Spectrophotometric Determination of Manganese in Ground Water in Shillong City Using Bismuthate Oxidation Method

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Abstract- **Spectrophotometric determination of Mn in ground water samples was performed employing the Bismuthate oxidation method and using the Systronic Model 166 and Visible Spectrophotometer. Thirty-six ground water samples were collected from different parts of the city of Shillong, Meghalaya, India and the depth of the sample sources ranges from 10 feet to 350 feet. The bismuthate oxidation method was first validated to check its efficiency and reproducibility. The minimum detection limit for Mn using this method was observed to be 0.1mg/L. The λ_{max} was also determined and it was found out to be 510nm. The efficiency of the method was about 98-99 %. The interference due to the presence of iron was also monitored and it was observed that iron concentration up to 5mg Fe /L did not interfere with the estimation. In this study, the concentration of Mn in the ground water sample was found to be ranged between Below Detection Limit (BDL) to 0.65mg/L. Detectable Mn concentration was observed in all the sampling sites except one location.**

Keywords- Bismuthate; Estimation; Ground; Manganese; Oxidation; Water

I. INTRODUCTION

Manganese is considered to be the 12th most abundant element in the biosphere. Its concentration in earth crust reaches as high as 0.098%. The concentration of manganese in the ocean crust is about 60% greater than that in the continental one (Seigel and Seigel, 2000). It is widely distributed in soil, sediment, water, and biological materials. Although manganese is essential for humans and other species of the animal kingdom as well as for plants, it is at higher level of toxicity. In man, chronic manganese excess affects the central nervous system, with the symptoms resembling those of Parkinson's disease. This is the reason why manganese belongs to highly toxic heavy metals. It can also affect the ecosystem negatively, accumulating in the food chain. Excess of manganese and iron in drinking water cause staining of kitchen utensils, bath accessories and clothes, as well as a yellowish water appearance and unpleasant taste and odour in food and drinks. Manganese and iron also contribute to water hardness, resulting in loss of pressure in pumps, water heaters and pipes (Vollmanova, et al., 2003). The determination of trace amounts of manganese in ground water is of extreme significance.

The levels of manganese in groundwater from natural leaching processes can vary widely depending upon the types of minerals present at the aquifer. Natural sources of manganese are more common in deeper wells where the water has been in contact with rock for a longer time. Manganese often occurs together with iron in groundwater but it usually occurs in much lower concentrations than iron (Schroeder et al., 1987).

The natural presence of manganese in rock and soil provides a source of manganese that may dissolve in ground and surface waters or may erode and deposit as sediment, with the subsequent potential for dissolution. Manganese accumulated in plant material also provides a source for dissolution during decomposition. In aquatic systems manganese solubility increases at low pH as well as under low oxidation-reduction potential, and is most commonly in the Mn (II) and Mn (IV) oxidation states. The presence of high concentrations of chlorides, nitrates and sulphates may increase manganese solubility, raising both aqueous mobility and uptake by plants. Manganese precipitates out in sediment mainly as Mn (IV) and re-solubilizes in water column mainly as Mn (II) (Moore, 1991).

Manganese is essential for normal development and body function across the life span of all mammals with some twenty identified functions in enzymes and proteins. The role of manganese, as a required co-factor for several enzymes, for example, represents one of the most important functions of this element in biochemistry. The mentioned functions are generally known for arginase, which is responsible for urea production in the liver, for superoxide dismutase, which is a very important antioxidant enzyme that catalyzes the conversion of superoxide radicals ($O_2^{\cdot-}$) to hydrogen peroxide and molecular oxygen in the mitochondria as well as for pyruvate carboxylase, an essential enzyme in gluconeogenesis. Mn contributes to maintain healthy nerves and immune system and helps in blood sugar regulation. It is involved in utilization of Vitamins B1 and E and it is required for normal bone growth or for avoiding blood clotting defects. Manganese is an antagonist of iron and can replace magnesium in certain enzymes and because of its similar ionic radius it can interfere with the metabolism of calcium. It is also essential for normal bone structure and the formation mucopolysaccharides. The main route of manganese absorption is the gastrointestinal tract, but absorption occurs via the lung as well. Manganese has been found in different oxidation states as Mn (II), Mn (III) and Mn (IV) in both animals and humans. The human body contains about 10-20 mg of Mn of which 5-8 mg are turned over daily. Only divalent Mn is absorbed by man. Principal food sources are green vegetables, nuts, whole-grain cereals and tea. The major storage of Mn is in the bones (about 50%) and its excretion is within the liver. In tissues, Mn may exist primarily in the form of Mn (II). Mn deficiency in human body is very rare because of its widespread presence in the human diet. However, when it does occur, Mn deficiency has been related with skeletal abnormalities, ataxia, alterations of reproductive function as well as lipid and carbohydrate metabolism, osteoporosis,

epilepsy, difficulties in wound healing, and impaired growth (HOWE, 2004).

Concentrations of manganese in open seawater range from 0.4 to 10 µg dm^{-3}. Concentrations of dissolved manganese in natural waters that are essentially free of anthropogenic sources can range from 10 to > 10000 µg dm^{-3}, while tap water can typically contain > 1 mg dm^{-3}. However, manganese concentrations in natural surface waters rarely exceed 1000 µg dm^{-3} but are usually lower than 200 µg dm^{-3}. Average levels in drinking water are 4µgdm^{-3} (Pearson & Greenway, 2005).

Small quantities of manganese are readily determined spectrophotometrically by the oxidation of Mn (II) to the intensely colored permanganate ion (MnO_4). Sodium Bismuthate ($NaBiO_3$) is an effective oxidizing reagent for this purpose. The manganese content is determined using a spectrophotometer from the absorbance of the permanganate solution at 510 nm. Manganous salts are oxidized to permanganic acid (Permanganic acid is stable in cold solution containing 20% – 40 % of nitric acid) by excess of sodium bismuthate in the presence of nitric acid as follows:

$$2Mn^{2+} + 5NaBiO_3 + 14H^+ = 2MnO_4^- + 5Bi^{3+} + 5Na^+ + 7H_2O$$

II. SAMPLE COLLECTION

The City of Shillong is the capital of Meghalaya, a North Eastern state in India surrounded by rivers on all sides. From the eastern to the northern part of the city flows the Umkhrah river and from the southern part to the western part of the city flows the Umshyrpi river and the two rivers meet at a junction known as Sonapani point and from there they discharge into the Barapani Dam. The rivers may act as charging source to the ground water in the city. Apart from this, the State as a whole is a heavy rainfall area. The main provider of drinking water in the city is the Public Health and Engineering Department and the Shillong Municipality. However the daily water requirement of the city is ever growing and with the growth of the population, the inhabitants of the city are now looking for other sources of water and their attention is now turn to the available ground water resource.

Ground water samples were collected once during the winter months of January 2012 and February 2012 from Thirty Six site all around the city of Shillong. The city was divided into five Zones (North, East, Central, South, and West Zones). The samples were collected from all types of ground water sources i.e. wells (Bore wells, Dug wells), underground springs ranging from depth of 10 feet to 350feet. The water samples were kept in polythene containers (500 mL) with the addition of 2 mL concentrated HNO3 at 2 mL in order to preserve the metals and also to avoid precipitation.

III. METHODOLOGY

Many methods are available for the estimation of manganese in different matrices, for example, there are Atomic Absorption Spectrophotometry, Neutron Activation Analysis Technique, DPAS Voltametry, Periodate colorimetry, Persulphate spectrophotometry, Formaldoxime (FAD) method and Pyridylazonaphthol (PAN) colorimetric method etc. But all these methods are quite expensive and require expert handling. However, the bismuthate method is very simple and accurate and very easy to perform. But it does have its limitation, which is, the sensitivity of the method is not very high. The minimum detection limit is 0.1mg/l. However, this shortcoming can be rectified by taking larger sample volume. All the analytical reagent used were i.e. KMnO4, HNO3, NaBIO3 and Manganese metal were all of extra pure grade.

A. Determination of λ_{max} for Spectrophotometric Estimation of Mn

A standard solution of concentration 1mg/L was prepared, by which the maximum absorbance wavelength (λmax) was determined as shown in Fig. 1. λmax was observed to be 510nm.

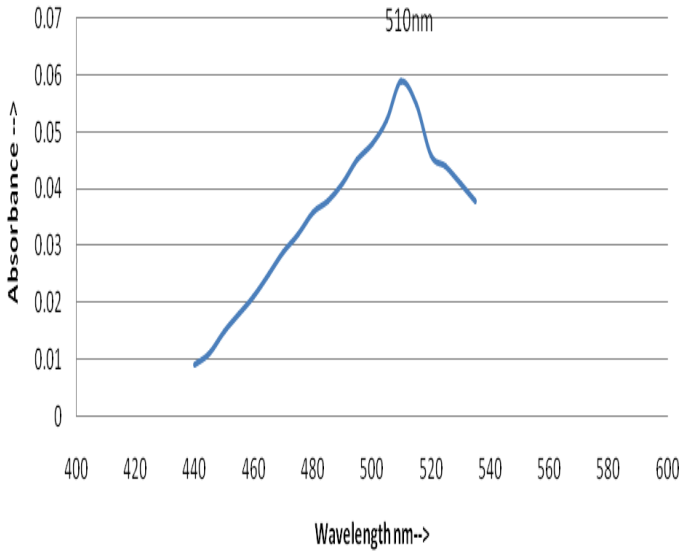

Fig. 1 Determination of the maximum absorbance wavelength

B. Standard Calibration of the Spectrophotometer for Mn Estimation

0.2876 g of potassium permanganate (of extra pure grade) is dissolved in 100 ml of distilled water. This is stirred until all the solid KMnO4 is dissolved. The solution contains 100 mg Mn/L. From this solution, appropriate volume is taken and diluted with distilled water in a 50ml volumetric flask to prepare a standard series of Mn as shown in Table I.

TABLE I STANDARD SERIES OF M_N PREPARED BY DILUTING STANDARD (100mg/L) KM_nO_4

Sl.No	Volume of Standard $KMnO_4$ Solution Taken (ml)	Final Volume Made (ml)	Concentration (mg/L)
1	0.1	50	0.2
2	0.3	50	0.6
3	0.4	50	0.8
4	0.5	50	1
5	1.0	50	2
6	2.0	50	4
7	3.0	50	6
8	4.0	50	8
9	5.0	50	10

Standard calibration of the spectrophotometer “Systronic Model 166” for the determination of Mn was performed. The absorbance of the prepared series was determined at 510nm and is depicted in Fig. 2 where it can be seen that the calibration curve obey the Beer-Lambert’s Law even up to a concentration of 10mg/L.

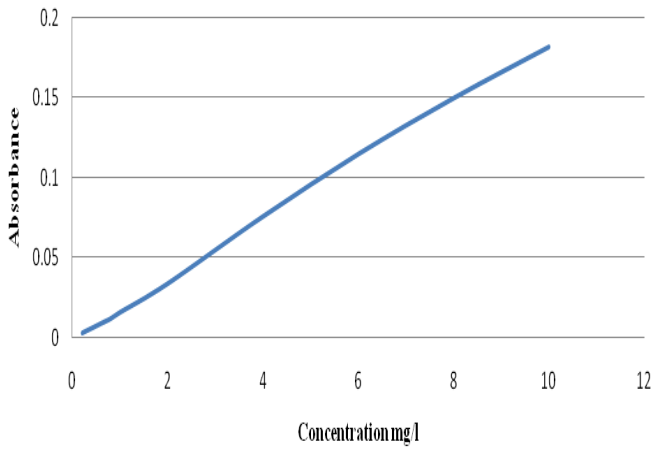

Fig. 2 Determination of standard calibration curve of Mn

C. Methodology for the Determination of Manganese

1mg of pure Mn metal is dissolved in 2ml conc. HCl and then diluted to 100ml with distilled water to make a solution whose strength is 10mg/L. From this solution, 1ml, 2ml, 3ml and 4ml is taken where 5 drops of Nitric Acid was added and made up to 50ml volume by adding distilled water in a volumetric flask. The final concentration of these four solutions was 0.2, 0.4, 0.6 and 0.8 mg/L. To these solutions, 0.01mg NaBiO3 was added and boiled for 45 minutes until effervescence ceases. The final volume was adjusted to 50ml by adding distilled water. The same method was run using distilled water blank. The solutions were cooled and allow standing for some time. The pink colored supernatant liquid is centrifuge and filtered through an ordinary filter paper to remove any adhering matter or any suspended solids that may interfere with the absorbance reading and to get a clear pink solution. The solutions having different color intensities were measure for their absorbance at 510nm where a straight line is obtained. The measured absorbance was found to match the standard absorbance and it was also observed that the percentage recovery yield was very high (almost 98-99%). At concentration lower than 0.1mg/L, it was observed that there is no color development. Thus, the minimum detection limit was set at 0.1mg/L. Study on the interference of different concentration of iron on the absorbance was also performed and it was seen that at acidic pH there was no interference from iron even at concentration of 5mg Fe /L.

The above method was applied to ground water samples. In this method 100ml of water sample was taken and acidified with HNO3 and then 0.01mg of NaBiO3 is added and boiled till effervescence ceases and then the volume was reduced to 50ml and cooled. The coloured supernatant liquid is then centrifuge, filtered through an ordinary filter paper and then the concentration of Mn is measured using a Systronic Model 166 and Visible Spectrophotometer. The observation and findings, and the concentration of Mn varying from different locations are depicted in Table II.

IV. RESULT AND DISCUSSION

In the present study, it can be seen that the concentration of Mn in all the ground water sampled around Shillong City ranges from Below Detection Limit (BDL) to 0.65mg/l. In the North zone the concentration ranges from 0.05 to 0.3 mg/l with a mean value of 0.12 ± 0.103, in the East zone it varies from 0.05 to 0.15 mg/l with a mean concentration 0.08 ± 0.033 mg/l, in the South zone the concentration observed lies between BDL to 0.35 mg/l with a concentration mean of 0.18 ± 0.12 mg/l and the West zone the concentration ranges from 0.05 to 0.65 mg/l with an average concentration of 0.16 ± 0.19 mg/l. From the central point or the reference point two samples were collected and the concentration was observed to range from 0.05 to 0.3 mg/l with a mean concentration of 0.18 ± 0.18 mg/l.

TABLE II MEAN CONCENTRATION AND CONCENTRATION RANGE OF M_N IN GROUND WATER SAMPLES COLLECTED FROM DIFFERENT ZONES DURING THE WINTER SEASON (JAN-FEB-2012)

Zones	Number of Sampling Locations	Concentration of Mn (mg/L)	Mean Concentration of Each Zone (mg/L)	Concentration Range of Each Zone (mg/L)
North	1	0.1	0.12 ± 0.103	0.05 to 0.3
	2	0.05		
	3	0.3		
	4	0.05		
	5	0.1		
	6	0.1		
	7	0.05		
	8	0.05		
	9	0.3		
East	1	0.1	0.08 ± 0.033	0.05 to 0.15
	2	0.1		
	3	0.05		
	4	0.05		
	5	0.05		
	6	0.08		
	7	0.07		
	8	0.06		
	9	0.15		
	10	0.05		
Central Point	1	0.05	0.18 ± 0.18	0.05 to 0.3
	2	0.3		
South	1	0.35	0.18 ± 0.12	BDL to 0.35
	2	BDL		
	3	0.25		
	4	0.15		
	5	0.05		
	6	0.1		
West	1	0.05	0.16 ± 0.19	0.05 to 0.65
	2	0.05		
	3	0.1		
	4	0.2		
	5	0.1		
	6	0.1		
	7	0.05		
	8	0.15		
	9	0.65		

The Bureau for Indian Standards (BIS) has set the desirable limit for Mn at 0.1 mg/l and the permissible at 0.3mg/l. Out of the total 36 ground water samples collected, 50% of the samples show Mn concentration below the BIS prescribed limit of 0.05mg/l, 25% exhibit values equal to the prescribed desirable limit (0.1mg/l), 8.33% contain Mn concentration higher than the BIS desirable limit (0.1mg/l) but still lower than the prescribed limit (0.3mg/l), 11.11% show concentration almost or equal to the prescribed limit (0.3mg/l) and 5.56% of the ground water samples have Mn

concentration well above the prescribed limit as per the BIS guidelines (Fig. 3).

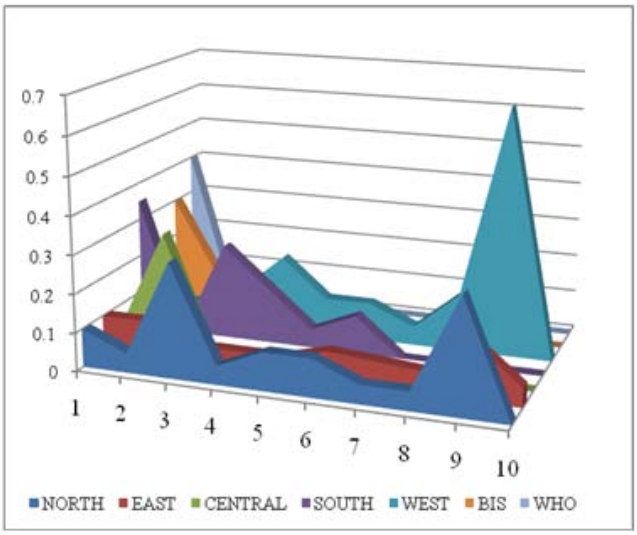

Fig. 3 Comparison of concentration of Mn in ground water samples in Shillong city with BIS (0.3mg/l) and WHO (0.4mg/l) prescribed limit

The World Health Organization (Howe, 2004) on the other hand has prescribed 0.4mg/l as the permissible limit for Mn in drinking water. All the ground water under investigation show Mn concentration well below the WHO prescribed limit (0.4mg/l) except for one location in the West zone where the concentration of Mn (0.65mg/l) was found out to be very much higher than the WHO limit.

In neutral conditions, the redox potential has a stronger influence on manganese mobility than pH. The concentration of manganese under aerobic conditions typical of shallow aquifers and surface water is generally low and as a rule do not reach detection limits. The reason is that in aerobic conditions, manganese is found in its stable oxidized form, generally as MnO2, which is highly insoluble. As water infiltrates downwards through soils and aquifers, the soil environment becomes more anaerobic and more reducing. The reduction reactions follow a sequence in which oxygen is removed first, followed by nitrate and manganese. Progressively more reducing conditions lead to the reduction of iron followed by sulphate. In these anaerobic conditions, manganese is released from minerals and reduced to its more soluble form, Mn (II). This form is apparently the most soluble one in most waters. Much higher manganese concentrations are therefore commonly found in anaerobic ground waters than in aerobic surface waters or shallow ones.

Similar distributions of Mn concentrations in groundwater used for drinking water have been reported elsewhere. In Sweden, the median Mn concentration in 12,000 sampled wells was 0.06 mg/l and around 20% of wells exceeded the Swedish recommended guideline of 0.3 mg/l (Ljung and Vahter, 2007). In a survey of 2160 private wells in the USA used for household drinking water, 5% of those tested had Mn concentrations greater than the health reference level (0.4 mg/l) and 21% had concentrations in excess of the USEPA Secondary Maximum Contaminant Level set for aesthetic quality and other non-health reasons (0.05 mg/l) (DeSimone, 2008). In a survey of total Mn (i.e. not filtered) from 10,000 groundwater sources in New Zealand, Daughney (2003) found that 39% exceeded 0.05 mg/l and 15% exceeded the WHO guideline of 0.5mg/l.

As previously mentioned, manganese is an essential element in humans and animals, functioning both as an enzyme co-factor and as a constituent of metalloenzymes. It has been implicated in carbohydrate metabolism, lipid and sterol metabolism and oxidative phosphorylation. Furthermore, experimental studies in animals suffering from manganese deficiency have suggested a role for manganese in the prevention of tissue damage following lipid peroxidation and in the normal functioning of the central nervous system. (Zidenberg & Keen, 1987) Gross deficiencies of manganese have never been observed in the general population, but a recent experimental study involving human subjects fed a manganese-deficient diet (0.11 mg/d) resulted in the development of dermatitis and hypocholesterolemia and elevated concentrations of serum calcium and phosphorus. (Friedman et al., 1987) In a recent comprehensive literature survey of studies of manganese metabolism in humans, it was concluded that previous estimates for a safe and adequate daily dietary allowance for manganese (2.5-5.0 mg/d) were too low, and a new range of 3.5-7.0 mg/d was recommended for adults (Zidenberg & Keen, 1987). A statistical analysis of the metabolic studies showed that a daily manganese intake of approximately 5 mg is required to consistently maintain positive balance.

If a daily water consumption of 2 litres and a manganese concentration of 0.05 mg/L in the ground water are assumed, the daily intake of manganese from Shillong city ground water would be approximately 0.1 mg. Actual daily intake of manganese from ground water varies considerably, depending on the sampling area in the city of Shillong.

Even though in some locations the concentration of Mn in the sampled ground water is high compared to others, still, this does not pose a threat to health of inhabitants of Shillong city through the daily intake of ground water with respect to Mn concentration.

V. CONCLUSION

Spectrophotometric determination of Mn in ground water samples was performed employing the Bismuthate oxidation method and using the Systronic Model 166, Visible Spectrophotometer. The bismuthate oxidation method was first checked for efficiency and reproducibility. The minimum detection limit for Mn using this method was observed to be 0.1mg/L. The λmax was also determined and it was found out to be 510nm. The efficiency of the method was about 98-99%. The interference due to the presence of iron was also monitored and it was observed that iron concentration even upto 5mg Fe /L did not interfere with the estimation. In this study, using this method, the concentration of Mn in the ground water sample was found to range between Below Detection Limit (BDL) to 0.65mg/L. Except in one location, Mn was detected in all the other sampling sites. Out of the total 36 ground water samples collected, 50% of the samples show Mn concentration below the BIS prescribed limit of 0.05mg/l, 25% exhibit values equal to the prescribed desirable limit (0.1mg/l), 8.33% contain Mn concentration higher than the BIS desirable limit (0.1mg/l) but still lower than the prescribed limit (0.3mg/l), 11.11% show concentration almost or equal to the prescribed limit (0.3mg/l) and 5.56% of the ground water samples have Mn concentration well above the prescribed limit as per the BIS guidelines. Only in one location the concentration of Mn (0.65mg/L) was observed to exceed the WHO limit of 0.4mg/L.

ACKNOWLEDGEMENT

The author would like to express deepest gratitude to Mr. R. Decruse, Head of the Chemistry Department of Lady Keane College, for encouraging and allowing carrying out the experiment in the Chemistry Laboratory. The author would also like to thank Mrs. C. Massar, Principal of Lady Keane College, for encouraging and motivating this research works.

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