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Determination of heavy and essential elements in tap water using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) in Kembata Tembaro Zone: SNNPR, Ethiopia

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Abstract

An appropriate level of concentration of elements in the human body is vital for its proper functioning. The measurement of both heavy and essential elements determines the quality of the water that tremendously correlated with the health of the consumers. In this study, the concentration levels of five essential metals (Na, K, Ca, Mg and Zn) and three heavy metals (Pb, Hg and Cd) were determined in the tap water by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) technique after pre-concentration and acid digestion. The result of the study had revealed that the concentrations of metals in the tap water samples (in mg/L) were in the ranges of: Ca (16.52-24.74), K (8.43-11.44), Mg (5.10-11.30), Na (18.89-28.62), Pb (0.02-0.03), Zn (1.22-2.44), Cd (0.01) and Hg (0.04-0.05). The concentrations of essential elements were very small as compared to their recommended value by USEPA/WHO while the concentration of heavy metals were above the maximum levels recommended by EPA, WHO and USEPA. Thus, it can be concluded that this water requires treatment for heavy metals before used by the community.

Keywords: Concentration, essential elements, heavy elements and limit recommended

Introduction

Water is one of the most essential elements to the life of human and livestock. Due to human and animal activities, it is usually contaminated with solid and human waste, effluents from chemical industries and dissolved gases (Jimoh and Umar, 2015). As it contains minerals and other biological compounds for proper functioning of the human body, drinking water is one of the essential needs for the human life (Albertini et al., 2007). Water quality varies depending on the sources, which is highly affected by both natural and human factors. Among the determining factors for the determination of quality of water is the concentration level of heavy metals. The difference in the concentration level of the metals may be due to geological and geographical factors; and sometimes it could be due to a difference in chemical treatment before supply (Zelealem and Panneerselvam, 2020; Elarina et al., 2014).

The availability of good quality water is an indispensable feature for preventing diseases and improving the quality of human life (Adefemi and Awokunmi, 2007). Trace elements often seem to be very insignificant; but they do have an important role in life at their appropriate concentration level in the human body. On the other hand, the presence of essential elements in drinking water can be crucial in the prevention of deficiency of essential elements in humans diets (Lekskulchai, 2015). Many of the minerals in water are required as micronutrients with a small amount. Concentrations of trace elements in water vary because of physiological, environmental and other factors (Sa'id, 2008). Some trace elements have several roles in living organism. Some are essential components of enzymes where they attract substrate molecules and facilitate their conversion to specific end products (Nielson, 2002).

Heavy metals that exist in our daily drinking water and tap water are highly dangerous to our health when they exceed the health based limits. Due to the bioaccumulation properties of heavy metal ions, drinking such water for a long period will seriously affect our health. The detection of heavy metal ions is important to avoid consuming the harmful ions unconsciously. This study, therefore, attempted the assessment of drinking water for certain heavy and essential elements so as to provide general information on the permissible levels.

Materials and methods

Study area description

The study was conducted in Damboya Woreda, Kembata-Tembaro Zone: SNNPR, Ethiopia. The sample Woreda lies between 7^{o}27" and 7^{0}42" latitude and 37^{0}8" and 38^{0}07" longitude. According to the agricultural office, the Woreda's total area is categorized under rural and urban settlements which is estimated to be 8318 sq. km with the density of 589p/ sq. km (CSA, 2007).

Sample collection and preparation

Three water sampling sites were randomly selected from the target Woreda: Urulicho, Lemecha and Kota Kombola. To draw the representative sample from each sampling site, 500 ml tap water was collected from each site. The water samples were collected in three liter plastics bottles.

Each sample bottle was washed with a brush and phosphate free detergent three times with tap water and was rinsed with respective water sample before use.

Apparatus and instruments

Plastic bottles were used to handle water samples. Beakers and volumetric flasks were used to handle chemicals and reagents during solution preparations. Measuring cylinders were used to measure volumes of the solutions. Pipette was used to suck solutions; while Pipette tips were used to avoid contamination of samples and reagents. Filter paper was used to filter residuals. Inductively coupled plasma optical emission spectroscopy (ICP-OES) (PerkinElmer, Inc. Shelton, CT, USA model ARCOSFHS12) equipped with WinLab32™ software (ICP Version 4.0) was used for recording the absorption of each metal of interest.

Reagents and chemicals

Reagents and chemicals used during the experimentation were in high-purity grade. In all dilutions and standard preparation, double distilled water and Nitric acid (NHO_3), Hydrochloric acid (HCl) and Hydrogen peroxide (H_2O_2) were used for digestion (Said and Jimoh, 2012).

Preparation of standard and spike solutions

To develop calibration curve, a series of eight standard solutions were prepared by appropriate dilutions from 1000 ppm stock standard solution for each metal analyzed in this work. For the spiking processes, a mixture of standard solution containing 1 mg/L of each (Na, Mg, Ca, K, Zn) and 4 mg/L Pb, Hg and Cd were prepared by serial dilution from 1000 mg/L stock standard solution in to 250 ml volumetric flask and diluting to the mark with double distilled water ((Jimoh and Sholadoye, 2011)

Digestion method

The water sample bottles were shaken thoroughly. A volume of 100 ml of the sample was measured using a 100 ml volumetric flask and poured into a conical flask and 5 ml of concentrated nitric acid was added. The mixture was heated slowly on a hot plate and evaporated about 20 ml ensuring that the water did not boil. A further 5 ml of concentrated nitric acid was added and the beaker was covered with a watch glass while the heating process continued. Nitric acid continuously added until the solution appeared light colored and became clear. Lastly, 2 ml of concentrated hydrochloric acid was added and heated slightly to dissolve any remaining residue. Few drops of hydrogen peroxide were then added to ensure complete digestion to have taken place. The solution was filtered and the filtrate was transferred to a 100 ml volumetric flask to cool and the filtrate was made up to the mark with distilled water (Radojovenic and Bashkin, 2006).

Method of validation

The proposed method was validated by evaluating different parameters such as: linearity, limit of detection (LOD), limit of quantification (LOQ), accuracy (in terms of recovery), instrument detection limit and precision (in terms of repeatability) (Chauhan et al., 2015).

Accuracy and precision

The accuracy and precision of the proposed procedure were evaluated by the analysis of matrix spike samples and laboratory control samples. Accuracy was evaluated through recovery studies of sample spikes. The precision was evaluated based on repeatability by estimating the relative standard deviation (RSD) of the recovery percentage for each spiked level.

In this study, the recovery test was done by spiking a suitable known quantity of metal standard solution into a test portion of the sample. The spiked and non-spiked samples were digested and analyzed using the same analytical procedure. The percent recoveries of the analyte were calculated by using equation 1 (Iqbal et al., 2010).

$$\%Recovery = \frac{spiked\ \ conc - \text{non spike cnc.}}{added\ coc} * 100$$

Limit of detection

The limit of detection (LOD) is taken as the lowest concentration of an analyte in a sample that can be detected, but not necessarily quantified, under the stated conditions of the test. LOD is calculated (Shrivastava and Gupta, 2011) as:

$$LOD = (\text{Standard deviation}) * 3$$

Limit of quantification

The limit of quantification (LOQ) is the lowest concentration of an analyte in a sample that can be quantitatively determined with acceptable precision and accuracy under the stated conditions of test. LOQ is calculated (Shrivastava and Gupta, 2011) as:

$$LOQ = (\text{Standard deviation}) * 10$$

Instrumentation and conditions

The instrument detection limit with respect to the wavelength of absorption was set according to the condition of the instruments manual. Table (1) displays the operating parameters setting.

Table 1. (ICP-OES) operating conditions

Operating parameters	Setting
Plasma power(w)	1400.00
Triplicates	3.00
pump speed(rpm)	30.00
Stabilization time (s)	10.0
Coolant Flow) (L/min)	13.00
Auxiliary flow(L/min)	0.80
Nebulizer pressure(bar)	1.96(2.00-4.00)
Nebulizer flow(L/min)	0.73
Main Argon Pressure(bar)	6.75(6.00-8.00)
Optic Temperature(℃)	15.05(14.00-16.00)
Flow light tube(L/min)	0.90(0.80-1.80)
Plasma viewing	Radial

Table (2) shows the instrument detection range. Absorptions were recorded at their maximum wavelength of absorption of each metal considered for analysis.

Table 2. Instrument detection range (mg/L) and absorption wavelength (nm)

Element	Absorption Wavelength	Detection Range
Ca	317.933	0.002263–120
K	766.491	0.05163–240
Na	589.592	0.0018–240
Mg	279.553	0.004031-120
Zn	213.856	0.0009-3.36
Pb	220.353	0.0007–1.68
Cd	231.604	0.0001 1.68
Hg	257.611	0.0028-3.84

Linearity

Calibration curves were prepared to determine concentration of each metal in the sample solutions. Calibration curves were constructed using eight series of working standard for each metal from which the linearity of the experiment was evaluated.

Statistical analysis

Data entry management and preliminary summaries were done on Microsoft Office Excel spread sheet. The mean and standard deviation of the data collected were determined using Microsoft Excel. All analyses were carried out in triplicates and the data presented as (mean ± standard deviation). One way analyses of variance (ANOVA) at $p < 0.05$ was used to determine mean values and statistically significant difference in the mean concentration of metals among the tap water samples.

Results and discussion

Results of method validations

Results of method validations computed according to equation (1-3) for each element measured in this work were displayed in Tables. Table (3) displays the linear equation from calibration curves. The values of limit of detection and limit of quantification were determined and presented in Table (4). The correlation coefficient for all the calibration curves was above 0.999 which shows that there was linear relationship between the concentration and intensity of metals' absorbance.

Table 3. Concentration of working standard solutions

Metal	Con. of intermediate standard solution (mg/L)	Concentration of working standard (mg/L)	(R^2)	Equation of calibration curve
Ca	100	2, 4, 6, 8, 10, 20, 40, 60, 80, 100	0.9999	Y=58981*x*+17382
K	200	4, 8, 12, 16, 20, 40, 80,120, 160, 200	0.998	Y=2556*x*+6573
Na	200	4, 8, 12, 16, 20, 40, 80,120, 160, 200	0.999	Y=22798*x*+17666
Mg	100	2, 4, 6, 8, 10, 20, 40, 60, 80, 100	0.999	Y=58971*x*+18083
Zn	5	0.056,0.112, 0.168, 0.56, 1.12, 1.68, 2.24 2.8	0.999	Y=11253*x*+3295
Pb	5	0.028,0.056, 0.084, 0.28, 0.56, 0.84, 1.12 1.4	0.999	Y=6683*x*+2353
Cd	5	0.028,0.056, 0.084, 0.28, 0.56, 0.84, 1.12, 1.4	0.9999	Y=84758*x*+2278
Hg	5	0.064,0.128, 0.192, 0.64, 1.28, 1.92, 2.56, 3.2	0.999	Y=15116*x*+5948

As can be observed from Table 4, the limit of detection (LOD) values for all the elements analyzed ranged from 0.0042–0.63 mg/L and the limit of quantification (LOQ) values for all the metals analyzed ranged from 0.014–2.1mg/L. The LOD and LOQ method obtained were low enough to detect metals presence of interest at trace levels in all samples.

Table 4. LOD and LOQ used for method validation in this work (n = 3)

Element	SB	LOD	LOQ
Ca	0.18	0.54	1.8
K	0.011	0.033	0.11
Na	0.012	0.036	0.12
Mg	0.0014	00042	0.014
Zn	0.07	0.21	0.70
Pb	0.21	0.63	2.1
Cd	0.007	0.021	0.07
Hg	0.137	0.411	1.37

SB= Standard solution of blank, LOD=Limit of detection, LOQ=limit of quantification (n=3)

The precision and accuracy of the proposed method were evaluated by means of matrix spike recovery tests. The recovery values of triplicate analysis of the matrix spike tap water were calculated using equation 1 and the RSD values were calculated using equation 2 and the results were presented in Table 5.

Table 5. Recovery and precision test results (Lemecha site)

Elements	Mean conc. in sample	Added conc.	Mean conc. in spike	RT (%)
Ca	16.62±0.30	100	114.74±0.60	98.12
K	8.78±0.02	125	138±1.60	103.38
Mg	5.10±0.08	100	105.42±0.25	100.32
Na	28.62±0.09	125	141.45±2.74	90.26
Pb	0.03±0.01	6.25	6±0.28	95.52
Zn	1.25±0.17	7.50	9.57±0.23	110.93
Cd	0.01±0.00	6.25	5.94±0.09	94.88
Hg	0.05±0.00	12.5	15.90±1.25	126.80

RT – recovery test

As can be seen in Table 5, the percentage recovery of the metal analysis in the tap water samples ranged between 90.26 – 126.80 percent. The matrix spike recovery obtained in this study falls within the acceptable range for a good recovery study. The high percentage recovery obtained from the study validates the accuracy of the method and the reliability of the levels of metal concentration in the study. The RSD values of the samples were < 10 %, indicating that the proposed method was precise.

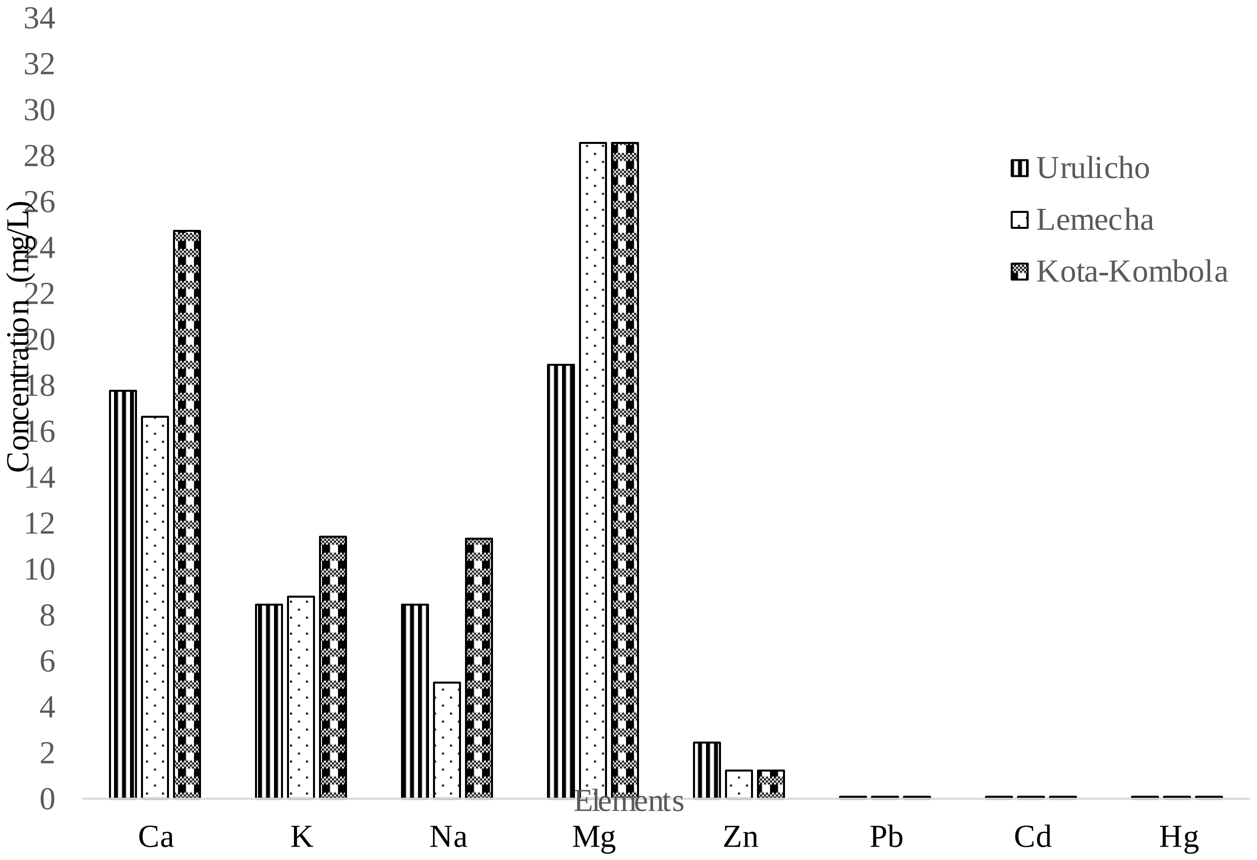

Figure 1. Comparisons of the obtained values for essential and heavy metals in the study

Concentration of metals

The concentrations of eight metals were determined in the study. Results for essential metals (Potassium, Calcium, Zinc, Manganese and Sodium) and heavy metals (Lead, Cadmium and mercury) are displayed in Table (6). The results indicated that the samples had variable concentration of analyte metals in the three location districts. Up on comparisons, almost all samples from Kota Kombola site have comprised more essential elements (Figure 1). All the analyzed metals were above the method detection limits of the instrument. The results determined from each sampling site were presented in terms of mean value in µg/L and standard deviation.

Table 6. Concentration (mg/L) (mean ± SD) of the elements in the study (n = 3).

Element	Urulicho	Lemecha	Kota Kombola
Ca	17.77±0.28	16.62±0.30	24.74±0.12
K	8.43±0.05	8.78±0.02	11.44±0.08
Na	8.44±0.10	5.10±0.08	11.30±0.08
Mg	18.89±0.20	28.62±0.09	28.57±0.14
Pb	0.02±0.00	0.03±0.01	0.03±0.00
Zn	2.44±0.41	1.25±0.17	1.22±0.27
Cd	0.01±0.00	0.01±0.00	0.01±0.00
Hg	0.05±0.00	0.05±0.00	0.05±0.00

SD - Standard deviation

Sodium (Na) content

As it can be seen from Table (6); the sodium content in the tap water samples ranged from 5.10 to 11.30 mg/L. The lowest concentration of sodium (5.10 mg/L) was found in samples collected from Lemecha site and the highest concentration of sodium (11.30 mg/L) was found in samples collected from Kota Kombola site. Whereas, Urulicho tap water contained (2.44 mg/L). The maximum value obtained in the study (11.30 mg/L) was near 5 % of the upper limit set by WHO (2011) for quality drinking water. Sodium at normal intake level is beneficial to healthy adults. However, people with heart disease or hypertension should reduce sodium intake to lower blood pressure (WHO, 1996).

Table 7. Upper limit for essential elements (mg/L) and heavy metals (µg/L) in quality standard of drinking water guidelines

Essential Elements		Heavy Metals				
Element	WHO (2011)	Metal	TBS (2008)	WHO (2011)	USEPA (2002)	EAS (2009)
Na	200	As	50	10	10	10
Mg	100	Cd	5	3	5	3
Ca	250	Hg	1	6	2	1
K	NE	Pb	50	10	15	1
Zn	5					

NE- Not established

Calcium (Ca) content

Calcium was the second most accumulated essential metal next to sodium in the tap water considered in this work. The concentration of calcium (Table 7) ranged from 16.62 mg/L to 24.74 mg/L. The concentration of all samples was within WHO (2011) upper limit and was 10% less than the limit. Long term consumption of water which had low minerals such as calcium, magnesium and fluorid may be responsible for different health related problems of which: Kidney stones, hypertension and stroke, insulin resistance and obesity could be mentioned (Mihayo and Mkoma, 2012; WHO, 2011).

Potassium (K) content

The concentration of potassium was found lower than sodium and calcium metals analyzed in the study. Mean potassium concentration ranged from 8.43 mg/L to 11.44 mg/L. There was significant difference ($p < 0.05$) in the content of potassium between the sampling sites. High-potassium diet lowers blood pressure in individuals with raised blood pressure. Prospective cohort studies and outcome trials show that increasing K intake reduces cardiovascular disease mortality. An increased K intake lowers urinary Ca excretion and plays an important role in the management of hyper calciuria and kidney stones and is likely to decrease the risk of osteoporosis (He and MacGreger, 2008). But, there is no upper limit set by WHO on potassium.

Magnesium (Mg) content

Magnesium level obtained in the study ranged from 18.89 mg/L to 28.62 mg/L. This value is within the upper limit set by WHO (2011). This element was found in abundant in the tap water samples considered in the study as compared to other essential elements. The maximum value of magnesium in the study was less than 15% of the upper limit set by WHO (2011).

Zinc (Zn) content

Zinc level ranged from 1.22– 2.44 mg/L as shown in Table (7). The concentration of zinc was the highest on samples in Urulicho and the lowest in samples from Kota Kombola. However, the concentrations of all samples were lower than WHO (2011) and USEPA's (2002) standard limit which is 5 mg/L. Usually zinc is introduced in tap water through corrosion of galvanized plumbing materials. Many galvanized pipes in old buildings were manufactured using zinc that probably contains high levels of lead, which is a common impurity in the zinc (Barnard, 1995).

Lead (Pb) content

In the studied tap water samples, the results of lead concentrations were 0.02, 0.03 and 0.03 mg/L in the sample sites of Urulicho, Lemecha and Kota Kombola, respectively (Table 7). The WHO (2011) recommended maximum limit of Pb for tap water is 0.01 mg/L. The concentration of lead in each sample had exceeded 0.001 mg/L EAS (2014), 0.01 mg/L WHO (2011) and 0.015 mg/L USEPA (2002) standard levels. Most Pb in drinking water comes from Pb lined pipes, lead solder and brass plumbing fixtures inside the apartment. The results of the study indicated that the water requires treatment regarding its Pd concentration.

Cadmium (Cd) content

The mean concentration of cadmium in the tap water samples analyzed in this study was 0.01mg/ L (Table 7). Cadmium is a non-essential element and is highly toxic to marine and freshwater aquatic life (Elarina et al., 2014). The concentrations of cadmium obtained in this study were higher than the recommended maximum limits for tap water. This indicates the water needs treatment for cadmium before being used.

Mercury (Hg) content

The mean concentrations of mercury in tap water samples were 0.05mg/L (Table 7). The maximum acceptable limit for mercury as per USEPA (2002) and WHO (2011) are 0.002 mg/L and 0.006 mg/L, respectively. However the observed concentration levels of Mercury in the study area was not within the permissible limits specified in the standard guidelines. Higher value of mercury is toxic and causes neurological damage, paralysis and blindness. This indicates the water needs treatment for mercury before being used

Conclusion

ICP-OES was used to determine three heavy (Pb, Hg and Cd) and five essential (Ca, K, Na, Mg and Zn) metals in tap water using Wet digestion method. There was variation on concentration of both essential and heavy metals in the three selected sites. The concentration of magnesium was the highest of the essential metals followed by calcium, while zinc was the least in essential metals. Among heavy metals, concentration of mercury was the highest followed by cadmium. However, the concentration of all the heavy metals measured in the study was higher than the limits set by different standard values. The presence of some heavy metals beyond permissible limits requires detailed further investigation by including other heavy metals.

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