RESEARCH ARTICLE

ICP/AAS ANALYSIS OF HAIR SAMPLES OF MINERS IN INDISCRIMINATE MINING AREA OF GOLD IN ABU HAMMED CITY, SUDAN.

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Manuscript Info	*Abstract*
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	In present study, human head hair samples were collected from River Nile State, Abu-hamad locality. The sampling area was divided in two locations with 30 samples were taken from Washer's (location one) and Evaporator's (location two). Inductively Coupled Plasma (ICP) was used to identify these elements (Ni, Cu, Pb and As) and Atomic Absorption Spectroscopy (AAS) used to determine the elements (Cu, Cd and Pb) in human hair samples. The mean elemental concentration of Ni, Cu, As and Pb in location one by ICP were 0.13, 0.10, 0.21 and 0.23 ppm while the mean elemental concentrations in location two were 0.14, 0.09, 0.23 and 0.30 ppm respectively. The mean elemental concentration of Cu, Cd and Pb in location 1 by AAS were 0.038, < LOD, < LOD ppm and 0.012 ppm while the mean elemental concentrations in location 2 were 0.027, 0.024, 0.069 ppm and 0.048 ppm respectively. The obtained results show that the lowest concentration values of elements were found in Location (Loc_1) compared to elemental concentration found in Location (Loc_2). The correlation for the various elements was determined. Also clusters analysis was performed. The enrichment factor (EF) of elements was calculated using Fe as a reference element. Comparisons between this study and data from literature were done.

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Introduction:-
Determination of trace elements in human hair is important in biological, medical, environmental and forensic science, as it represents an interesting biological matrix for the studies in both, the inorganic and organic field[1]. Occupational exposure to metals increases the body burden and subsequently health hazards. Excess concentration of metals causes such as kidney damage, gastrointestinal disturbance, renal failure, dermatitis, respiratory disorder and lung cancer.

Heavy metal pollution and the resulting effects represent a challenge currently facing developing countries, Sudan included. This is reinforced by the fact that metal poisoning is difficult and expensive to assess in developing countries due to the limited resources. Hence there is need to increase the level of understanding and assessment of environmental risk exposure to heavy metal pollution in Sudan.

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The metals may enter the human body through food, air, water and absorption through the skin. Industrial exposure accounts for common route of exposure in adults while ingestion is the common route of exposure in children.
 Using hair as a way to detect trace metal exposure is appealing because it is easily and non-invasively sampled, transported, handled, and analyzed [2].The World Health Organization (WHO), Environmental Protection Agency (EPA), and International Atomic Energy Agency (IAEA) have recommended the use of hair as an important biological material for worldwide environmental monitoring [3] .

 Many analytical techniques such as Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), X-ray Fluorescence, Neutron Activation Analysis (NAA) and Proton Induced X-ray Emission (PIXE) and Energy Dispersive X-ray Fluorescence (EDXRF) techniques have been widely used for analysis of heavy metals in human hair due to its high sensitivity, low detection limit. The objectives of this study are to measure the levels of Cu, Cd, Ni, Pb and As in human hair among indiscriminate mining of gold workers in Abu hammed city as bio indicator, to identify percentageof Cu, Pb, Ni , Cd and As and compare the elemental concentrations obtained with data from literature.

Materials and Methods:-
Sampling
The research has covered 30 people who Indiscriminate mining of gold workers, the sample collected by stainless scissor. The age of subjects range from 21-30 to 51-60 years. Length varies between 3 and 5 cm 0.5-2.0g of hair samples were collected in polyethylene bags, which will be thoroughly closed and labeled. A participants were randomly selected using the lottery method with replacement at the time of data collection and consented to the study, after the purpose of the study have been explained to them.

Samples preparation
The washing procedure was carried out as per the recommendation of international atomic energy agency (IAEA).Hair samples 100mg were weighing near the scalp following the sequence acetone – deionized water - deionized water – deionized water – acetone. Washed samples were oven-dried at 60 8C for 24h and then weighed. For wet ashing, 2 ml of HNO_3 (65% nitric acid) were added to each sample, in graduated tubes. Tubes were screw capped and the acid was allowed to react in a sand bath at approximately $60\ ^0$ C. Samples were allowed to cool and dropwise addition of 1 ml aliquots of H_2O_2 was made until a clear solution was obtained. Samples were diluted to a final volume using deionized water. Sample blanks were prepared following the same procedure .The samples are ready for ICP and AAS measurement.

ICP and AAS measurements
The concentrations Cu, Pb, Ni , Cd and As, were determined by inductively coupled plasma atomic emission spectrometry and flame atomic absorption spectrometry . Considering the importance of quality assurance, a parallel routine check of the accuracy and precision of quantified results was ensured.

Results and Discussion:-
Elemental concentrations in human hair samples:
The average concentrations of Cu, Cd, Pb, Ni and As is quantified using ICP and AAS techniques in hair samples of miners in Abu hamed indiscriminate mining areas in different locations (Loc 1 & Loc 2) and their standard deviation are presented in Table 1& 2, respectively. However, the average concentrations of all elements in hair samples location 2 were significantly higher than those hair samples form location one.

Hair samples are good indicators for certain toxic elements, when using hair samples, the external contamination is the main problem. In spite of the external contamination and lack of standardized methodology, the World Health Organization (WHO), Environmental Protection Agency (EPA), and International Atomic Energy Agency (IAEA) have recommended the use of hair as an important biological material for worldwide environmental monitoring.

The elemental concentration (ppm) of these elements (Cu, Cd, Pb, Ni and AS) in human hair by ICP and AAS samples from different locations are presented in Table (3 & 4), respectively.ICP results shows that the concentration of Cu in location one ranges between 0.07-0.13 ppm with an average value of 0.12 ppm. Pb concentration ranges between 0.12-0.36 ppm with an average value of 0.20 ppm. The concentration of Ni ranges between 0.07-0.20 ppm with average value of 0.10 ppm. As concentration ranges between 0.10-0.33 ppm with an

average value of 0.22 ppm. In location two, the concentration of Cu in location one ranges between 0.006-0.23 ppm with an average value of 0.14 ppm. Pb concentration ranges between 0.02-0.92 ppm with an average value of 0.23 ppm. The concentration of Ni ranges between 0.01-0.40 ppm with average value of 0.09 ppm. As concentration ranges between 0.02-0.70 ppm with an average value of 0.30 ppm. The AAS results, in location one, the concentration of copper ranges between 0.003 and 0.113 ppm with mean value of 0.038 ppm. Hh_{13} sample showed the highest concentration while Hh_{110} and Hh_{111} samples showed the lowest value. Cadmium concentration was less than detection limits in all the analyzed samples in this location, except the sample Hh_{14}. The concentration of lead is less than detection limits in all samples in location one. Nickel concentration ranges between 0.013 ppm and 0.136 ppm with mean value of 0.053 ppm. Hh_{18} recorded the highest concentration value, while Hh_{13} sample recorded the lowest value. The concentration of copper in location two ranges between 0.016 ppm and 0.049 ppm with mean value of 0.027 ppm. Hh_{210} sample showed the highest concentration while Hh_{214} sample showed the lowest value. Cadmium concentration ranges from 0.002 ppm to 0.065 ppm with mean value of 0.024 ppm. $Hh_{2\,4}$ showed the highest concentration while Hh_{110} showed the lowest value. The concentration of Lead ranges from 0.025 ppm and 0.298 ppm with mean value of 0.069 ppm. Hh_{22} recorded the highest concentration value, while the samples Hh_{113} recorded the lowest values. Nickel concentration ranges between 0.020 ppm and 0.062 ppm with mean value of 0.040 ppm and standard deviation 0.012 ppm. Hh_{15} recorded the highest concentration value, while Hh_{11} sample recorded the lowest value. In location one, the elements follows this order Cd > Pb > Cu > Ni, while in location two following this order Cd > Cu > Ni > Pb. The results of elements analyses indicated that Pb is higher in location two compared to its value which measured in location one. Nickel concentration is higher in location one than it's concentration in location two.

Correlation Analysis
Table 5 & 6 summarizes the correlation between the elemental concentrations data for human hair samples in location 1 & 2 respectively. The coefficient between Ni–As, Ni–Pb and As-Pb was positive and statistically significant in location one, while also the coefficient between Ni-Cu, Ni-As, Ni-Pb, Cu-As, Cu-Pb and As-Pb was positive and statistically significant in location two. These correlations may be due to the natural geochemical background. The same correlations were found in Loc1 & Loc 2, but in Loc2 was found an extra correlation of Cu with these elements Ni,Cu and Pb it may be due to the high temperature of consummation process in gold mining. It has been reported that several factors such as gender, age and geographic location affect heavy metals levels in human hair.

Cluster Analysis
The cluster analysis was applied using the SPSS package for the data obtained. Fig (2) shows the Cluster grouping of elements in human hair samples. The clustering procedure generated three groups of samples. The cluster 1 includes Cu and Pb which reflects the similarity in the concentration in human hair samples. Cluster 2 includes Cd and Ni and Cluster 3 includes only As which enriched in sample may due to combustion of ore in mining activity.

Enrichment factor (EF):
Table 7shows concentration of the elements compared to crustal abundances from Mason (40). The enrichment factor (EF) is the enrichment of the element in hair compared to that in Earth's crust, using Fe as a reference element. An enrichment of unity indicates a soil-derived element, whereas elements derived from high temperature combustion processes will be more volatile and haveenrichment factors significantly above one. EF calculation showed that Cu and Ni is significant enriched, while the other elements Cd, As and Pb is extremely high enriched.

Comparison of elemental concentration between this Study and data from literature[4-10]:
Table 8 shows the comparison of elemental concentration between this study and data from literature. Generally, the average concentrations of Pb were higher in Kenya and Libya than the values in India, Egypt, Poland, Nigeria, China and this study. Cd concentrations in India, Egypt, Poland, Libya and this study are less than the concentration in Kenya, Portugal. Nigeria and China. The concentration of Cu in Kenya. Poland, China. India, Egypt and Portugal is higher compared to Nigeria and this study.

Table 1:-The average elemental concentrations (ppm) ± SD of analyzed elements in hair samples using ICP in different locations

	Number of samples	Cu	Pb	Ni	As
Loc 1	11	0.12±0.05	0.20±0.08	0.10±0.03	0.22±0.09
Loc 2	15	0.14±0.14	0.23±0.25	0.09±0.08	0.30±0.34

Table 2:-The average elemental concentrations (ppm) ± SD of analyzed elements in hair samples using AAS in different locations

	Number of samples	Cu	Pb	Cd
Loc 1	11	0.04±0.05	<LOD	<LOD
Loc 2	15	0.03±0.01	0.07±0.07	0.02±0.03

Table 3:-Summary of statistical data for elemental concentrations (ppm) in hair samples in different locations using ICP

Location	N of samples	elements	Min	Max	Mean
Loc1	11	Cu	0.07	0.13	0.12
		Pb	0.12	0.36	0.20
		Ni	0.07	0.20	0.10
		AS	0.10	0.33	0.22
Loc2	15	Cu	0.006	0.23	0.14
		Pb	0.02	0.92	0.23
		Ni	0.01	0.40	0.09
		As	0.02	0.70	0.30

Table 4:-Summary of statistical data for elemental concentrations (ppm) in hair samples in different locations using AAS

Location	N of samples	elements	Min	Max	Mean
Loc1	11	Cu	<LOD	0.11	0.04
		Pb	<LOD	<LOD	<LOD
		Cd	<LOD	0.06	<LOD
Loc2	15	Cu	<LOD	0.05	0.03
		Pb	0.03	0.30	0.07
		Cd	<LOD	0.07	0.02

Table 5:-Correlation between the elemental concentrations data for human hair samples in location 1

	Ni	Cu	As	Pb	Cd
Ni	1				
Cu	0.615	1			
As	**0.987**	0.438	1		
Pb	**0.996**	0.542	**0.997**	1	
Cd	***	***	***	***	1

Table6:-Correlation between the elemental concentrations data for human hair samples in location 2

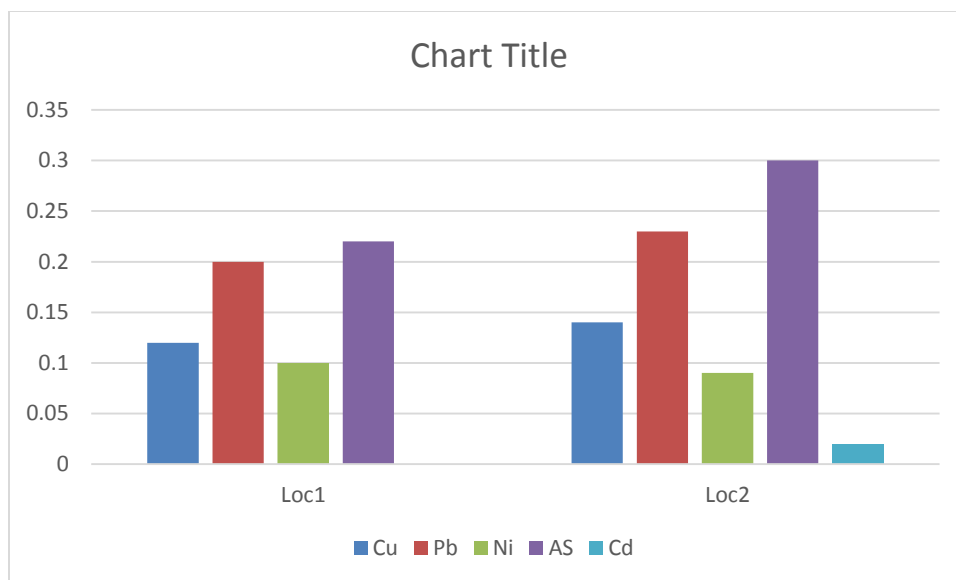|	Ni	Cu	As	Pb	Cd
Ni	1				
Cu	**0.998**	1			
As	**0.999**	**0.996**	1		
Pb	**0.997**	**0.993**	**0.999**	1	
Cd	-0.082	-0.041	-0.099	-0.077	1

Fig 1:-Mean elemental concentrations (ppm) of Cu, Pb. Ni, As and Cd in hair samples in different locations
Dendrogram using Average Linkage (Between Groups)
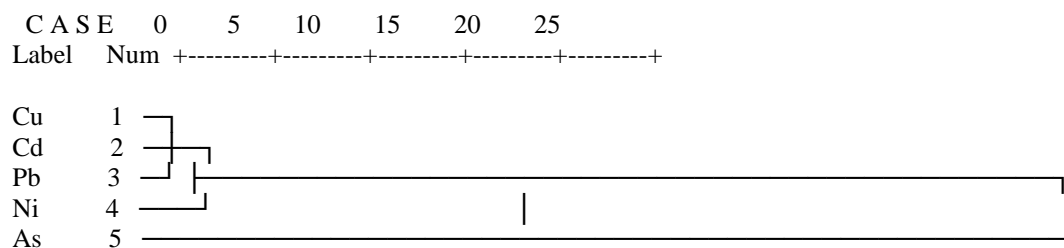   Rescaled Distance Cluster Combine

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  C A S E    0     5     10    15    20    25
  Label   Num  +---------+---------+---------+---------+---------+

  Cu      1  ─┐
  Cd      2  ─┤ ┌─────┐
  Pb      3  ─┘─┘     ├────────────────────────────────┐
  Ni      4  ─────────┘           │                    │
  As      5  ─────────────────────────────────────────┘
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Fig 2:-Cluster analysis

Table 7:-Enrichment factor for analyzed elements:

Element	EF
Cu	8.07
Ni	10.18
Cd	>40
As	>40
Pb	>40

Table 8:-Comparison of elemental concentration between this Study and data from literature**:**

Country	Pb	Cd	Cu	Ni	As
Egypt	5.95	0.44	10.6	-	
Kenya	52	2.22	24	-	
Portugal	-	0.17-1.52	7.7-27.2	-	
China	1.62	0.9	12	0.94	0.18
India	8.03	0.4	14.7	-	
Poland	4.8	0.55	7.2	-	
Nigeria(µg/g)	65.4	1.2	117.2	26.4	-
Libya	24.95	0.53	-	-	
This Study	0.6	0.02	0.12	0.13	0.44

Conclusion:-

In this study, heavy metals (Cu, Pb, Ni, Cd and As) were determinedin human hair samples using Inductively Coupled Plasma (ICP) and Atomic Absorption Spectrometry (AAS) techniques. The results showed that samples from location one has the lowest concentrations values compared to samples from location two. The mean elemental concentrations of all elements analyzed in this study were less than data from literature.

Recommendations:
1. Awareness of dangers of toxic elements especially miners.
2. Flow an occupational safety rules in traditional mining.
3. New studies may nesessate more sampling with comparative groups and modern instrumental analysis for new locations to achieve good results and good indication for protecting the human and environment.

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