $Ce(SO_4)_2$ were added.

After drying, the samples were mixed to homogeneity and pastilled as described above.

Apparatus

A sequential X-ray fluorescence spectrometer with the dispersal of the wavelengths, with a rhodium lamp, (*PHILIPS* model *PW2400*) was used.

Programme parameters of the XRF spectrometer for qualitative and quantitative analysis are shown in Table 1.

Results

12 elements: Na, Mg, P, S, K, Ca, Mn, Fe, Cu, Zn, Sr, and Pb were analyzed in 62 hair samples.

13 elements: Ca, P, Na, Mg, Zn, S, K, Al, Fe, Ni, Cu, Sr, Pb were analyzed in 38 teeth samples. Each sample was analyzed 6 times. The results are presented in Tables 2 and 3.

To verify the results, a part of the samples was analyzed by ICP-OES. AAS method was used for Na and K. The results are shown in Table 4.

Table 1. Programme parameters of the qualitative and quantitative XRF analysis.

Element	X-ray tube voltage [kV]	X-ray tube current intensity [mA]	Crystal	Collimator	Detector	Angle [°2θ]
Sr	60	50	LiF 200	150 µm	scynt.	25.1288
Pb	60	50	LiF 200	150 µm	scynt.	33.8706
Zn	60	50	LiF 200	150 µm	scynt.	41.7426
Cu	60	50	LiF 200	150 µm	flow	44.9984
Fe	60	50	LiF 200	150 µm	flow	57.4698
Mn	60	50	LiF 200	150 µm	flow	62.9632
Ca	30	100	LiF 200	150 µm	flow	113.0100
K	25	120	LiF 200	150 µm	flow	136.6732
S	24	125	PE 002	550 µm	flow	75.8234
P	24	125	PE 002	550 µm	flow	89.4582
Mg	24	125	PX1	550 µm	flow	22.3966
Na	24	125	PX1	550 µm	flow	26.9418

Table 2. Concentration of the elements in human hair.

No.	S	Ca	Na	Mg	P	K	Mn	Fe	Cu	Zn	Sr	Pb
	[%]	[mg/g]	[mg/kg]									
Mean value n = 6	3.79	1.30	88.3	48.7	110.9	22.6	3.57	36.3	7.95	162.1	7.50	11.6
Minimum	1.83	0.099	21	10	55	5	1	15	2	45	1	2
Maximum	4.30	2.762	148	168	157	40	6	54	15	246	18	18

Table 3. Concentration of the elements in human teeth.

No.	Ca	P	Mg	Na	Al	S	K	Fe	Ni	Cu	Zn	Sr	Pb
	[%]			[mg/kg]									
Mean value n = 6	40.9	16.72	0.25	62.9	191.66	491.7	243.7	46.6	2.5	4.4	802.2	66.7	17.1
Minimum	28.1	11.50	0.2	30.8	57.06	302.4	142.8	4.4	0.7	0.9	83	37.2	4.6
Maximum	46.9	17.50	0.3	369.7	344.35	696.6	374.2	364	2.9	9.9	4387.1	140.8	44.1

As shown in the tables, a satisfactory correlation of the results was obtained in most cases.

Cd, Cr, Ni concentration in all samples and Mn concentration in some of the samples were below detection limit for X- ray method. The results from ICP method were taken into consideration (Table 4).

Discussion

There have been many studies concerning hair and teeth sample analysis. Most often heavy metals content was determined in the samples. In our work the X-ray apparatus parameters were worked out to analyze a wide spectrum of macro and micro elements. Correlations between the concentration of elements and origin (sex, age and place of residence of the volunteers) and type of samples (hair, teeth) were found. The results are presented in Table 5 (a and b).

A lower concentration of Na, K and S was found in women's hair. The concentration of Mg, Sr, Cd, Cr and Ni was lower in men's hair. The content of Fe and Cd in hair increases with age, the content of Ca and Ni de-

Table 4. Comparison of the results obtained from hair samples analyses by means of XRF and ICP methods.

Sample no.	Element	XRF			ICP-OES (AAS for Na and K)		
		Mean value [mg/kg]	SD [mg/kg]	RSD [%]	Mean value [mg/kg]	SD [mg/kg]	RSD [%]
10	Na	68	3.01	4.41	70	2.94	4.20
	Mg	142	7.34	5.18	145	3.90	2.69
	P	100	6.09	6.07	104	2.50	2.41
	K	14	5.01	36.15	18	0.98	5.44
	Ca	352	12.09	3.44	355	4.57	1.29
	Mn	< LLD*	< LLD*	< LLD*	0.83	0.02	2.40
	Fe	37	1.86	5.08	36	0.36	1.00
	Cu	6	0.89	14.91	5.8	0.10	1.73
	Zn	148	14.50	9.80	158	2.38	1.51
	Sr	13	2.23	16.91	13	0.31	2.36
	Pb	4	1.86	50.22	3.4	0.24	7.00
	Cd	< LLD*	< LLD*	< LLD*	0.185	0.07	37.84
	Cr	< LLD*	< LLD*	< LLD*	2.82	0.39	13.83
	Ni	< LLD*	< LLD*	< LLD*	0.62	0.14	22.58
15	Na	99	2.07	2.08	103	6.21	6.03
	Mg	17	0.98	5.84	15.122	0.20	1.32
	P	114	3.37	2.95	115.12	1.80	1.56
	K	18	5.34	29.12	15	0.20	1.33
	Ca	184	4.05	2.20	185.16	13.00	7.02
	Mn	< LLD*	< LLD*	< LLD*	0.576	0.05	8.68
	Fe	31	1.64	5.39	33.119	0.57	1.72
	Cu	8	0.41	5.21	7.899	0.34	4.30
	Zn	199	12.28	6.16	191.25	2.04	1.07
	Sr	2	0.41	22.27	2.326	0.02	0.86
	Pb	9	3.48	38.43	5.958	0.89	14.94
	Cd	< LLD*	< LLD*	< LLD*	0.27	0.01	3.70
	Cr	< LLD*	< LLD*	< LLD*	1.784	0.38	21.30
	Ni	< LLD*	< LLD*	< LLD*	1.053	0.17	16.14
18	Na	52	1.86	3.56	54	0.44	0.81
	Mg	52	2.00	3.85	55.305	0.80	1.45
	P	97	1.86	1.93	94.91	8.90	9.38
	K	21	3.55	16.55	20	0.61	3.05
	Ca	1479	11.46	0.78	1481.15	66.70	4.50
	Mn	2	0.41	22.27	1.187	0.06	5.05
	Fe	39	1.26	3.24	38.349	1.04	2.71
	Cu	11	0.82	7.65	10.773	0.33	3.06
	Zn	126	4.34	3.45	127.85	3.14	2.46
	Sr	6	0.52	8.15	6.517	0.08	1.23
	Pb	6	1.63	29.41	6.115	0.97	15.86
	Cd	< LLD*	< LLD*	< LLD*	0.259	0.04	15.44
	Cr	< LLD*	< LLD*	< LLD*	4.888	0.32	6.55
	Ni	< LLD*	< LLD*	< LLD*	3.418	0.27	7.90

Table 4 continues on next page...

19	Na	29	0.84	2.94	29	0.58	2.00
	Mg	35	1.03	2.98	38.628	1.19	3.08
	P	112	1.94	1.74	110.43	5.17	4.68
	K	6	2.84	51.49	8	0.60	7.50
	Ca	2259	28.15	1.25	2217.5	106.20	4.79
	Mn	5	0.41	7.90	4.923	0.68	13.81
	Fe	32	0.75	2.36	30.584	1.21	3.96
	Cu	6	0.52	8.15	5.639	0.28	4.97
	Zn	213	25.97	12.20	230.62	1.14	0.49
	Sr	7	0.42	6.14	6.1	0.35	5.74
	Pb	2	0.75	33.80	2.245	0.52	23.16
	Cd	< LLD*	< LLD*	< LLD*	0.225	0.04	17.78
	Cr	< LLD*	< LLD*	< LLD*	1.952	0.12	6.15
	Ni	< LLD*	< LLD*	< LLD*	1.317	0.05	3.80
23	Na	31	1.21	3.95	29	1.16	4.00
	Mg	55	1.17	2.13	53.698	0.31	0.58
	P	113	4.72	4.20	110.53	1.80	1.63
	K	10	1.86	17.79	12	0.19	1.58
	Ca	1062	67.61	6.37	1035.1	21.60	2.09
	Mn	< LLD*	< LLD*	< LLD*	0.442	0.07	15.84
	Fe	22	1.72	7.77	22.604	0.27	1.19
	Cu	13	0.63	4.87	13.274	0.53	3.99
	Zn	190	10.71	5.63	193.78	1.10	0.57
	Sr	5	0.41	8.45	5.206	0.06	1.15
	Pb	3	1.52	60.66	1.695	0.89	52.51
	Cd	< LLD*	< LLD*	< LLD*	0.029	0.00	0.00
	Cr	< LLD*	< LLD*	< LLD*	1.702	0.20	11.75
	Ni	< LLD*	< LLD*	< LLD*	0.182	0.10	54.95

* < LLD - below limit detection

creases with age and the content of K and Cr increases and then decreases at the age of about 60. This is consistent with the results obtained by other authors who investigated Ca content in hair and arteries by means of ED XRF [17].

The influence of the environment is demonstrated in the example of Ca and Pb content in samples. As expected, a higher concentration of Pb appeared in hairs of people who lived in contaminated areas (Gliwice). The concentration of Ca in hairs may depend on age, sex, health condition as well as the degree of hardness of water in place of residence of the volunteers. Lower concentrations of Ca were found in hairs of people living in cities where water is less hard (Pyskowice, Tychy). No correlations were found for other elements.

Several correlations between sex, age of volunteers or environmental conditions and the content of elements in human teeth were also found. Slightly higher concentrations of Al were found in women's teeth. It could be caused by the use of cosmetics (lipsticks). A higher concentration of Pb and Fe can be observed in men's teeth (Fig. 2).

The contents of Mg, Fe and Cu in samples correlated with the age of the volunteers, for Sr the correlation was reversed. The highest contents of Pb were found in samples from people aged between 36-60. The fact may be connected with exposure at work. Until the present, the correlation between the Pb concentration and age was monitored in bones but not in teeth.

Higher contents of Zn and S were observed in the samples from the inhabitants of Katowice, where the metallurgical industry and a high level of pollution are present. There were no differences in Pb levels in the samples from the remaining cities.

Concentrations of elements were determined in incisors, premolar and molar teeth. The highest levels of Mg, Zn, Fe, Pb, Na, K and the lowest levels of Sr were found in incisors. In molar teeth the levels of S, Al, Sr were highest and the levels of Na, K, Pb, Cu, Fe - lowest. In premolar and molar teeth the contents of Mg, Zn, Sr, Cu, Fe were approximately the same. The concentrations of Al, K, Na, S in premolar teeth were approximately the same as in incisors. Higher contents of Zn and Pb for smokers were confirmed (Fig. 3)

Table 5a. Obtained correlations between element contents in hair.

Element [mg/kg]	Sex dependence		Environmental dependence			Age dependence			
	Females	Males	Gliwice	Pyskowice	Tychy	<15	15-35	36-60	>60
Na	63.17±3.41	92.00±5.43	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
K	12.01±0.61	26.75±1.47	n.c.	n.c.	n.c.	21.52±1.18	27.04±0.66	28.10±0.70	25.01±0.88
S	$3.38 \cdot 10^4 \pm 19.94 \cdot 10^2$	$4.04 \cdot 10^4 \pm 23.03 \cdot 10^2$	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Mg	117.85±14.02	24.68±2.30	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Sr	12.97±0.77	4.66±0.25	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
Ca	n.c.*	n.c.	$1.53 \cdot 10^3 \pm 84.15$	$1.12 \cdot 10^3 \pm 42.56$	$1.29 \cdot 10^3 \pm 63.21$	1.70±0.11	1.52±0.08	0.83±0.06	0.55±0.05
Pb	n.c.	n.c.	11.96±0.78	9.20±0.41	17.12±0.71	n.c.	n.c.	n.c.	n.c.
Fe	n.c.	n.c.	n.c.	n.c.	n.c.	26.29±1.29	33.66±1.72	49.58±3.10	52.70±3.95
P	n.c.	n.c.	n.c.	n.c.	n.c.	88.48±6.64	113.1±6.33	133.1±7.72	107.5±5.38
Cd	$0.205 \pm 4 \cdot 10^{-3}$	$0.192 \pm 5 \cdot 10^{-3}$	n.c.	n.c.	n.c.	0.151±0.01	0.197±0.01	0.348±0.02	0.379±0.03
Cr	4.48±0.22	3.78±0.20	n.c.	n.c.	n.c.	2.95±0.14	3.79±0.20	6.34±0.32	3.29±0.16
Ni	$1.18 \pm 8 \cdot 10^{-3}$	$0.803 \pm 4 \cdot 10^{-3}$	n.c.	n.c.	n.c.	1.00±0.07	1.06±0.05	0.654±0.03	0.546±0.03

*n.c. - no correlation

Table 5b. Obtained correlations between element contents in teeth.

Element [mg/kg]	Kind of tooth			Age dependence				Environmental dependence		Sex dependence		Smoking- dependence	
	Incisors	Premolar	Molar	<15	15-35	36-60	>60	Katowice	Gliwice	Females	Males	Smokers	Non-smokers
Mg	2282±114.1	1794±80.7	1939±67.9	1735±200.6	1728±98.3	2015±92.2	2299±130.7	n.c.	n.c.	n.c	n.c	n.c	n.c
Zn	1636±188.1	663.0±37.1	759.3±44.9	n.c.*	n.c.	n.c.	n.c.	1018±128.6	264.1±40.4	n.c	n.c	1530±102.3	842.1±76.5
Fe	78.48±10.59	48.66±2.68	45.15±2.26	53.30±3.13	53.20±4.71	42.09±2.81	101.4±8.62	n.c.	n.c.	44.53±2.60	67.32±1.54	n.c	n.c
Sr	91.64±4.67	103.7±5.91	114.3±5.72	116.6±7.98	123.8±11.7	98.48±12.7	98.56±8.87	n.c.	n.c.	n.c	n.c	n.c	n.c
Pb	22.19±1.05	15.40±0.21	14.75±0.30	14.16±0.80	11.67±0.40	30.67±2.65	18.35±1.01	17.12±0.53	18.07±0.23	17.71±1.15	27.29±1.40	37.20±9.93	15.40±8.25
S	534.1±45.4	415.8±28.9	617.7±33.1	n.c.	n.c.	n.c.	n.c.	703.1±35.9	468.0±42.6	n.c	n.c	n.c	n.c
Al	117.7±7.83	102.8±5.96	151.0±9.06	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	130.3±0.75	127.3±0.81	n.c	n.c
Na	3684±25.8	3630±18.1	3495±52.4	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c	n.c	n.c	n.c
Cu	8.40±0.47	9.40±0.31	7.86±0.28	4.560±0.42	5.78±0.49	7.97±0.75	8.93±0.52	n.c.	n.c.	n.c	n.c	n.c	n.c
K	257.4±14.5	252.2±21.6	229.6±11.7	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c	n.c	n.c	n.c

*n.c. - no correlation

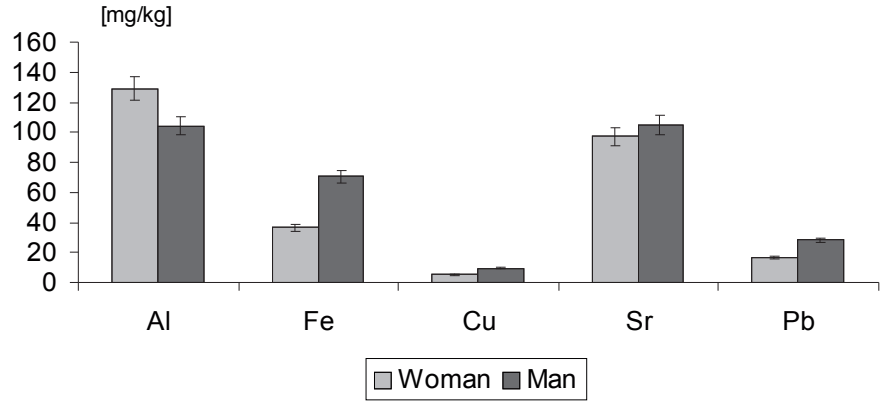

Fig. 2. The relationship between the contents of elements in teeth and sex of volunteers.

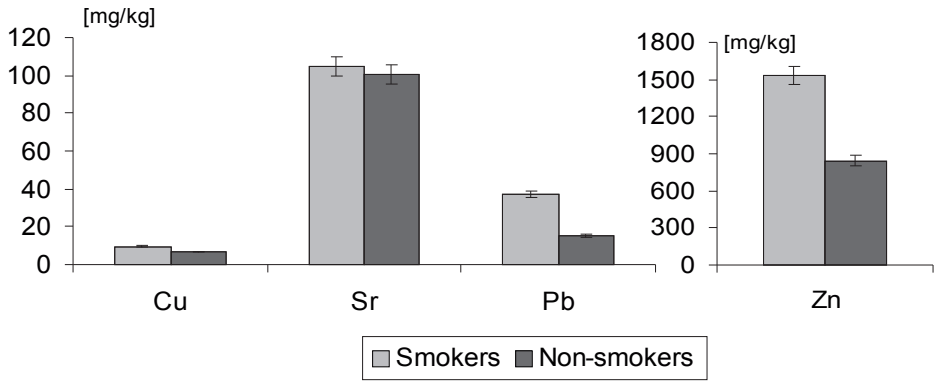

Fig. 3. The relationship between the contents of elements in chain smokers' and non-smokers' teeth.

Conclusion

The procedure of samples preparation and determination of wide spectrum of elements in human hair and teeth was worked out during our study. The use of certified reference materials allowed us to enhance the calibration of the X-ray spectrometer and to validate the analytical procedure.

The reliability of the results obtained by XRF analysis were verified by means of the ICP-OES method.

In summary, the XRF method can be used for simultaneous analyses of matrix elements as well as trace elements in biological samples.

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