



# Concentration of some heavy metals in Egyptian human hair

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## Abstract

In this work, Flame Atomic Absorption Spectrometry (FAAS) was applied for the determination of Cu, Fe, Mg, Mn, Ni, and Zn in twenty –four hair samples. The samples were collected covering different ages and gender. The samples are divided as, seventeen samples from people which assumed to be environmentally healthy (control) and seven samples from different worker’s people such as Iron worker, Cement worker and Duco worker (exposed). Samples were brought into solution using HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. In three example samples the molecular structure of the human hair was studied using Fourier Transformer Infrared Spectrometer (FTIR) in the range of 200- 4000 cm<sup>-1</sup>. The contamination of the sample was discussed for different samples.

**Keywords:** Human Hair, Heavy Metals, FAAS, FTIR.

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## 1. Introduction

In the last few decades the analytical study of concentrations of the minor and trace elements in biological and human samples have become very important. Occupational diseases, poisoning, and environmental diseases are accurately diagnosed by using trace elemental analysis of human biological samples and the state of health can be characterized with the analytical results[1]. The importance of these examinations is attested to by the fact that there are several trace elements in the human body that are important in the biochemical processes. An excess or absence of these essential trace elements causes serious problems in the physiology of the body. Thus, it is very important to check regularly trace element Concentrations in the body. Trace element analysis of biological samples is a considerable challenge to analytical studies.

The accurate and sensitive determinations of trace elements are the important part of analytical chemistry studies. [2-4] Flame atomic absorption spectrometry (FAAS) is relatively simple and available technique in many laboratories for heavy metal determination. [5-10] Because of the large amount of organic substances in the samples, digestion or ashing is required prior to analysis and the low concentrations of the measured elements demand well-organized [11].

Interest in human hair as a clinical sample has increased in recent years due to certain advantages offered by human hair over other clinical specimens such as blood or urine samples. Hair offers a good way of discerning long-term variations in trace element concentration by providing a better assessment of normal trace element concentrations [12].

The advantages of analysis of hair over blood and urine samples for the determination of metals are (I) the concentrations of most of the trace elements are higher in hair than in other human materials; (II) specimens can be collected more quickly and easily than specimens of blood, urine or any other tissue and also special storage conditions are not needed; (III) unlike blood, hair is an inert and chemically homogeneous sample ;and (IV) serum and urine concentrations provide both an acute index and also over a relatively short time period whereas the concentrations in hair provide a retrospective index of trace element supplies[13] .

Keratin is one of the most abundant proteins, being the major component of hair, feathers, nails and horns of mammals, reptiles and birds. The disposal of keratin wastes such as fiber byproducts from the wool textile industry, poor quality raw wools not fit for spinning, horns, nails and feathers from butchery, involve complex environmental and economic aspects. Moreover, pooling and processing of keratin wastes could allow a better exploitation of such a large amount of biomass, considering that the total amount of these materials has been estimated more than 3 million tons per year [14].

The essential element of the structure of the keratin macromolecule is the way of alignment of amino acids residue along its chain. The sequence of amino acids defines the possibility of intermolecular links, the molecular cohesion of the keratin and the access of amino acids to the chemical reaction [15].

The aim of the present work is to determine the concentration of heavy metals in human hair and its molecular structure.

## 2. Experimental

### 2.1. Sample preparation

To remove the external contamination from samples, washing technique should be applied such that it will remove only the surface external contamination without extracting metals from the samples or depositing metals on them. According to Harrison and Tyree [16] detergent washing reduced the element concentrations more than the organic washing. However for heavy metals, washing procedures do not essentially influence their concentrations because of the strong complex with the disulfide groups in keratin proteins [17]. Therefore, acetone was used in this study as washing liquid to remove the external contaminates. The samples were cut in pieces as small as possible, washed three times with acetone, and rinsed three times with deionized water. After washing, the hair samples were dried in an electric oven 60°C and protected in polyethylene bags until analysis.

Apportion of 0.5 gm of the dried sample weight in a clean glass beaker, followed with 20 ml (HNO<sub>3</sub>) and 10 ml (H<sub>2</sub>O<sub>2</sub>) [12]. It was heated gently on a hot plate at 150°C until evaporated to near dryness for three hours. Further 10 ml of HNO<sub>3</sub> and 10 ml hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) were added to the residue and evaporated to near dryness to ensure the complete dissolution. Distilled water is then added to the sample, and completed to 50 ml, in a volumetric flask to obtain a clear solution.

For IR study the samples were measured using KBr disc technique. 200 mg of (KBr) mixed with sample and pressed under pressure 10 tons held for 5 minutes and then slowly released a disc diameter of 13 mm.

## 3. Apparatus

Thermo-Elemental S4 full automatic atomic absorption spectrometer equipped with deuterium continuum background corrector. A burner-nebulizer (100 mm with single slot for air acetylene C<sub>2</sub>H<sub>2</sub>) was utilized as an absorption cell. The light sources were Thermo- Elemental hollow cathode lamps. All measurements were the average of three 3s integrations and a blank measurement was made between every solution measurement. Jasco 300E Fourier transform infrared spectrometer was used in the present work.

## 4. Results and discussion

### 4.1. Concentration of determined elements

In order to construct the analytical calibration curve standard solutions in increasing concentration were nebulized at the operating conditions (according to manufacture guide). The absorbance were determined and plotted against the concentrations. Under the same operating conditions, the sample solutions were nebulized and the absorbance was determined. It would be mentioned here that the determined absorbance is the value after reject incompatible readings (incompatible reading means scattering more than 95%). Obtained concentrations of the determined elements in hair samples for control and worker group are present in Tables 1 and 2. The values listed are the mean values of ten replicate determinations.

It was observed from the obtained results that the concentration of the determined elements (Cu, Fe, Mg, Mn, Ni and Zn) in samples of control group is lower than the obtained one of worker's. The higher concentration for metals in worker's hair may be due to contamination from their area. Also it was observed that the average concentration for all elements in all ages for hair samples of Duco worker's is higher, except for Zn. The average concentration of Zn in hair samples for Iron workers is higher than the average concentration of other elements in Duco and Cement worker's hair samples.

## 5. Metal concentration in relation to ages

The relation between the concentration of the determined elements in control hair samples and their ages are illustrated in Fig (1, 2). It was observed that the behaviors of Cu, MN Ni Zn and Mg are similar, but the concentration of Fe at age 30 years decreases. This may be due to the manner of the nutrition of the donor's at this age.

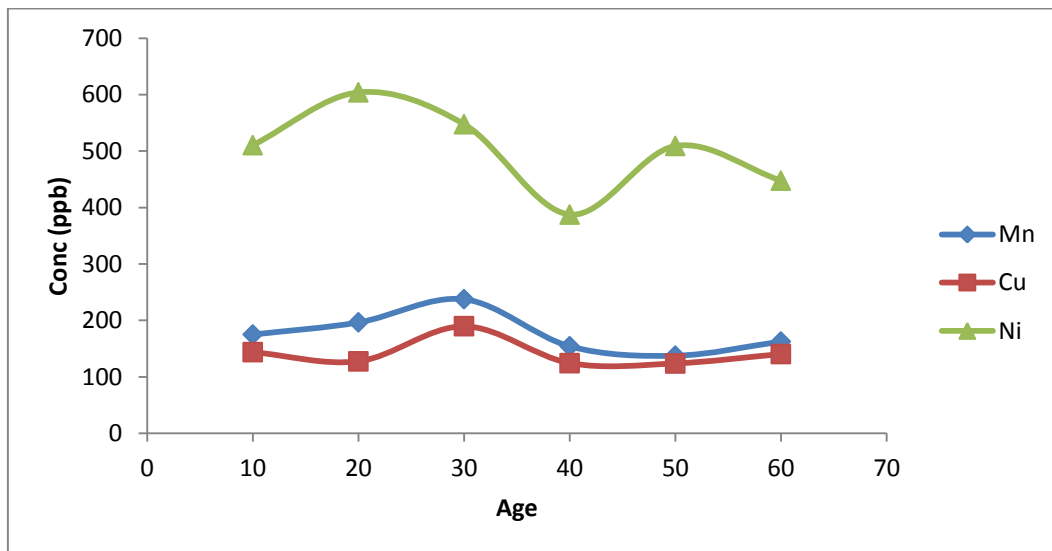
**Table 1:** Concentration in ppb for Detected Elements in Human Hair for (Control Group)

sample	Age (year)	Concentration in ppb					
		Cu	Fe	Mg	Mn	Ni	Zn
1	6	151 ± 7	5018 ± 251	2167 ± 108	163 ± 8	514 ± 25	1353 ± 68
2	10	100 ± 5	4754 ± 238	6207 ± 310	163 ± 8	500 ± 25	1937 ± 97
3	14	112 ± 5	4441 ± 222	2760 ± 138	200 ± 10	517 ± 25	1995 ± 100
4	15	122 ± 6	4425 ± 221	3039 ± 152	137 ± 7	535 ± 27	1933 ± 97
5	20	98 ± 5	6375 ± 319	4286 ± 214	262 ± 13	561 ± 28	1652 ± 83
6	21	162 ± 8	2548 ± 127	3660 ± 138	174 ± 9	578 ± 29	1877 ± 94
7	24	114 ± 6	3359 ± 168	3355 ± 168	225 ± 11	742 ± 37	2023 ± 101
8	26	130 ± 7	2381 ± 119	4104 ± 205	225 ± 11	618 ± 31	2077 ± 104
9	27	125 ± 6	4337 ± 217	3976 ± 199	350 ± 17	519 ± 26	1937 ± 97
10	28	151 ± 8	3190 ± 159	2742 ± 137	137 ± 7	506 ± 25	1639 ± 82
11	35	121 ± 6	4645 ± 232	3849 ± 142	163 ± 8	494 ± 24	1709 ± 85
12	36	108 ± 5	2067 ± 103	3840 ± 142	137 ± 7	487 ± 24	1606 ± 80
13	37	142 ± 7	5024 ± 251	2975 ± 149	163 ± 8	482 ± 24	1750 ± 88
14	45	118 ± 6	5932 ± 297	2285 ± 114	112 ± 6	528 ± 26	1898 ± 95
15	48	108 ± 5	2138 ± 107	3512 ± 176	163 ± 8	490 ± 24	1782 ± 89
16	50	125 ± 6	4982 ± 249	3461 ± 173	157 ± 5	441 ± 22	1605 ± 80
17	66	155 ± 8	4046 ± 202	4427 ± 221	163 ± 8	454 ± 23	1734 ± 87

**Table 2:** Concentration in ppb for Detected Elements in Human Hair for Workers Group

sample	Age (year)	Concentration in ppb					
		Cu	Fe	Mg	Mn	Ni	Zn
1	32	193 ± 10	6935 ± 347	6657 ± 333	138 ± 7	491 ± 25	3445 ± 172
2	36	263 ± 18	6900 ± 345	5579 ± 280	371 ± 19	454 ± 23	1765 ± 88
3	13	212 ± 11	7967 ± 398	6228 ± 311	288 ± 14	466 ± 23	2353 ± 118
4	30	292 ± 15	6468 ± 323	6086 ± 304	725 ± 36	462 ± 23	3261 ± 163
5	44	200 ± 11	6375 ± 319	5770 ± 289	230 ± 12	472 ± 24	1497 ± 75
6	16	508 ± 25	7960 ± 398	6038 ± 302	525 ± 26	542 ± 27	2324 ± 116
7	25	350 ± 18	7245 ± 362	7154 ± 358	500 ± 25	453 ± 23	2548 ± 123

iron worker ( 1 , 2 ) – cement worker ( 3 , 4 , 5 ) – duco worker ( 6 , 7 ).

**Fig. 1:** Relation between Ages of Human Hair and Metal Concentration (Cu, MN and Ni)

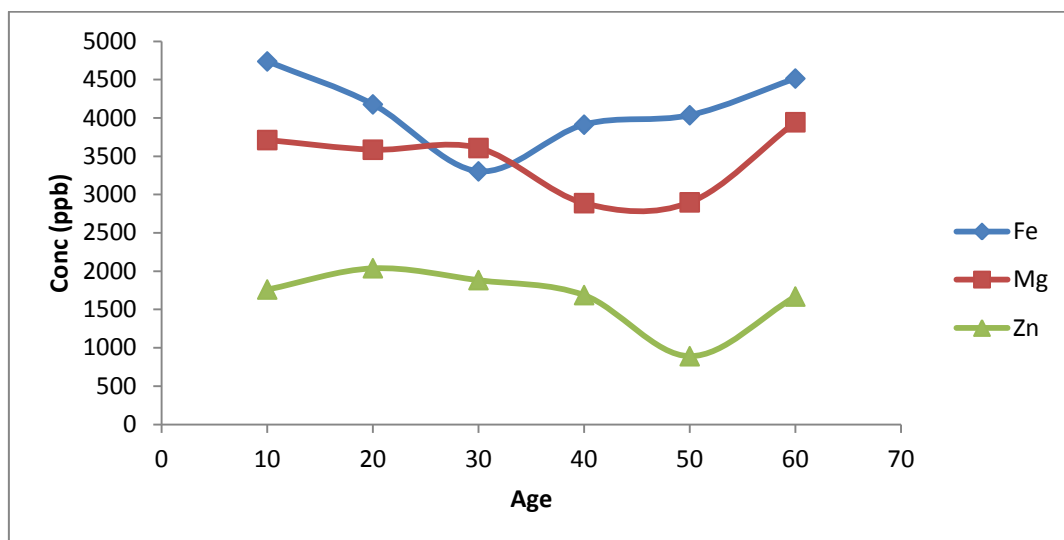


Fig. 2: Relation between Ages of Human Hair and Metal Concentration (Fe, MN and Zn).

## 6. FTIR spectra of hair samples

The infrared absorption spectra for control and worker hair samples were measured in the wavenumber ranging from 200- 4000  $\text{cm}^{-1}$ . The spectra were recorded in two ranges from 200-400  $\text{cm}^{-1}$  and 400-4000  $\text{cm}^{-1}$  Fig. (3, 4) respectively. In Fig. (3) A new band appeared at 230, 219  $\text{cm}^{-1}$  in worker sample (b,c), this band may be due to M- N stretching vibration indicating the interaction between the metal and nitrogen atom. Fig. (4a) shows a strong and medium absorption bands appeared at 3785 and 3323  $\text{cm}^{-1}$ , these bands due to N-H stretching vibration symmetric and asymmetric. The first one shifted to lower wavenumber in Fig. (4 b, c ), it appeared at 3778, 3781  $\text{cm}^{-1}$  respectively, but the band at 3323  $\text{cm}^{-1}$  is shifted to higher wavenumber in (b, c) it appeared at 3413,3424  $\text{cm}^{-1}$  respectively. Due to C-H bending in – plane, strong band appeared at 1440 $\text{cm}^{-1}$  Fig. (4a), this band appeared at 1432  $\text{cm}^{-1}$  Fig. (4b). A band appeared at 652  $\text{cm}^{-1}$  in Fig. (4a) which characteristic to C-H rocking vibration shifted in Fig. (4b, c) to higher wavenumber it appeared at 668, 775  $\text{cm}^{-1}$ . An absorption band appeared at 1812  $\text{cm}^{-1}$  of strong intensity assigned to C=O stretch vibration Fig. (4a) is shifted to lower wavenumber in Fig. (4b, c) and appeared at 1629-1710  $\text{cm}^{-1}$ . This shift is due to the interaction between oxygen of the carbonyl group and metal. In control hair sample Fig. (4a) band appeared at 543  $\text{cm}^{-1}$  which related to C-C bending vibration is shifted to higher wavenumber in worker hair samples (4 b, c) and appeared at 592, 568  $\text{cm}^{-1}$ .

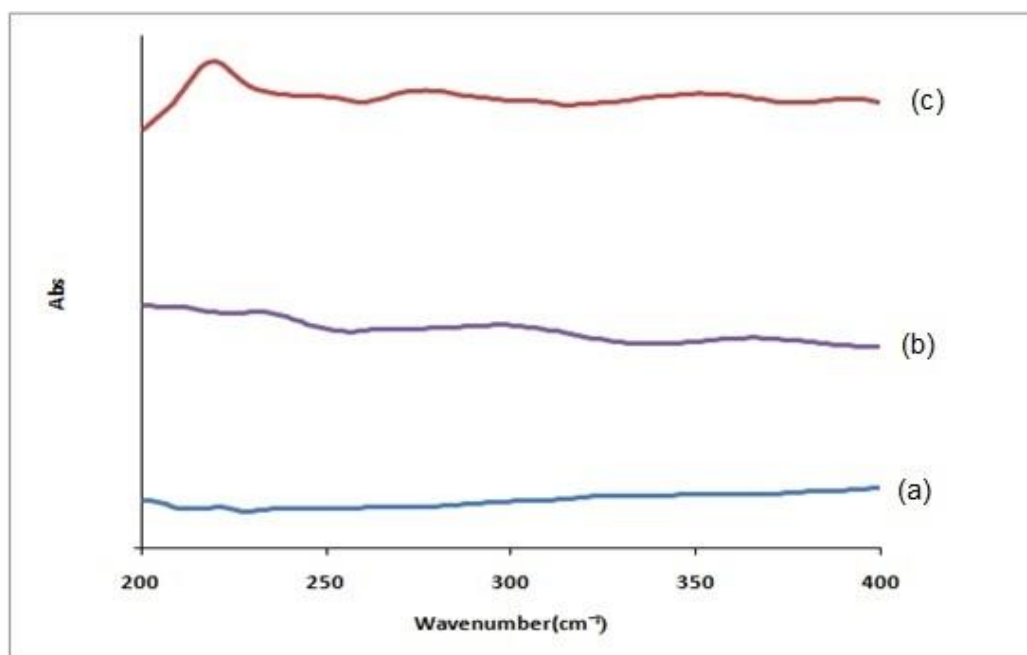


Fig. 3: FTIR Spectrum of (A) Control Sample and (B, C) Worker Hair in the Range (200-400)  $\text{Cm}^{-1}$

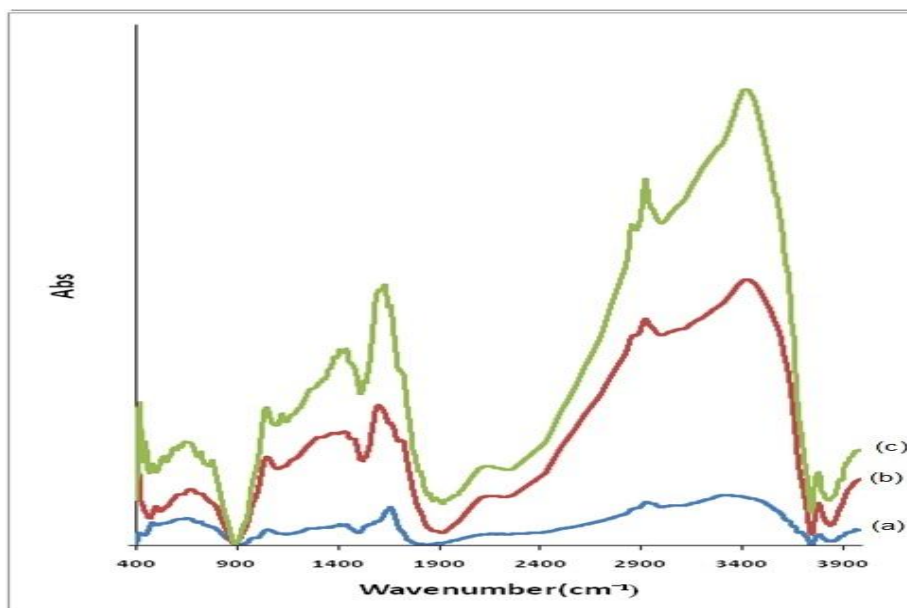


Fig. 4: FTIR Spectrum of (A) Control Sample and Worker Hair in the Range (400-4000)  $\text{Cm}^{-1}$

To indicate the existence of interaction between metal in worker hair samples and both oxygen and nitrogen in keratin, the ratio ( $R_1$ ,  $R_2$ ) the absorbance of the N-H band at  $3323 \text{ Cm}^{-1}$  and C=O band at  $1812 \text{ Cm}^{-1}$  to C-H band at  $2927 \text{ Cm}^{-1}$  was calculated. The C-H band at  $2927 \text{ Cm}^{-1}$  was taken as a reference in the ratios  $R_1$  and  $R_2$  since this band is not affected by contamination. The results are illustrated in Table (3).

Table 3: The Absorbance Ratios  $R_1$  and  $R_2$  for the Worker Hair Samples

Sample	(N-H/C-H)	(C=O/C-H)
	$R_1$	$R_2$
(a)	1.1634	0.054116
(b)	1.737	0.69031
(c)	2.60285	1.49017

## 7. Conclusion

The results obtained for the concentrations of metal in different samples of human hair revealed that the concentration of these elements for all worker's hair samples are significantly higher than the control samples. Also no clear correlation was observed for the ages or gender.

The limits of detection lie between 0.066 ppb for Mg to 0.012 ppb for Zn. The values obtained for precision lie between 0.2% to 3.1% for Mg and Zn respectively indicates the reliability.

The results obtained from atomic spectrometric techniques agree very well with the results obtained from FTIR.

The presence of the studied heavy metals in human hair depend on environmental exposure. This study proved that human scalp hair could be used successfully as a biological indicator for the assessment of heavy metal pollution.

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