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Atomic Absorption Spectrophotometric determination of Cadmium using biological materials

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ABSTRACT: *Cadmium is an extremely toxic metal hazardous to human health commonly found in industrial workplaces. Due to its low permissible exposure limit, overexposures may occur even in situations where trace quantities of cadmium are found. Cadmium is used in many industrial processes, such as constituent of easily fusible alloys, soft solder, electroplating, deoxidizer in nickel plating engraving process, electrodes for vapor lamps, photoelectric cells, nickel cadmium storage batteries, iron and steel factories, phosphate fertilizers and in zinc production. Most of the cadmium absorbed from the lungs or the intestine will initially be deposited in the liver, binding to a low molecular weight protein metallothionein, which has a high binding capacity for cadmium, zinc and copper. Later on Cd is transferred from the liver to the kidneys and eventually accumulates in the kidney cortex. Approximately one third of the body burden is found in the kidneys at long term low level exposure. Through metallothionein storage and transport of Cd takes place. Absorption of Cd from GI tract is about 5-8% .*
A serious form of Cd poisoning called the itai-itai disease has been reported from Toyama region of Japan. Hazards of Cd exposure include glomerular and tubular renal damage with proteinuria, depressed growth, enteropathy, anaemia, poor bone mineralization, severe kidney damage, cardiac enlargement, hypertension, foetal malformation, osteomalacia, osteoporosis, vulnerability to fractures, pain in back and legs and an early death.This paper gives some findings about cadmium concentrations using biomonitoring.
KEYWORDS: *Atomic Absorption Spectrophotometer, Cadmium, hair , nails*

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I. Introduction

Mankind has made enormous progress in several fronts since stone-age to make life comfortable and luxurious. And this progress is interminable. However, we homo-sapiens sometimes forget that everything comes at a cost, and later realize that the cost paid is too much sometimes. Everyone is aware of the adverse effects on the environment caused by industrialization and other advancements, the same environment which is essential for the survival of humans or any other kind of life on earth. So, there is a dire need to understand the harmful effects of this development and understand the limits which should be followed to give mother nature the time to heal herself. Apart from defining these limits we need to understand what kind of toll our health is paying for this advancement. Humans are now exposed to many chemicals because of many industrial and agricultural activities. Some of these chemicals are lethal, while some are beneficial in limited quantities and harmful in large quantities. Exposure could occur via inhalation, injection, ingestion or even skin-contact. Some of these exposures could lead to physical and psychological issues. So, there is a need to establish limits of exposures which could serve as standards to determine what kind of exposure for a given time could be hazardous to human body [1-3].

Metal has a significant role in the history of man. Over the years, man has made significant advancements in the field of industrial development and civilization. The impact of human activity on the environment has been profound. It has caused the balance between nature and humans to be disturbed. The rapid industrialization and the release of chemicals have greatly impacted the environment. This has substantially increased the chance of human exposure to these elements through inhalation, ingestion or skin contact. Many of the elements are now present in the human body.The most prevalent use of biological monitoring is element analysis in human tissues for the purpose of detecting, diagnosing, and assessing exposure to elements in the workplace [4-6].

Cadmium is an extremely toxic metal hazardous to human health commonly found in industrial workplaces. Due to its low permissible exposure limit, overexposures may occur even in situations where trace quantities of cadmium are found. Cadmium is used in many industrial processes, such as constituent of easily fusible alloys, soft solder, electroplating, deoxidizer in nickel plating engraving process, electrodes for vapor lamps, photoelectric cells, nickel cadmium storage batteries, iron and steel factories, phosphate fertilizers and in zinc production1. Exposure to cadmium is common for the workers of general industries, shipyard employees, construction industries and the agricultural industries. Workers can be exposed to cadmium coming in air from the smelting and refining of metals, or from the air in plants that make cadmium products such as batteries, coatings, or plastics. Workers can also be exposed when soldering or welding metal that contains cadmium. In human tissues Cd has been shown to be bound predominantly to a protein called metallothionein. Cadmium content of air in non-polluted areas although negligible, may play a significant role in the dispersal of Cd within the environment. Most of the cadmium absorbed from the lungs or the intestine will initially be deposited in the liver, binding to a low molecular weight protein metallothionein, which has a high binding capacity for cadmium, zinc and copper. Later on Cd is transferred from the liver to the kidneys and eventually accumulates in the kidney cortex. Approximately one third of the body burden is found in the kidneys at long term low level exposure. Through metallothionein storage and transport of Cd takes place. Absorption of Cd from GI tract is about 5-8% Cadmium can cause damage in the environment even at low concentrations and can pose serious risks to human health. These risks could be short term or long term. Symptoms of exposure include nausea, vomiting, abdominal cramps, diarrhoea, short breath, headache, fever and choking fits. A serious form of Cd poisoning called the itai-itai disease has been reported from Toyama region of Japan. Hazards of Cd exposure include glomerular and tubular renal damage with proteinuria, depressed growth, enteropathy, anaemia, poor bone mineralization, severe kidney damage, cardiac enlargement, hypertension, foetal malformation, osteomalacia, osteoporosis, vulnerability to fractures, pain in back and legs and an early death. The tolerable limits of Cd as laid down by WHO and Indian Standards of Institution are 0.05 mg/m^3[7-11].

II. Experimental

2.1Sample Collection

The Hair and fingernail specimens used for assessment of Cd were obtained from male subjects working in different sections of roadways, carriage and locomotive workshops, lead battery factory and tooth power manufacturing unit. The samples were collected with the help of sterilized stainless-steel scissors. A questionnaire was got filled up by each subjects for knowing the personal, medical and environmental history of subjects. Samples of age and sex matched subjects were also collected as controls.

2.2 Sample solution preparation and Cadmium determination

The collected samples were washed with triton X-100, deionized water and acetone, dried and finally converted to a water clear solution by using wet acid digestion procedure as described in chapter III. The quantitative analysis of Cd in solution of hair and nail samples was performed with atomic absorption spectrophotometer (AAS), ECIL Model –with air acetylene flame. Cadmium hollow cathode lamp was set at a wave length 228.8 nm with an integration time 5 sec for each measure. Other parameters set were lamp current at 3.5 mA and spectral bandwidth 0.5 nm.

2.3 Calibration

Standard solutions prepared from stock solution containing 1000 ppm of cadmium were used for the calibration of instrument. These standard solutions are aspirated on flame under similar conditions as those as described for sample solution of hair and nails. Absorption curve was obtained by plotting the absorbance of solution v/s concentration of standard solutions.The sensitivity for the standard conditions is about 0.02-3µg/ml Cd for 1% absorption.

III. Results and discussion

Hair and fingernail cadmium levels of male subjects of different age groups working in different environments were assessed. They have been further classified with respect to different parameters. The mean cadmium levels and standard deviation of hair and nail samples as a function of different age groups are shown in TABLE1and 2. As is very clear from the table, the mean Cd level continuously increases with age upto 31-40 .

Table 1-Range and mean cadmium levels (µg/g) in hair and fingernails of subjects of varying age groups

Age group in years	No. of samples	Hair		No. of samples	Fingernails	
		Range (µg/g)	Mean ± SD (µg/g)		Range (µg/g)	Mean ± SD (µg/g)
11-20	25	0.13-0.68	0.33±0.19	25	0.29-0.85	0.77±0.14
21-30	20	0.16-0.69	0.59±0.11	20	0.11-0.80	0.49±0.19
31-40	35	0.23-1.02	0.68±0.17	35	0.60-1.78	1.33±0.36

41-50	30	0.16-0.69	0.41±0.17	30	0.93-1.23	0.95±0.05
51-60	20	0.12-0.53	0.36±0.11	20	0.36-1.11	0.79±0.27

Table 2- Range and mean cadmium levels (µg/g) in hair and fingernails of subjects of varying age groups

Age group in years	No. of samples	Hair		No. of samples	Fingernails	
		Range (µg/g)	Mean ± SD (µg/g)		Range (µg/g)	Mean ± SD (µg/g)
11-20	25	0.13-0.68	0.33±0.19	25	0.29-0.85	0.77±0.14
21-30	20	0.16-0.69	0.59±0.11	20	0.11-0.80	0.49±0.19
31-40	35	0.23-1.02	0.68±0.17	35	0.60-1.78	1.33±0.36
41-50	30	0.16-0.69	0.41±0.17	30	0.93-1.23	0.95±0.05
51-60	20	0.12-0.53	0.36±0.11	20	0.36-1.11	0.79±0.27

Hair and fingernail cadmium levels of male subjects of different age groups working in different environments were assessed. They have been further classified with respect to different parameters. As is very clear from the table, the mean Cd level continuously increases with age upto 31-40. years. No definite trend was observed for Cd concentrations in different age of subjects by Ashraf et al[12]. Age dependence of Cd and Pb in hair of both sexes (aged 2 to 98 years) has also been studied by Petering et al [13]. They found that Cd in hair of males increased with age up to 20 years and probably remained at an elevated level or decreased slightly thereafter.TABLE3 gives the mean cadmium levels and standard deviation of hair and nail samples of subjects with respect to smoking habit in different age groups. No definite trend could be observed for Cd levels in hair and nails of smokers and non-smokers.The student 't' test between smokers and non-smokers clearly show that Cd concentration reflected in human hair and nails are influenced by smoking Table 3. Smoking was found to be a contributing factor to higher bioaccumulation of Cd in hair as has been reported by other researchers also[14-16].

Table 3 Range and mean cadmium levels (µg/g) in hair and fingernails of subjects of varying age groups as a function of smoking habit

Subjects	Age group in years	No. of Samples	Hair		No. of samples	Fingernails	
			Range (µg/g)	Mean ± SD (µg/g)		Range (µg/g)	Mean ± SD (µg/g)
Smokers	11-20	20	0.09-0.14	0.10±0.01	20	0.23-0.86	0.76±0.18
Non-Smokers	11-20	20	0.09-0.20	0.11±0.02	20	0.29-0.85	0.77±0.13
Smokers	21-30	30	0.15-0.33	0.26±0.05*	30	0.26-0.82	0.67±0.19*
Non-Smokers	21-30	30	0.06-0.17	0.14±0.02	30	0.18-0.48	0.32±0.09
Smokers	31-40	30	0.12-2.12	1.19±0.83*	30	0.63-2.74	2.13±0.83*
Non-Smokers	31-40	30	0.11-0.50	0.45±0.07	30	0.22-1.07	0.91±0.23
Smokers	41-50	25	0.06-0.78	0.58±0.19*	25	0.49-1.03	0.89±0.12*
Non-Smokers	41-50	25	0.08-0.76	0.43±0.16	25	0.19-0.77	0.53±0.19
Smokers	51-60	25	0.27-1.37	0.90±0.39*	25	0.48-1.02	0.98±0.11*
Non-Smokers	51-60	25	0.07-0.69	0.61±0.12	25	0.29-0.72	0.39±0.16

Lekouch et al[17] have also reported higher level of Cd in hair of smokers as compared to non-smokers but their levels were found to be non-significant (smokers 3.5+1.1 and non-smokers 2.7+0.6). In general, smokers had higher Cd levels than non-smokers in hair and blood and these differences were significant in many cases as reported by Hartwell et al [18]. Rauhamaa et al [19] have reported in their study that in one pack a day, smokers inhale about 0.9 µg cadmium daily during smoking. Smoking did not affect Cd concentrations in hair studies by Moon et al[20] and Ahmed and Elmubarak[21].

IV. Conclusion:

Cadmium levels increase with age upto 40 years of age nearly following which no definite pattern was observed. Cadmium is significant in smokers relative to non-smokers.

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It is based on the analysis of human tissues and fluids, and it is the only direct technique of establishing whether people are exposed to specific substances, their magnitudes and change with time, if any. Biomonitoring has become a more helpful tool in recent years as the ability to measure increasingly small amounts of substances in the human body.Hair and nails are commonly employed in forensic research to demonstrate the poisoning of the human body by numerous poisonous metals such as As, Cd, Cr, Pb, Hg, and Ni. Hair and nail analyses are now widely recognised as a valuable tool for epidemiological investigations as a general screening method. However, no comparable studies on nails have been conducted8-9. The assessment of the risks of adverse health effects from environmental hazards is a developing public interest topic with a considerable body of research in various domains. It requires recognising the link between environmental hazard exposure and understanding about the source and nature of the danger. Various environmental samples, as well as tissue and fluid samples from animals and plants, have been used in studies to analyse trace element levels10-11. In assessing the environmental risk to toxic metals, where the exposure is infrequent and highly variable, hair and nail metal contents could provide a better estimate for long term risk to the general public when compared to the blood metal levels12-16.Analytical techniques are valuable in the study of workplace monitoring in the mining, refining, and metalworking industries, providing useful data in the assessment of potential health impacts. Toxic heavy metals, as well as trace elements that may cause harm, can be detected in airborne particulates and human tissues using neutron activation analysis (NAA) using research nuclear reactors42, other modes of activation analysis (e.g. with photons)43, particle induced X ray emission (PIXE) analysis, nuclear microprobe techniques, and X ray fluorescence (XRF). Mandal et al determined arsenic in human hair and nail using HPLC-inductively coupled argon.

Human dietary cadmium intake shows regional differences. Cadmium intake in some European countries, New Zealand and the United States is on the average 15-20 μg/day, whereas it is several times higher in Japan. Analysis of rice from several countries indicates that the daily intake of cadmium might be high in Taiwan, Singapore and Java4-5.

Drinking water also contributes relatively little to the average daily intake. A survey of U. S. Community water supplies revealed an average cadmium concentration of 1.3μg/L. On the basis of an average adult consumption rate of 2 L/day drinking water contributes not more than 3-4ug/day to the average total cadmium intake6.

It is well established that increasing the cadmium content of soil increases the cadmium of plants grown in those soils. Cadmium uptakes by plants vary with soil characteristics (particularly pH) and the type of plant. In general, leaves, roots including tubers and seeds accumulate the largest amount of cadmium. An extensive report on the uptake of cadmium by plants has been published by Council for Agricultural Science and Technology7. High soil and water concentration can lead to significant accumulation of Cd in food. Plants usually show a higher tolerance to Cd than mammals and this fact may contribute to the increased accumulation of Cd in the food chain8-9.

The amount inhaled from the air is in most circumstances insignificant compared with that ingested with food, with the exception of heavy smokers who have a cadmium intake of 3 to 5µg/day or more from this source alone 10-13. One cigarette contains about 0.5-1.5 µg Cd of which 10% is inhaled 14,11. Some reports also confirm the high body burden of Cd in smokers15. Such inhaled cadmium is absorbed much more efficiently than ingested cadmium.

Absorption has been shown to be enhanced by dietary deficiencies of calcium (Ca), iron (Fe) or protein17. Cd is distributed to all major organs, but liver and kidneys are the main storage sites. Cd is stored to a lesser extent in the pancreas, salivary glands, skeletal muscle and testes 18 and excreted in urine (20%), bile and faeces (80%). Other minor routes for the removal of absorbed Cd are peculiar to females. Breast milk usually contain less than 1 ppb Cd 19.