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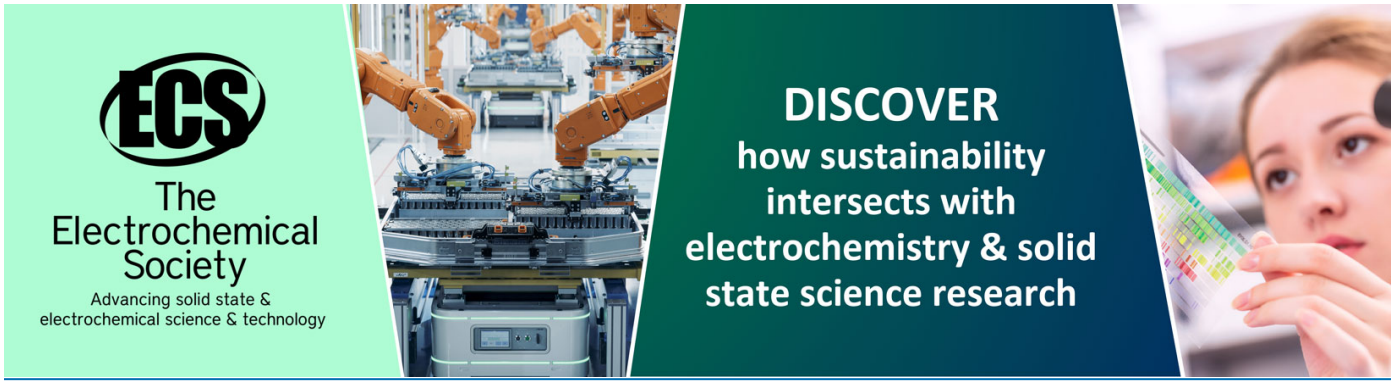

Determination of arsenic and cadmium as toxic metals in human blood samples collected from targeted people of Sana'a governorate

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Abstract. This study was amid to assess Arsenic and Cadmium in whole blood in participate with occupational and environmental exposure to toxic metals. Metals were determined by inductively coupled plasma – optical emission spectrometry ICP-OES after digested by dry ashing in the microwave muffle for 99 samples collected at different stations and occupations in Sana'a, Yemen and applying biomonitoring human model BHM on the evaluation of metallic toxicity among a human population. From the results, it is noted that the range and average concentrations measured in ppb were 0.41-2.43 for Cadmium, 0.59-1.22 for Arsenic. It can be concluded that Cadmium contaminating blood samples. However, the possibility of Arsenic poisoning cases might be encountered in the future unless it would be avoided. The concentrations of Arsenic in some many categories lying within the normal ranges and slightly approaching the hazard limits. Interestingly, the hazard trend of metallic toxicity was increased in the order: Arsenic > Cadmium and that younger and junior workers of unsafe harder occupations.

Keywords: Blood, Toxic Metals, Biomonitoring Human Model, Dry Ashing, Inductivity Coupled Plasma - Optical Emission Spectrometry.

1. Introduction

Heavy elements pollution are also called toxic metals that is serious and severe problem for plants, humans and animals such as arsenic and cadmium. That compounds to accumulate within living ecosystems, it has reached a high level on the environment. A person is considered to be a victim of this environmental burden if this exposure to environment pollutants causes long-term risks and hazardous conditions. Exposure to these toxic metals to various adverse effects observed in plants, animals, or humans and the environment as a whole. It is interesting to note that such toxic elements reach our blood and body tissues from around environment polluted by these toxic elements, i.e., air by breathing [1], water by drinking, washing [2] and food by eating [3].

Workers in various fields of worker are exposed to toxic metals from environmental or occupational pollution. Many Sources of exposure to Arsenic As, drinking water, and foods, such as vegetables and meat [4], wine drinking and tobacco [5]. Many industrial processes such as metal plating and the production of nickel-cadmium batteries, plastics, pigments and other synthetics. The

main sources of exposure to Cadmium Cd is specific professional atmospheres, diet, drinking water, and tobacco [6]. From food, particularly leafy vegetables, grains and cereals [7].

Many of studies have shown the heavy metals contamination water, plant and foods [8-11]. Conducted many analytical researches about contamination of heavy metals on blood in many countries of the word in Nigeria and Saudi Arabia [12,13]. Also, a study worked on blood in Ibb governorate, Yemen [14]. It has been reported that prolonged exposure to heavy elements induces serious diseases including liver failure, disorder, cardiovascular disease, bone disease, central nervous system disorder and cancer. In addition, it can cause hypertension, metabolic syndrome and abnormal cognitive function. Furthermore, the toxic effect of heavy elements is especially critical for children and pregnant women [15].

Chronic Arsenic exposure results into dermatologic changes and Cardiovascular effects and various malignancies and teratogenic in animals. Exposure to Cadmium toxicity causes *itai-itai* disease and renal abnormalities, chronic rhinitis and other effects. Cd is one of six substances banned by the European Union's Restriction on Hazardous Substances RoHS directive due to its carcinogenic potential in humans as it may cause cancers of lung, prostrate, pancreas and kidney [6]. Many recent studies have been carried out on the risks and effects of toxic elements on the human health [16].

Results of studies on the adverse effects on human health have been summarized in numerous reports published by International Organizations, e.g. the World Health Organization WHO and the International Agency for Research on Cancer IARC, or governmental agencies such as the centres for Disease Control and prevention CDC in the United States [17]. This research concerned with providing data bases related to determination of metallic toxicity among human population. We worked to present the applications of analytical chemistry and its roles in treatment. Our aim is to educate people and workers on danger of pollution with toxic metals and its impact on them in the long run and doing educational courses in cooperation with the ministry of environment and media.

2. Materials and Methods

2.1. Collection of blood samples

A 99 blood samples were collected from different workers aged 15-55 yrs and the working period from 1-35 yrs working in the different occupations like, Yemen Standardisation Metrology and Quality Control Organization Laboratory workers, Welders, Bus drivers, Pregnant, Street vendors and shopkeepers, Paint workers, Traffic policemen and petrol station workers from Sana'a governorate, Yemen. By ICP-OES technique which is found in YSMQCO laboratory, Sana'a, Yemen, the concentrations of Arsenic and Cadmium in the blood was measured.

2.2. Preparation of standard solutions

A 100 mL standard solutions of Arsenic and Cadmium each of which in concentrations of 0.2, 0.4, 0.6, 0.8 and 1.0 ppb (µg/L) were prepared by diluting with distilled water the corresponding commercially provided stock solutions of 1,000 ppb concentration.

2.3. Preparation of blood sample solutions (Dry ashing and Ash treatment)

Amount of blood samples 2.0 mL were taken into a dry clean ceramic crucible. A 3.0 mL of nitric acid 69 v/v% were added into the crucible and then heated on a hot plate at temperatures in the rang 50–200^{o}C until the sample content turns into a dry black coal. The resultant dry black coal was kept in a dryer for 15 min and then burned in the microwave muffle furnace at temperature ranging from 450 to 550^{o}C for 16 hrs until a reddish – brown ash was formed. The resulting sample ash was thereafter kept in the dryer. Then 2.0 mL of nitric acid 69 v/v% were added into the crucible containing the dry ash content of a blood sample. The mixture was heated on the hot plate until the ash becomes fully soluble in the acid. After cooling, the acidified ash solution was ultrasonically mixed for 15 min and was diluted up to 25 mL with deionized water. The blood sample solution was filtered and kept in plastic tubes ready for ICP-OES measurements. All glassware used in this procedure were soaked overnight in 50% nitric acid and rinsed in distilled / deionized water.

2.4. Analytical measurements

The ICP-OES instrument was well calibrated to operate at a flame temperature of 10,000ºC with a constant flow rate of 10 L min^{-1} for running the solutions. A series of standard solutions in a consequent concentrations 0.2, 0.4, 0.6, 0.8 and 1.0 ppb and blood sample solutions were injected systematically into the instrument, using deionized water as washing solution after each injection. The readings were collected at different wavelengths 188.980 and 214.439 nm for Arsenic and Cadmium, respectively. The measurements were repeated three times n = 3 for both standard solutions and sample solutions.

2.5. Statistical analysis

The data collected for three replicates n = 3 of both standard solutions and blood sample solutions were statistically treated using Varian's ICP-Expert 4.1.0 software program installed in ICP-EOS instrument and Origin pro 8 program. The concentrations of toxic metals were evaluated from the relevant calibration equations at acceptable levels of precision and accuracy.

3. Result and discussion

Statistical and analytical parameters for the determination of Arsenic and Cadmium by ICP-OES technique are summarized in table 1. The determination method was found to be at a satisfactory, acceptable levels of accuracy and precision, as clearly evidenced by the expected results obtained from the analysis of a suitable number of reference samples containing such metals whose concentrations lying within the same measurement range [18]. As a result, it began in practice to visualize the target samples and divided them in to different occupational categories and analysed and interpreted us on the type of professions, sex, age, time period for work and smoking. The results of the concentrations of toxic metals such as Arsenic and Cadmium in whole blood samples are showed that containing a large amount from Cadmium and a little amount from Arsenic.

Table 1. Statistical parameters of measured metals obtained from standard calibration method using linear least – squares fitting it.

Parameters	As	Cd
Concentration range (ppb)	0.2-1	0.2-1
Emission wavelength (nm)	188.980	214.439
Calibration equation	y=133.0158×-2.86995	y=5923.368×-138.8174
Error % (Slope)	3.6876	190.44638
Error % (Intercept)	2.44608	126.32784
Detection limit (ppb)	0.021576	0.023435
Correlation factor (R)	0.99693	0.99588
F value	1301.12504	967.36855
P value	4.68589×10^{-5}	7.30246×10^{-5}

From our work noted that the risk of Cadmium poisoning was observed in among several occupational categories, a large amount of Cadmium was noted in four blood samples from welders and moderately in one blood sample from bus drivers, one blood sample from paint workers and one blood sample from petrol station workers with the average Cd concentrations ~ 2.43, 0.41, 0.42 and 0.44 ppb, respectively. While the all occupational categories were showed that containing amount from Arsenic concentrations which lie in the allowed normal rang. Both Arsenic and Cadmium results summarized in table 2 and figure 1.

Table 2. Estimated values of As and Cd concentrations in blood samples for all targeted occupation category.

Categories	As				Cd			
	Range	No of blood samples	As Average cons (ppb)	SD	Range	No of blood samples	Cd Average cons (ppb)	SD
YSMQCO laboratory workers	Oar	*	*	*	Oar	*	*	*
	Iar	12	0.6	0.0086	Iar	26	0.21	0.0003
Welders	Oar	*	*	*	Oar	4	2.43	0.0013
	Iar	4	1.16	0.0105	Iar	7	0.22	0.0002
Bus drivers	Oar	*	*	*	Oar	1	0.41	0.0002
	Iar	2	0.59	0.0122	Iar	9	0.22	0.0004
Pregnant	Oar	*	*	*	Oar	*	*	*
	Iar	1	0.65	0.0117	Iar	10	0.21	0.0003
Street vendors and shopkeepers	Oar	*	*	*	Oar	*	*	*
	Iar	5	0.8	0.0131	Iar	8	0.21	0.0003
Paint workers	Oar	*	*	*	Oar	1	0.42	0.0001
	Iar	14	0.87	0.0125	Iar	14	0.23	0.0003
Traffic policemen	Oar	*	*	*	Oar	*	*	*
	Iar	7	0.99	0.0102	Iar	12	0.17	0.0003
Petrol station workers	Oar	*	*	*	Oar	1	0.44	0.0002
	Iar	6	1.22	0.015	Iar	6	0.21	0.0003

Oar: Over allowed range;
Iar: In allowed range;
* Not observed react;
Normal range of As in whole blood = 0.49-4.18 ppb [20].
Normal range of Cd in whole blood = 0.029-0.316 ppb [20].

It is worthwhile to mention that the average metal concentrations and relevant average standard deviations SD were obtained from the corresponding concentration range estimated for each group. However, the values of average standard deviations are over all found to be a quite enough low, indicating somewhat satisfactory and acceptable levels of accuracy and precision for all metal concentrations determined [19]. Also, the Cd poisoning cases are reported intensively in seven blood samples targeted from males category at the age category 15-30 yrs were found to be containing Cadmium in the average Cd concentration ~ 1.57 ppb, while not observed that in the blood samples containing Cadmium in the female category and age categories 31-45 and 46-55 yrs. The results of both Arsenic and Cadmium as summarized in table 3, figures 2 and 3.

Table 3. Estimated values of As and Cd concentrations in blood samples among sex, age, working periods and smoking categories.

Categories		As				Cd			
		Range	No of blood samples	As Average cons (ppb)	SD	Range	No of blood samples	Cd Average cons (ppb)	SD
Sex	M	Oar	*	*	*	Oar	7	1.57	0.0304
		Iar	49	0.88	0.0105	Iar	76	0.21	0.0006
	F	Oar	*	*	*	Oar	*	*	*
		Iar	2	0.57	0.0093	Iar	16	0.21	0.001
Age	15-30 yrs	Oar	*	*	*	Oar	7	1.57	0.0023
		Iar	51	0.88	0.0115	Iar	35	0.2	0.0003
	31-45 yrs	Oar	*	*	*	Oar	*	*	*
		Iar	*	*	*	Iar	34	0.22	0.0002
	46-55 yrs	Oar	*	*	*	Oar	*	*	*
		Iar	*	*	*	Iar	23	0.21	0.0002
Working periods	1-10 yrs	Oar	*	*	*	Oar	6	1.52	0.0026
		Iar	51	0.88	0.0115	Iar	34	0.22	0.0002
	11-20 yrs	Oar	*	*	*	Oar	1	1.87	0.0004
		Iar	*	*	*	Iar	23	0.21	0.0002
	21-35 yrs	Oar	*	*	*	Oar	*	*	*
		Iar	*	*	*	Iar	35	0.2	0.0003
Smoke	Smokers	Oar	*	*	*	Oar	3	1.21	0.0004
		Iar	30	0.98	0.012	Iar	54	0.21	0.0003
	Non Smokers	Oar	*	*	*	Oar	4	1.83	0.0014
		Iar	21	0.7	0.0108	Iar	38	0.22	0.0002

Oar: Over allowed range;
Iar: In allowed range;
* Not observed react.

In the present study, it is worthwhile to monition here that the three and six blood samples targeted from workers shorter period category 1-10 yrs, are much more exposed to the Cadmium poisoning with the average Cd concentrations ~ 1.52 ppb. However, reporting one Cadmium poisoned sample of the working period 11–20 yrs was found to be Cadmium poisoned the average Cd concentration ~ 1.87 ppb. While the workers longer period category 21-35 yrs was not observed containing Cadmium. As well as, both smokers and non-smokers categories were noted that contain a large amount of Cadmium in blood samples. It is important to that three and four blood samples targeted from smokers and non-smokers categories are found to be Cadmium poisoned with the average Cd concentrations ~1.21 and 1.83 ppb, respectively.

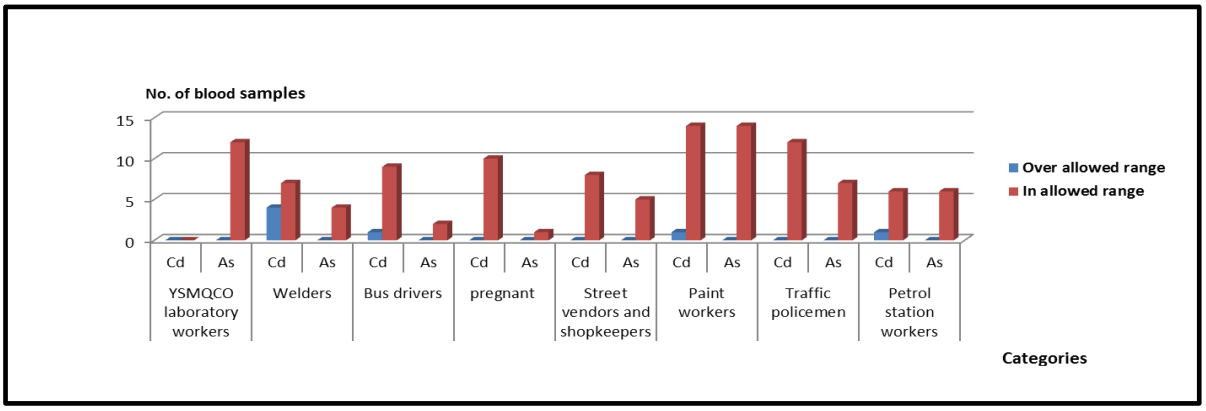

Figure 1. Distribution of estimated As and Cd concentrations in blood samples among all targeted occupation category.

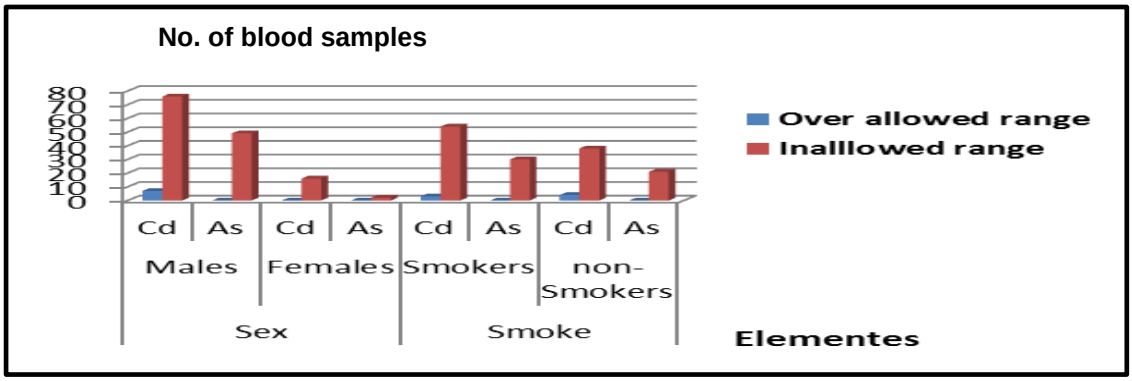

Figure 2. Distribution of estimated As and Cd concentrations in blood samples as a function of sex for males and females and Smoke for smokers and non-smokers categories.

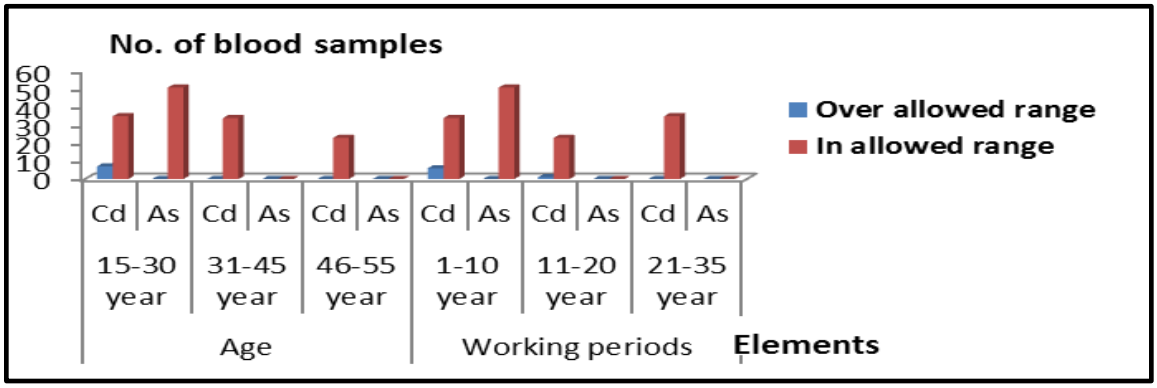

Figure 3. Distribution of estimated As and Cd concentrations in blood samples as a function of age from 15-30, 31-45 and 46-55 yrs and working period from 1-10, 11-20 and 21-35 yrs categories.

Where the allowed normal range of Cd in whole blood according to WHO = 0.024-0.316 ppb [20]. All concentrations of Arsenic blood samples were found to be lie with the allowed normal range for male and female at age 15-30 yrs only and working periods 1-10 yrs only and smokers and non-smokers categories. Where the allowed normal range of As in whole blood according to WHO = 0.49-4.18 ppb [20]. The investigation of the metallic toxicity in human blood samples among different sex, age,

period working and smoking categories is also a significant strategy performed in several bio monitoring studies [12, 21-23]. In addition, the presence of Cd has been reported in several James Ensor's paintings as a bright yellow pigment [24] and some other industrial paints [7]. Cd has also been found to be included beside Pb in Arabian petroleum products [25]. The analysis of the results demonstrated that in comparison concentrations of both metals Arsenic and Cadmium, the workers exposed to Cadmium showed significantly higher Cd levels in whole blood, significantly lower As levels in whole blood. So, Cd is more contaminated than As in blood.

4. Conclusion

It can be concluded that Cd poisoning samples were remarkably reported among welders, bus drivers, paint workers and petrol station workers specifically within males aging in the range of 15-30 yrs, whose working period lying in the ranges of 1-10 and 11-20 yrs, as well as among both smokers and non-smokers. However, the possibility of As poisoning cases might be encountered in the future unless it would be avoided. That was clearly evident in the estimated concentrations of As in some many categories lying within the normal ranges and slightly approaching the hazard limits. Interestingly, the hazard trend of metallic toxicity was here found to increase in the order: As > Cd and that younger and junior workers of unsafe harder occupations were reported to be the major population exposed to As and Cd contamination or at the risk of pollution which could be attributed to carelessness's, dangerous tasks undertaken, and following up no necessary precautions and safety productions of work. Finally, the national researchers and research scholars of the same interest are also strongly invited to conduct similar investigations on the same/some other toxic metals in various governorates of Yemen using more advanced, very precise analytical techniques, such as ICP-OES so as to obtain a clearly complementary picture of the environmental pollution by toxic metals in our country and to suggest applicable and protective solutions for toxic metals pollution problem.

Acknowledgement

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