International Journal of the Physical Sciences Vol. 6(8), pp. 2090-2094, 18 April, 2011
Available online at http://www.academicjournals.org/IJPS
DOI: 10.5897/IJPS11.073
ISSN 1992 - 1950 ©2011 Academic Journals

Full Length Research Paper

Heavy metals Mn, Fe, Ni, Cu and Zn in human hair samples using energy dispersive X-ray fluorescence analysis

Jauharah Md Khudzari[2], Husin Wagiran[1], Md. Imam Hossain[1,3]*, Noorddin Ibrahim[1] and Mohd Arif Agam[2]

[1]Department of Physics, Universiti Teknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia.
[2]Faculty of Science, Technology and Human Development, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Malaysia.
[3]Department of Physics, Shah Jalal University of Science and Technology, Sylhet 3114, Bangladesh.

Accepted 21 March, 2011

This paper presents the results of analysis of energy-dispersive X-ray fluorescence (EDXRF) applied on the human hair. We determined the concentrations of heavy metals Mn, Fe, Ni, Cu and Zn of 29 hair samples of sanitation workers and 5 samples of students were assumed to be environmentally healthy group. The accuracy and precision of the method for the elements were evaluated through the analysis of a standard hair sample. We compared the concentrations of human hair from an occupationally exposed group of sanitation workers and a control group (students). The hair of the exposed group showed a range of concentrations of 6-28 ppm Mn, 20-195 ppm Fe, 258-549 ppm Ni, 452-1182 ppm Cu and 334-1556 ppm Zn, while that of the control group has a range of 7-26 ppm Mn, 22-61 ppm Fe, 309-558 ppm Ni, 438-700 ppm Cu and 224-876 ppm Zn.

Key words: Human hair, heavy metal, EDXRF, sanitation worker, concentration.

INTRODUCTION

Everyday handling of solid waste from dawn to dusk by sanitation workers does not only expose them to air pollution, but also to chemical waste and poisonous gases. Studies have shown that solid waste does contain heavy metals and exposure to them can cause health problems. Diseases from poisonous gases and micro-organisms in the air near garbage dumps and poisoning by polluted underground water and soil may result in serious health problems (Issever and Gul, 2002). Pollution is any substance in the environment, which causes objectionable effects, impairing the welfare of the environment, reducing the quality of life and may eventually cause death (Duruibe et al., 2007). Heavy metal can also remain unchanged in the environment for years and may pose threat to human and other organisms. This is a sound motivation for investigating the elements contained in human hair especially in a group that gets exposed to heavy metals during their working hour.

Interestingly, small amounts of heavy elements are common in our environment and diet and are actually necessary for good health, but large amounts of heavy elements may cause acute or chronic toxicity (poisoning). Heavy metals toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer’s disease, muscular dystrophy, and multiple sclerosis. Heavy metals enter the body via inhalation, ingestion, and skin absorption. If heavy metals enter and accumulate in body tissue faster than the body’s detoxification pathways, a gradual build up of these toxins will occur. Heavy metals can be emitted into the environment by both natural and anthropogenic causes. Therefore, it is important for us to inform ourselves about the heavy metals and to take protective measures against excessive exposure.

The research of trace elements in hair sample has

*Corresponding author. E-mail: imamhossain@utm.my. Tel: +6075534062. Fax: +6075566162.

been continually a subject of interest in the biomedical and environmental sciences. It is widely known that the trace element concentrations in the body are potentially pertaining to the concentration of trace elements of the hair (Cho et al., 1997; Eltayeb and Van Grieken, 1988). Moreover, this kind of sample can be taken, transported and stored easily. In 1993, Diaz-Barriga et al. reported that analysis in some hazardous samples taken from a landfill for toxic waste showed the waste was rich in heavy metals. Furthermore, Agusa et al. (2003) determined the presence of 11 trace elements (V, Cr, Mn, Co, Cu, Zn, Mo, Ag, Cd, Sb and Pb) in hair samples of the population living nearby and in soil from dumping sites and control sites of India and Vietnam. Most of the studies reported on sanitation health problem used questionnaire and interview as their method to collect response and data (Dall'Agnol and Fernandes, 2007; Ferra et al., 2009; Wang et al., 2009). In this paper, heavy metal concentrations in human hair from sanitation workers and students in Johor Bahru, Malaysia were measured to see the contamination level using energy-dispersive X-ray fluorescence (*EDXRF)* analysis.

METHODOLOGY

Sample collection and preparation

29 hair samples from sanitation workers and five environmentally healthy students were collected. The samples were cut about 200-250 mg by using stainless steel scissor and were sealed in transparent plastic bag. Each sample was given a code number to correspond to the respondent's. Simultaneously, their age, working duration, year of working experience and health history were recorded. The samples were washed according to the recommendation of *International Atomic Energy Agency* (IAEA). Therefore, in this research, they were first washed once in ethanol, then thrice in distilled water, once again in ethanol and followed finally in distilled water, accordingly. They were placed in Petri dishes and dried under infrared lamp for three hours at Nuclear Laboratory, Universiti Teknologi Malaysia. Then, the hair samples were filled in the XRF cups to contain at least 0.5 inches (1.3 cm) of the cup.

Sample analysis by X-50 Mobile XRF

The analysis was done at the XRF Laboratory in Oceanography Institute, Universiti Terengganu Malaysia. This study used X-50 Mobile (Innov-X System, United States) due to its powerful specification. It is the first EDXRF in the world, produced by Innov-X that performs the capability bench top and features true portability. Before running tests on samples, quality assurances energy calibration check was performed. Testing of SiO_2 blank provided with the analyzer was used to detect any contamination on the analyzer window or other component that was sent by the X-rays.

The calibration verification of samples for two minutes test was performed using standard reference National Institute of Standards and Technology (NIST) that is SRM 2711 Montana Soil. This X-50 Mobile had an excitation system of 50 Kv and 200 µA. Primary beam filters were arranged in six positions for optimal performance across the periodic table. However, in this study copper filter was used due to the chosen mode. Soil mode was chosen, as it was equivalent to samples with light matrix such as thin human hair since matrix effect could be negligible. This small and lightweight X-ray tube was made from tantalum. It has a close coupling of collimator and target, close coupling of source to detector that give benefits such as portability, versatility, and higher x-ray output with lower power tube.

Moreover, it has stable output that yields low detection limit and long battery life due to low power consumption. This analyzer provides clean spectrum and short sampling time due to low spectral contamination and high X-ray output, respectively. In addition, the EDXRF detection system uses high purity Si PiN diode detector which delivers <190 eV resolution. The whole analysis was done by MobiLab Elemental Analysis System complimented in the X-50 Mobile system and easily identified and quantified elements with sensitivity that was up to part per million (ppm). Other than that, its overall sample turnaround time was very fast. All these factors contributed to a significant reduction in the analytical cost per sample compared to any other elemental analysis techniques.

In brief, the EDXRF method was preferred because of the easy portability and good quality performance. Moreover, this technique is a non-destructive testing, which does not destruct or destroy physical and properties of sample. Hair sample can be directly tested without preparation with any chemical solvent prior to testing.

RESULTS AND DISCUSSION

We determined the concentration of heavy metals in human hair samples from sanitation workers and students (control group). The precision and accuracy of the X-50 Mobile was tested by analyzing NIST standard SRM 2711 Montana Soil, and found that it has good agreement with the certified value within 2% deviation. The data have been presented by arithmetic mean (MEAN), standard deviation (SD), geometric mean (GM) and 95 per cent confidence interval (CI). We detected 12 heavy metals in hair samples, out of those five elements; Mn, Fe, Ni, Cu, and Zn to be presented in this paper. This is due to the factor that these named elements have quantified data for all samples, i.e. not below the limit of detection (LOD). Figure 1 shows the energy spectrum of the elements taken from sample of worker #1 with range of 5 to 10 keV.

Tables 1 and 2 show raw data for workers group and control group respectively, which list individual concentration for detected elements Mn, Fe, Ni, Cu, and Zn, together with their MEAN, SD, GM and 95% CI. There is no correlation for the elements content in the hair as a function of sampling data. The standard deviations of the measurement for most of the elements are at an acceptable level, indicating the precision of the method. In sample #6 of worker group, the maximum concentration value is 1556 ± 44 ppm for Zn. The hair of the exposed group shows a range of 6-28 ppm Mn, 20-195 ppm Fe, 258-549 ppm Ni, 452-1182 ppm Cu and

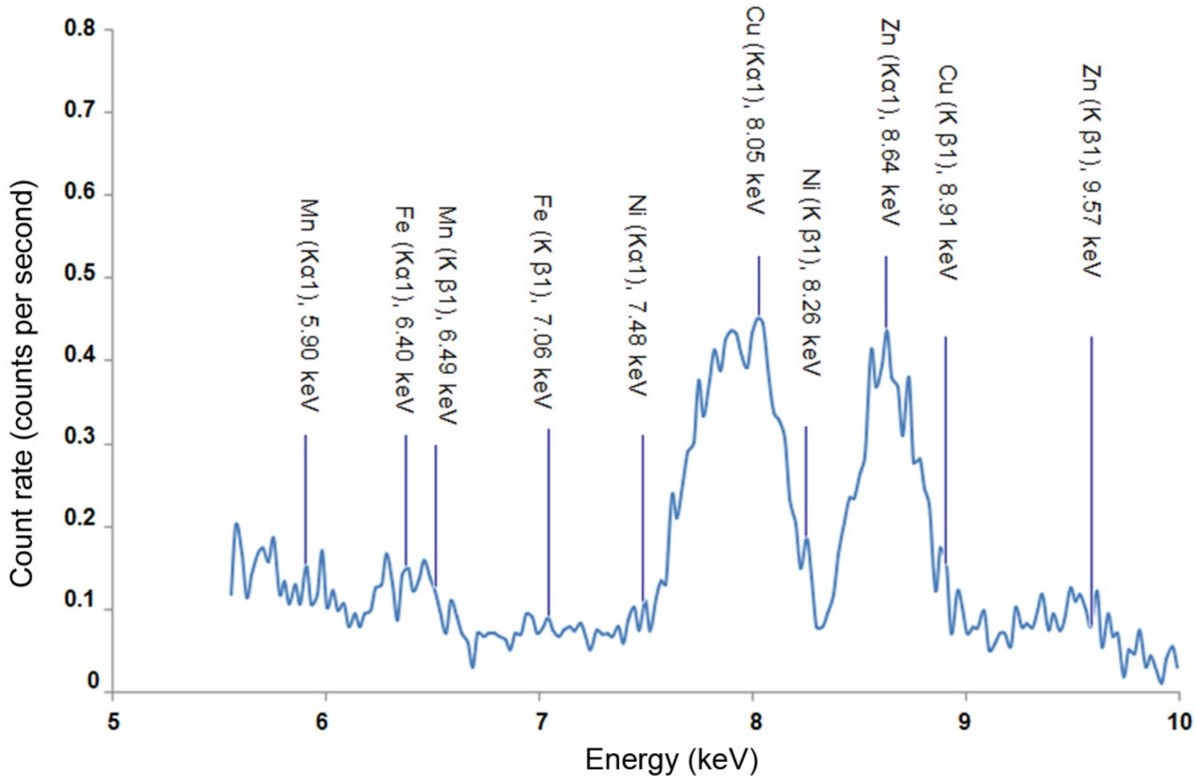

Figure 1. Spectrum of heavy elements detected in human hair sample.

Table 1. Raw data for sanitation workers group with individual concentration for detected elements; Mn, Fe, Ni, Cu, and Zn.

Sample #	Age (year)	Exposure duration (year)	Concentration (ppm)				
			Mn	Fe	Ni	Cu	Zn
1	39	4	27 ± 4	72 ± 6	515 ± 52	1047 ± 63	845 ± 44
2	52	10	7 ± 2	62 ± 4	304 ± 31	605 ± 37	334 ± 23
3	30	1	16 ± 3	49 ± 4	374 ± 39	725 ± 45	774 ± 34
4	26	3.5	12 ± 2	49 ± 4	421 ± 37	706 ± 43	791 ± 32
5	29	4.4	10 ± 2	56 ± 4	359 ± 36	814 ± 43	629 ± 29
6	34	4.2	28 ± 3	107 ± 6	549 ± 43	1017 ± 51	1556 ± 44
7	29	0.6	8 ± 2	37 ± 4	342 ± 35	718 ± 41	493 ± 27
8	29	1.5	16 ± 3	75 ± 5	351 ± 37	984 ± 47	911 ± 35
9	28	5.3	9 ± 2	28 ± 3	316 ± 30	692 ± 35	543 ± 24
10	36	10	6 ± 2	21 ± 3	351 ± 32	735 ± 37	519 ± 25
11	31	10	8 ± 2	21 ± 3	329 ± 30	656 ± 35	367 ± 22
12	24	0.6	17 ± 3	48 ± 4	340 ± 35	853 ± 43	626 ± 29
13	47	10	22 ± 3	58 ± 5	427 ± 44	886 ± 53	797 ± 38
14	30	1	8 ± 2	20 ± 4	353 ± 35	636 ± 40	732 ± 30
15	40	2	18 ± 3	57 ± 5	339 ± 39	1028 ± 51	961 ± 37
16	28	9	18 ± 3	62 ± 5	453 ± 43	1058 ± 54	687 ± 36
17	23	1	16 ± 3	53 ± 5	446 ± 47	844 ± 56	1004 ± 43
18	45	12	16 ± 3	58 ± 4	382 ± 39	826 ± 47	443 ± 29
19	36	0.7	11 ± 2	59 ± 4	412 ± 38	889 ± 46	837 ± 33
20	23	0.4	10 ± 2	48 ± 4	387 ± 37	685 ± 43	530 ± 29
21	39	3	35 ± 4	113 ± 7	525 ± 53	1106 ± 66	1473 ± 54
22	36	3	13 ± 3	52 ± 6	328 ± 47	852 ± 60	675 ± 42

Table 1. Contd.

23	33	4	8 ± 2	43 ± 4	258 ± 30	615 ± 36	1042 ± 30
24	29	1	<LOD	29 ± 4	313 ± 35	603 ± 40	443 ± 27
25	48	13	17 ± 3	28 ± 4	295 ± 40	774 ± 51	544 ± 34
26	24	3	17 ± 4	64 ± 6	437 ± 52	897 ± 64	835 ± 46
27	36	3	23 ± 3	90 ± 6	481 ± 47	1182 ± 59	1282 ± 46
28	22	1.3	27 ± 4	195 ± 8	526 ± 49	810 ± 56	709 ± 40
29	51	13	6 ± 2	31 ± 3	352 ± 30	452 ± 33	397 ± 22
MEAN	34	5	15	58	388	817	751
SD	9	4	8	35	77	175	307
GM	-	-	14	51	381	799	697
Range	22 - 52	0.4 - 13	6 - 28	20 - 195	258 - 549	452 -1182	334 - 1556
95% CI	-	-	12 - 18	45 - 71	359 - 418	751 - 884	634 - 868

Table 2. Heavy metals Mn, Fe, Ni, Cu, and Zn measured in control group.

Sample #	Concentration (ppm)				
	Mn	**Fe**	**Ni**	**Cu**	**Zn**
N1	9 ± 2	22 ± 3	309 ± 29	498 ± 32	383 ± 21
N2	26 ± 4	61 ± 5	558 ± 46	700 ± 50	876 ± 38
N3	14 ± 3	33 ± 4	436 ± 38	447 ± 40	466 ± 28
N4	7 ± 2	30 ± 4	420 ± 35	489 ± 38	224 ± 23
N5	11 ± 2	32 ± 3	360 ± 31	438 ± 32	343 ± 21
MEAN	13	36	417	514	458
SD	8	15	94	107	249
GM	12	34	408	507	413
Range	7 - 26	22 - 61	309 - 558	438 - 700	224 - 876
95% CI	4 - 23	17 -54	300 - 533	382 - 647	149 - 768

334 - 1556 ppm Zn, while that of the control group has a range of 7 - 26 ppm Mn, 22 - 61 ppm Fe, 309 - 558 ppm Ni, 438 - 700 ppm Cu and 224 - 876 ppm Zn.

The impact of age and work period on element concentrations was investigated. We did not found any correlation of concentrations of heavy metals influence of age and working periods. Out of the five elements, Mn shows the highest standard deviation. This might be as a result of dust contamination because the exogenously deposited elements were not removed completely during washing of the hair.

Comparison for the MEAN of each element in the two groups was performed as shown in Figure 2. The SD for each element within each group is high because of the variation in the hair element content among individuals. The mean concentrations are: Mn (15 ± 8) ppm, Fe (58 ± 35) ppm, Ni (388 ± 77) ppm, Cu (817 ±175) ppm, Zn (751 ± 307) ppm for sanitation workers group and Mn (13 ± 8) ppm, Fe (36 ± 15) ppm, Ni (417 ± 94) ppm, Cu (514 ± 107) ppm, Zn (458 ± 249) ppm for control group, respectively. Mean concentrations of Fe, Cu and Zn in workers are found to be significantly higher and in contrast, Ni is significantly lower compared to the control group. Moreover, the MEAN of Mn is almost the same in both groups while that of Cu is the highest among five detected elements in the hair samples of the both groups. Significant elevated concentration of three metals Fe, Cu and Zn suggests the possible uptake from exposure of sanitation worker during working. On the other hand, the concentrations of two elements Mn and Ni suggest that sanitation workers might get exposed to them not during the course of their work.

Conclusion

We reported five heavy metals Mn, Fe, Ni, Cu, and Zn in human hair samples of both sanitation workers and the

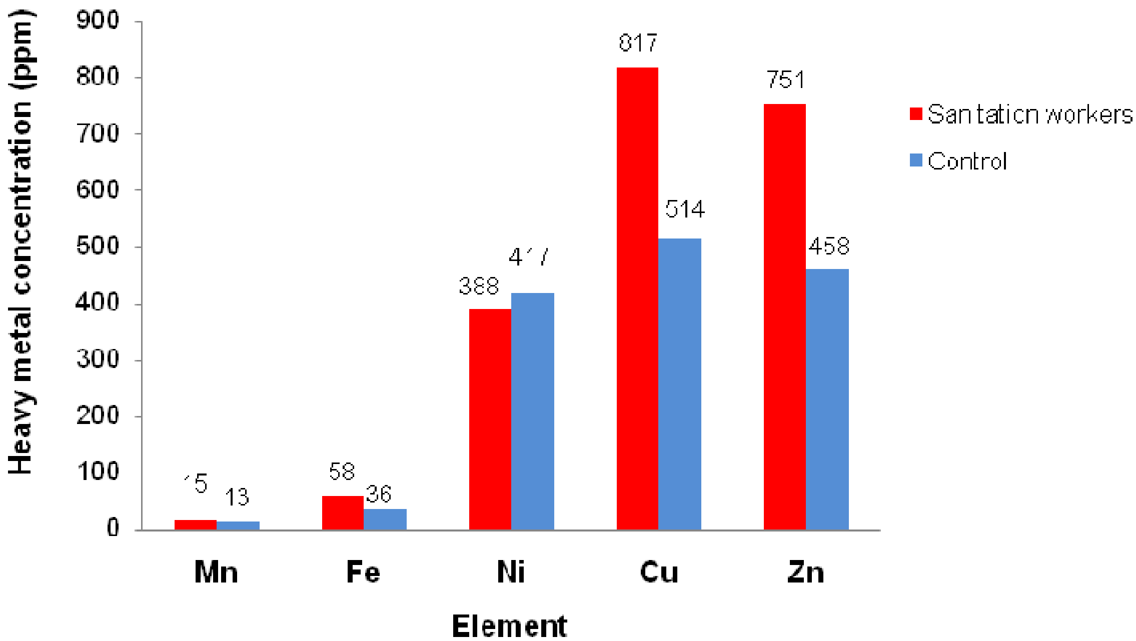

Figure 2. Comparison of mean concentration between sanitation workers and control group.

control group. The mean concentrations for these elements are: Mn (15 ± 8) ppm, Fe (58 ± 35) ppm, Ni (388 ± 77) ppm, Cu (817 ± 175) ppm, Zn (751 ± 307) ppm for sanitation workers group. Moreover, for control group, the mean concentrations are: Mn (13 ± 8) ppm, Fe (36 ± 15) ppm, Ni (417 ± 94) ppm, Cu (514 ± 107) ppm, Zn (458 ± 249) ppm. The concentrations of Fe, Cu and Zn are much higher in the sanitation worker group, suggesting the possible uptake from exposure during working. The concentrations of Mn and Ni elements indicate that the workers do not get exposed to these toxic elements during the course of their work.

REFERENCES

Agusa T, Kunito T, Nakashima E, Minh TB, Tanabe S, Subramanian A, Viet PH (2003). Preliminary studies on trace element contamination in dumping sites of municipal waste in Indian and Vietnam. J. De Phys., IV:JP.107: 21-24.

Cho SY, Awh OD, Chung YJ, Chung YS (1997). Trace element exposure in man by instrumental neutron activation analysis of hair. J. Radioanal. Nucl. Chem., 217(1): 107-109.

Dall'Agnol CM, Fernandes FDS (2007). Health and self-care among garbage collector: Work experiences in a recyclable garbage cooperative. Saludy auto cuidado entre minadores de basura: Vivencias en el trabajo en una cooperative de basura recyclable. 15(SPEC. ISS): 729-735.

Diaz-Barriga F, Santos MA, Yanez L, Cuellar JA, Ostrosky-Wegman P, Montero R, Perez A, Ruiz E, Garcia A, Gomez H (1993). Biological monitoring of workers at a recently opened hazardous waste disposal site. J. Exposure Anal. Environ. Epidemiol., 3(Suppl. 1): 63-71.

Duruibe JO, Ogwuegbu MOC, Egwurugwu JN (2007). Heavy metal pollution and human biotoxic effects. Int. J. Phys. Sci., 2(5): 112-118.

Eltayeb MAH, Van Grieken RE (1988). Preconcentration and XRF-determination of Heavy Metals in hair from Sudanese populations. J. Radio anal. Nucl. Chem., 131(2): 331-342.

Ferra H, Nadal N, Schuhmacher M, Domingo M (2009). Monitoring metals in blood and hair of the population living near a hazardous waste incinerator: Temporal trend. Biol. Trace Elem. Res., 128(3): 191-199.

Issever H, Gul H (2002). Health problems of garbage collectors in Istanbul. Indoor Built Environ., 11(5): 293-301.

Wang T, Fu J, Wang Y, Liao C, Tao Y, Jiang G (2009). Use of scalp hair as indicator of human exposure to heavy metals in an electronic waste recycling area. Environ. Pollut., 157(8-9): 2445-2451.