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Determination The Level Of Some Heavy Metals (Mn And Cu) In Drinking Water Using Wet Digestion Method Of Adigrat Town

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ABSTRACT: The study was undertaken to assess the status the metals in drinking water in the urban areas (Adigrat town) of the Tigray region, northern Ethiopia. A total of 7 drinking water samples were collected from the town. All the samples were analyzed for the two elements of Cu and Mn, using standard procedures and the results were compared with other international standards and WHO guideline values. Therefore, the results of the present study have shown the concentration all metals values (Mn with range of **0.139 to 0.427** mg/L and Cu with the range of **0 to 0.68** mg/l) were below the WHO (2009) recommended maximum admissible limits. Further works should be carried out in the toxic metal (like Pb, Cd, Cr etc) to check whether concentration is below or above the permissible level set by WHO guideline value.

Key words; - heavy metals, water, health and WHO

1. INTRODUCTION

1.1 . Background of the study

Heavy metals are produced from a variety of natural and anthropogenic sources; they are indeed intrinsic natural constituents of our environment. In environments, however, metal pollution can result in from direct atmospheric deposition, geologic weathering or through the discharge of agricultural, municipal or industrial waste products [1]. The known fatal effects of heavy metal toxicity include damaged or reduced mental and central nervous function and lower energy level. They also cause irregularity in blood composition, badly effect vital organs such as kidneys and liver. The long-term exposure of these metals result in physical, muscular, and neurological degenerative processes that cause Alzheimer's disease (brain disorder), Parkinson's disease (degenerative disease of the brain), muscular dystrophy (progressive skeletal muscle weakness), and multiple sclerosis (a nervous system disease that affects brain and spinal cord) [2]. Toxicity can result from any of the heavy metals but eight of them are considered by the Agency for toxic substances and disease registry in the top 20 hazardous substances list. These metals include arsenic, cadmium, chromium, cobalt, copper, lead, mercury and platinum [3]. Water is the most abundant substance on the earth's surface that is essential for the survival of all known forms of life. Water plays an important role in the world economy, as it functions as a solvent for a wide variety of chemical substances, industrial cooling and transportation. More than 70% of freshwater is consumed by agriculture [4]. Drinking water is obtained from a variety of sources like wells, tube wells, rivers, lakes, reservoirs and ponds. That poses the greatest risk to human health due to contamination of these sources. Water pollutants mainly consist of heavy metals, microorganisms, fertilizers and thousands of toxic organic compounds. Heavy metals in water occur only in trace levels but are more toxic to the human body [5]. So far, no sufficient study has been conducted on heavy metal contamination of drinking water of the Adigrat town. For this reason, due emphasis is given to the analysis of these contaminants. Heavy metals normally occurring in nature are not harmful to our environment because they are only present in very small amounts [6]. However, if the levels of these metals are higher than the recommended limits, their roles change to a negative dimension. Human beings can be exposed to heavy metal ions through direct and indirect sources like food, drinking water, exposure to industrial activities and traffic [7]. Drinking water is one of the important sources for heavy metals for humans. Concentration of the heavy metal ions in drinking water are generally at mg/l (ppm).

2. Methodology

2.1. Description of Study Area

The sample for this study was collected from Adigrat town. The town is located in the Northern part of Ethiopia, Tigray region 898km far from Addis Ababa and 115 km away from North of Mekelle city. It is found between $14^{o}16.453'$N latitude and $39^{o}27.654'$E longitude with altitude of 2457meters above sea level.

2.2 Chemicals

Distillated water, de-ionized water, concentrated HNO_3, stock solutions of $CuSO_{4;}$ $MnSO_4$ was used in the experiment.

2.3 Apparatus and instruments

Poly ethylene bottle, different size volumetric flasks, beakers, pipettes, thermometer, filter Paper No.41 and flame atomic absorption spectrophotometer (FAAS).

2.4. Sample Collection

Water samples were collected in 1 liter capacity plastic bottles. Before sampling, the bottles were washed with detergent followed by tap water and finally several times rinsed with distilled water. The source for all water samples was tape water supplied by Municipal Corporation. The water at the sample site (k1, K2, k3, k4, k5, k6 and k7) was allowed to flow for some time then the bottles was rinsed thrice with this water and 1 liter was taken as sample from each source of water. The samples were properly tagged. These samples were air tightened and stored in a refrigerator till the complete analyses were carried out [8].

2.5. Water sample digestion (wet digestion)

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The metal percentage found in water was estimated by digestion of the water sample 50 ml by digestion in 3 ml concentrated HNO_3 and 3 ml H_2O_2 below 80^{o}c for one hour until a clear solution was observed. The clear solution was diluted to 50 ml volumetric flask to make solution of known concentration and blank digestion was also carried out in the same way [6].

2.6. Preparation of Standard solutions

Determination of the metal concentration in the experimental solution was based on the calibration curve. In plotting the calibration curves copper and manganese stock solutions of 1000 ppm were prepared by dissolving sulfate salts of Cu and Mn. Blank solutions were prepared for the methods and, for the standard working solutions, to prepare 100 ppm, 10 mL of the standard Cu and Mn stock solution were pipetted and added into 100 mL calibrated flasks finally diluted with de-ionized water and the solution was mixed thoroughly. Next, to prepare 50 ppm standard solution of each metal, 50 mL of each of 100 ppm stock solution was pipetted into 100 mL volumetric flasks and diluted with de-ionized water. Finally standard working solution pipetted from 50 ppm standard solution into 50 mL calibrated flasks and made up to volume with De-ionized water (Table 2.1) [9].

2.7. Analytical procedure for heavy metal analysis by FAAS

Water samples were analyzed for heavy metals using FAAS. The heavy metals analysis adjustment of the operating condition was very essential target. Wavelength, slit width, limit of detection was adjusted for the analysis of the metals Mn and Cu. 1000 mg/l Standard solutions of metals was prepared in 10ml HNO_3 (0.1N) for calibration curve from the standard salt of each metal in 1000 ml volumetric flask. From this stock solution 100 mg/l of each metal was freshly prepared by diluting in 100 ml volumetric flask with distilled water and then the working solution (10 mg/l) of each metal was prepared. For the determination of these metals, four solutions was prepared for each sample from each source and four standard solutions was made for each metal which is shown below and rinse blank (distilled water) was used to flush the uptake system to reduce memory interferences [10].

Table 2.1. Standard concentration of the metals to be analyzed by FAAS

Metals	Concentration of standards (mg/l)
Mn	0.1, 0.2, 0.4, 0.8
Cu	0.1, 0.5, 1 ,2

Table 2.2. Standard conditions used in determination of different elements and their detection limits using atomic absorption spectrometer.

Element	Wave length(nm)	Method detection limit (ppm)	Lamp current (mA)	Slit width (nm)
Mn	275.9	0.01	5	0.2
Cu	324.8	0.02	4	0.5

Finally, the data was statistically analyzed using Axel and Origin.

3. RESULT AND DISCUSSION

3.1. Calibration of the instrument

Calibration of the instrument (AA 240**)** was done by the standards prepared before the determinations were done. Because the qualities of results obtained for heavy metals analysis using FAAS are seriously affected by the calibration and standard solution preparation procedures. The standards were prepared from the 100 mg/L of the elements which were prepared prior by taking 10 ml from the stock standard solutions containing 1000 mg element/L, in 10 ml of HNO_3, of the metals and concentrations of the working standards for each trace metals are listed in Table 3.1. The calibration curves of each of the metals (Mn and Cu) intended to be determined and the linear Regression (equation, 2) is given below.

$$y = A + Bx \quad (2)$$

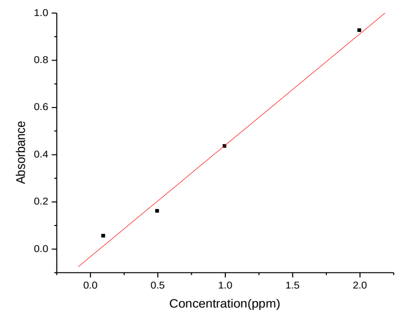

Fig.3.1. Calibration curve for Cu using FAAS.

Table 3.1. Linear Regression for the calibration curve of Cu standards using FAAS

Parameter	Value	Error
A	-0.03209	0.03487
B	0.47233	0.03041

R	SD	N	P
0.99588	0.04321	4	0.00412

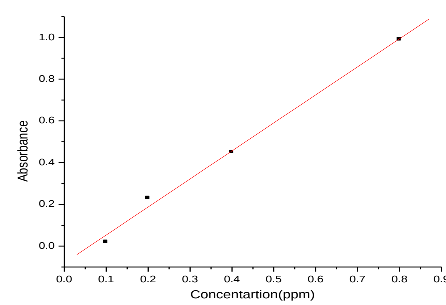

Fig.3.2. Calibration curve for Mn using FAAS

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Table 3.2. Linear Regression for the calibration curve of Mn standards using FAAS

Parameter	Value	Error
A	-0.0813	0.03305
B	1.34348	0.07171

R	SD	N	P
0.99716	0.03845	4	0.00284

3.2. Concentration of Cu and Mn using FAAS in water

As can be seen the calibration curve of Cu and Mn from the above plots and using their respective calibration equation of each metal, the concentration of each metal in samples of the town were calculated from their corresponding absorbance value. Table 3.3 shows mean concentrations of these metals investigated in the water in Adigrat, Ethiopia. The values are given as mean ± SD and the results are means of three replicates**.**

Table 3.3. Mean* (±SD) values of heavy metals concentration in water of town

Area of sample	Mn (mg/L)	Cu (mg/L)
K1	0.295 ± 0.010	ND
K2	0.265 ± 0.018	0.4 ± 0.011
K3	0.427 ± 0.005	0.43 ± 0.029
K4	0.177 ± 0.017	0.67 ± 0.010
K5	0.139 ± 0.019	0.345 ± 0.001
K6	0.236 ± 0.033	0.62 ± 0.041
K7	0.221 ± 0.002	0.68 ± 0.003

*Values are mean of the three determinations at 95 % confidence level,

ND: not detectable, k: Keble

This means: $$\mu = \bar{X} \pm \frac{ts}{\sqrt{n}} \qquad (3)$$

Where: μ - the expected value of the determination

$\bar{X}$ - mean of the replication

t- Statistical factor whose value is determined by number of samples and the desired confidence level

s- The standard deviation of the measured value

n- The number of replicate measurement

3.3. Distribution of heavy metals in water of Adigrat town

All water samples collected from the study areas shows the presences of Cu and Mn and all were found to be above their detection limits, except for Cu from Kebles one which is not detectable. Comparison of the level of metal in water sample of the seven Keble's are given in figure 3.3 and 3.4 respectively.

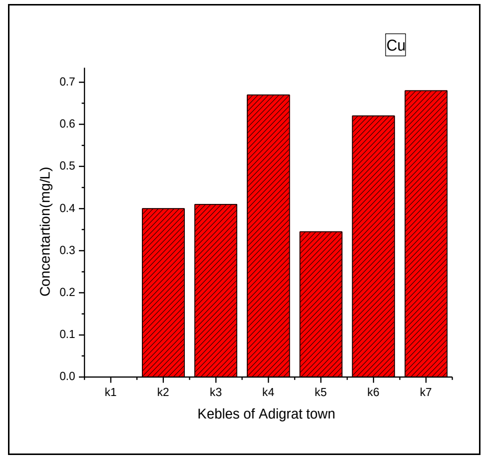

Fig. 3. 3. Distributions of Cu concentration on the water

As shown in the above figure, the concentration Cu is varied from 0 to 0.68 mg/l in all samples and its concentration have slight difference between the Keble's of the town. The difference was found in the order of K7 > K4 > K6> K3> K2> K5, but Keble one was found below the detection limit. In general, the concentration of copper was below the permissible level in all water sample of town and there is no any health effect based on this result.

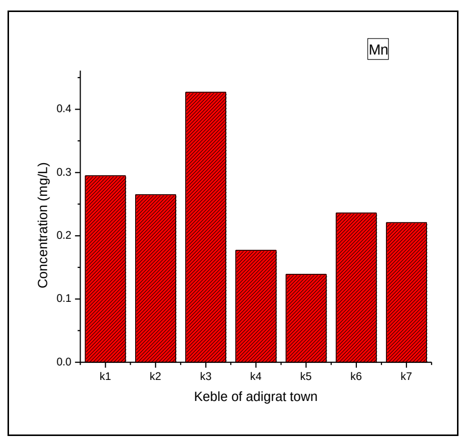

Fig. 3. 4 `Distributions of Mn concentration on the water

In each and every one sample, Mn content was low as compared to Cu as you can from table 3.3. The ranges was varied from 0.139 to 0.427 mg/L and Keble three provided maximum of 0.427 mg/L while its minimum concentration

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was found in Keble five. The concentration of Mn was in the order of k3 > k1 > k2 > k2 >k6 > k7 > k4 >k5. In general, the concentration of manganese was found below the permissible level in all water sample of town.

3.4. Comparison between the average heavy metal content of drinking water of this study with that of literature and WHO values

There are some reports from different countries on the analysis of the metal contents of the drinking water**.** It is important to compare the result obtained from the analysis of the water sample in this study with the values sited in other countries and WHO guideline values. Currently, all of the concentrations of heavy metals that are determined in this study were in the permissible range of the international guidelines listed below.

Table 3. 4. Comparison of the results obtained by current study with results from other countries in mg/L of analytes.

Country		Analytes	
		Mn (mg/L)	Cu (mg/L)
Present study	K1	0.295 ± 0.010	ND
	K2	0.265 ± 0.018	0.4 ± 0.011
	K3	0.427 ± 0.005	0.43 ± 0.029
	K4	0.177 ± 0.017	0.67 ± 0.010
	K5	0.139 ± 0.019	0.345 ± 0.001
	K6	0.236 ± 0.033	0.62 ± 0.041
	K7	0.221 ± 0.002	0.68 ± 0.003
Ghana [11]		0.30	0.20
Romania[12]		0.45	0.24
Turkey [13]		0.79	0.95
Iran [14]		0.524	0.304
(WHO) Permissible level [15]		0.85	1.00

K: Keble, WHO: world health organization, mg/l –milligram per litter From the Table 3.4, concentration of magnetism in all Kebles except in Keble three have smaller than when we compare with the other countries and WHO guideline value listed in above table. However, the concentration of copper that was obtained in this study is higher than to Ghana, Romania, and Iran but smaller than to turkey and the permissible value set by WHO guideline value.

3.5. Conclusion and recommendation

The main goal of this paper was to assess the status of drinking water quality in Adigrat town located northern Ethiopia, with special emphasis on trace heavy metals. A total of 7 drinking water samples were collected from Keble's of the town. All the samples were analyzed for two heavy metals (Cu & Mn,) using standard procedures. The concentrations of the investigated metal in the drinking water samples from Adigra /Ethiopia were found below the guidelines for drinking water given by the World Health Organization (WHO). In general, the concentration of the metals in this study was below the guideline value for drinking waters set by the World Health Organization (WHO). Therefore, it was safe drinking and there is no any health effect according metals what we have studied here. Lastly the researcher recommends the following

- Further works should be carried out in the toxic metal (like Pb, Cd, Cr etc) to check whether concentration is below or above the permissible level set by WHO guideline value.
- It also support further study to be conducted on other physical, chemical and biological parameters of significant health concern and on identification of potential sources of the contaminants including heavy metal contaminants.

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