A Comparative Study on the Determination of Fe in Groundwater by Different Methods

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Abstract. Three different experimental methods were used to analyse iron content in groundwater samples drawn from various spots of Mirzapur, a southeastern part of Rajshahi City, Bangladesh. These included UV-visible spectrophotometry, atomic absorption spectrophotometry, and titrimetric methods. As many as 20 water samples were collected from randomly selected domestic water supply tubewells throughout the area. Iron content was found to range between 0.052 - 5.890 ppm, 0.060 - 6.060 ppm, and 0.139 - 5.584 ppm by the spectrophotometric, atomic absorption spectrophotometric, and titrimetric methods, respectively. The values obtained with the three different methods were, fairly comparable and lie within the fringe of experimental deviations.

Keywords: drinking water, Fe determination, metal contamination, toxic effect, groundwater iron

Introduction

Iron is an essential mineral for living beings. The total iron content of a normal adult body is about 4 to 5 g. The primary function of iron is to form haemoglobin, which carries oxygen in the blood in the form of oxyhaemoglobin. Myoglobin is an iron containing chromoprotein, like haemoglobin, which combines with oxygen and acts as an oxygen store for muscles. It is also involved in the process of cellular respiration.

The probability of changes in the groundwater quality, particularly with respect to heavy metal contamination, has increased significantly during the recent years. Iron, among the heavy metals, may be present in concentrations that may be either in the beneficial or the toxic range. As per international standards, the permissible limit of Fe in drinking water is 0.3 mg/l, while 1.0 mg/l is rated as excessive (WHO, 1971). The US public health safety standards specify 0.3 mg/l of iron (USEPA, 1979). Groundwater in the excessive rainfall areas contains iron in toxic amounts. In deep tubewells, iron exists as ferrous ion, which on coming in contact with air rapidly changes to light yellow-orange colour due to oxidation and precipitates as ferric hydroxide. Such waters are extremely harmful for drinking.

Some recent studies carried out in Bangladesh have indicated iron contamination in groundwater (Khan *et al.,* 2003; Samad *et al.,* 2003; Tareq and Rahman, 2002). Rahman *et al.* (2000) studied the underground-water quality of Tongi, Gazipur District, Bangladesh. The study reported that Fe contamination was within the permissible limit. Alam and Anam (1991)

have studied the chemical characteristics of groundwater samples collected from some deep and hand-operated tubewells around Dhaka City, Bangladesh. Water available in Gorakhpur, India is moderately hard and contains appreciable content of Fe (Srivastava *et al.,* 2001). Raveendran and Ismail (1991) have studied the quality of groundwater in Bahrain. Recently, Chilton (2003) reported that underground aquifers are the major sources of municipal and industrial water supplies. Some of the world's largest cities (Beijing, Buenos Aires, Dhaka, Lima, Mexico City) draw heavily from them, while some of the fastest growing cities are completely dependent on groundwater. Groundwater from aquifers beneath or close to Mexico City, for example, provides the city with more than 3.2 billion litres per day. However, as the groundwater pumping increases to meet the growing water demand, it can exceed the rates at which the aquifers are replenished. In fact, water level of several urban aquifers have shown long-term decline. Since Fe is an important water mineral, the present study was carried out to compare three different methods, namely, spectrophotometric, atomic absorption photometry, and titrimetry for proper assessment of the quality of groundwater with respect to this important water constituent.

Materials and Methods

Twenty groundwater samples were collected from hand-operated tubewells of Mirzapur area of Rajshahi City, during October-November, 2002 (Fig.1). For the purpose, those wells were selected that were under constant use and were free from external pollution. The samples were collected in plastic containers during running condition of the wells. These tube-

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wells were in use from 6 months to as many as 20 years. The depth of the tubewells ranged between 100-150 ft. The plastic containers were let to stand overnight with 7% HNO_3, washed with soap-water and then with distilled water, before use for
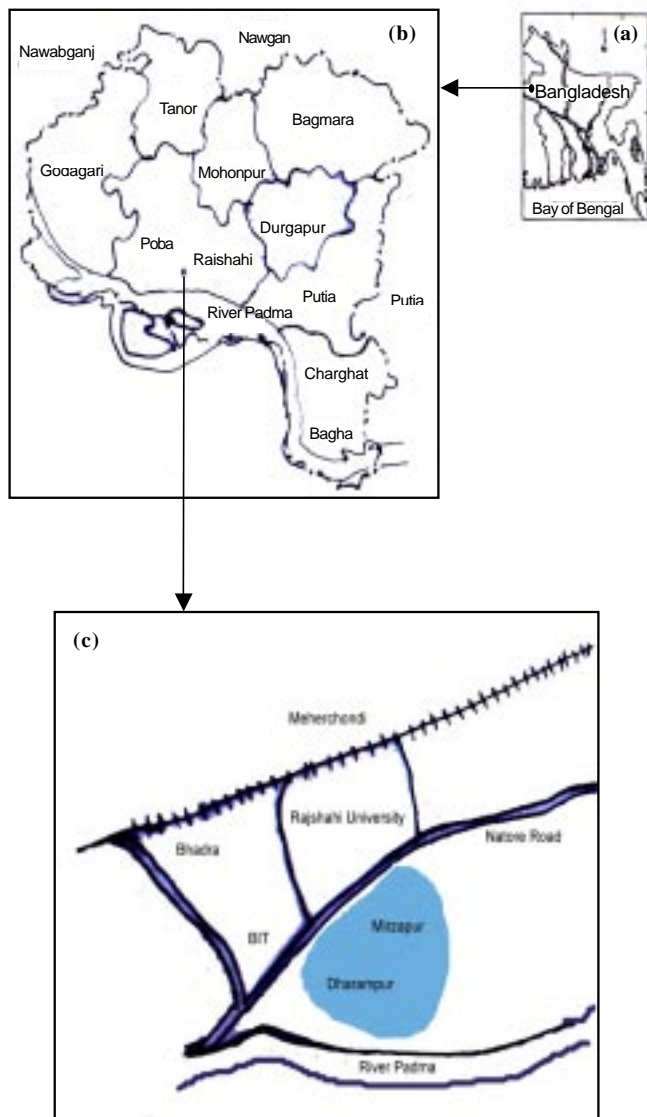
collecting water samples. Every tubewell was pumped for 5 min per 50 ft depth, before commencing with the sample collection, which were then collected in the sample containers, thoroughly rinsed before hand three times with the corresponding tubewell water.

Physical properties, including pH and electrical conductivity values were determined electrometrically using digital pH meter (S-3C, Rex, Shanghai, China) and digital conductivity meter (HI9033, Hanna, Singapore). Iron was determined by three different methods, namely, UV-visible spectrophotometric (using model ANA-75), atomic absorption spectrophotometeric (using model Perkin-Elmer 3110, USA), and titremetry. In the spectrophotometric procedure, iron was determined by the thiocyanate method; in the atomic absorption spectrophotometeric method, iron was determined directly with an air acetylene flame and single hollow cathode lamp; and in the titrimetric method, iron was measured by using standard potassium dichromate solution for titration and sodium diphenylamine sulphonate as the indicator. In the case of spectrophometric method, the absorbance of the samples was measured at 480 nm and in the case of atomic absorption spectrophotometric method, the reading of the samples was taken at 248.3 nm. In both the cases, standard solutions of Fe were used to make calibration curves.

Results and Discussion

A selected set of international drinking water regulations representing pH and Fe range of constituents in respect of health or aesthetic impacts are given in Table 1. A critical examination in respect of these values reveals that the pH of water samples used in the present study ranged from 7.42 to 8.6, which indicate that the groundwater of the area was alkaline in nature and within the safe limit for drinking (Table 2). The alkaline nature may be due to the abundance of Ca, Mg, Na and HCO_3^- ions present in the sampled water. BWPCB (1976) and WHO (1971) have recommended the standard values of pH in the range of 6.5 to 9.2 for potable water. The presently observed values of pH further indicate that the groundwater of this area is also suitable for irrigation purpose as a whole.

Fig. 1. Map of the study area, southeastern part of the Rajshahi City, Bangladesh; (a) Bangladesh, (b) Rajshahi City, (c) study area.

Table 1. Standard values of pH and Fe content, internationally accepted for potable water

| pH/Fe | USEPA (1979) | | WHO International (1971) | | | European Community | | | |
	Recommended	Maximum permissible range	Recommended	Maximum permissible range	WHO European (1970)	Guide levels	Maximum permissible	USSR (1975)	Norway
pH	6.5 - 8.5	-	7.0 - 8.5	6.5 - 9.2	-	6.5 - 8.5	9.5	-	8.0 - 8.5
Iron (mg/l)	0.3	-	0.1	1.0	0.1	0.05	0.2	0.3	<0.1

The electrical conductivity (EC) values of groundwater of Mirzapur area varied from 694 to 1185 μScm^{-1}. The EC values reported by Costa *et al.* (1985) were also in the same range, which is an indication of a comparatively high mineralisation of the groundwater. The present EC observations (Table 2) revealed that maximum number of tubewells had water in the high salinity (C3) range, while some were (samples 5, 6, 10, 15) in the medium salinity (C2) class, in accordance with the classification of Richards (1968). Theoretical and experimental values of Fe measured by the titration method are presented in Table 3, from which it may be concluded that the method was sufficiently precise.

A comparison of the data for the contents of Fe (using different methods), pH and EC values are tabulated in Table 2 and Fig. 2. It is evident from Table 2 that the lowest values were obtained with sample no.1, and the highest with sample no.16. For sample no.1, the spectrophotometric method gave values

Table 2. Values of pH, EC and Fe and in the tubewell water sam-ples of Faridpur area, Rajshahi, Bangladesh

Sam-ple no.	Depth of the tubewell (ft)	pH	EC (μScm^{-1})	Iron (ppm)		
				sectrophoto-metric method	AAS method	titrimetric method
1	135	7.61	989	0.052	0.060	0.139
2	134	8.01	787	0.052	0.090	0.195
3	115	7.95	859	2.306	2.560	2.401
4	150	7.96	767	0.098	0.130	0.140
5	130	8.02	697	2.273	2.320	2.234
6	150	7.89	694	0.153	0.140	0.195
7	145	7.97	935	0.114	0.120	0.140
8	100	8.6	777	0.151	0.130	0.176
9	115	7.90	938	3.320	3.990	2.792
10	110	8.13	703	1.220	1.060	1.780
11	106	7.8	980	0.077	0.080	0.140
12	120	7.5	798	0.687	0.770	0.410
13	130	8.01	829	0.165	0.140	0.223
14	125	7.32	1010	0.140	0.160	0.230
15	140	7.76	740	0.185	0.150	0.223
16	135	7.54	1054	5.890	6.060	5.584
17	130	7.78	1180	3.170	3.050	2.792
18	110	7.97	823	0.105	0.120	0.149
19	135	7.42	1185	2.720	2.690	2.596
20	120	7.92	928	3.070	3.140	3.350

AAS: atomic absorption spectrophotometric method

Table 3. Theoretical and experimental values of Fe measured by titrimetric method

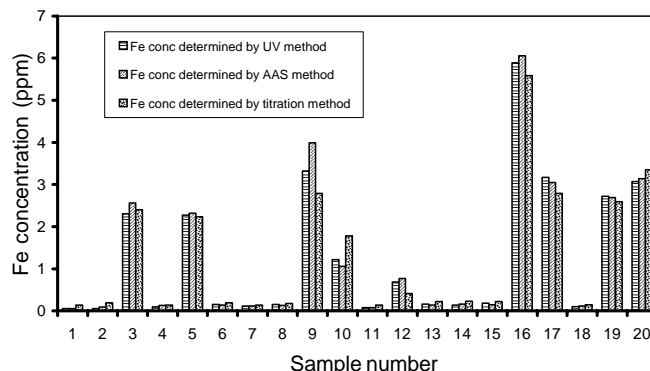| Theoretical value of Fe	Experimental values of Fe
0.5 ppm	0.577 ppm
1 ppm	0.885 ppm
1.5 ppm	1.499 ppm
2 ppm	1.907 ppm

Fig. 2. Iron contents as determined by different methods in the tubewell water of Rajshahi City, Bangladesh.

of 0.052 ppm, atomic absorption spectrophotometric method 0.060 ppm, and titrimetric method 0.139 ppm. The values are comparable and the average iron content in tubewell no.1 was 0.083 ppm. However, values obtained with spectrophotometric and atomic absorption spectrophotometric methods were closer in comparison to that obtained with titrimetric method. Sample no.16 gave values of 5.890, 6.060 and 5.584, respectively, with spectrophotometric, atomic absorption spectrophotometric and titrimetric methods. The values are fairly comparable and the average iron concentration was 5.844 ppm. However, again the value obtained with titrametric method was somewhat diffirent from the other two values, indicating that the titrimetric method was less precise. A critical examination of the entire range of observations presented in Table 2, lead to a similar conclusion, as stated above. It may be noted that the titrimetric method depends on colour change and the end point was detected visually. Fig. 2 gives a good comparison of the three methods investigated. A general conclusion can, nevertheless, be drawn that the three methods were fairly comparable, with insignificant variations and the values obtained were within the fringe of experimental error.

The following observations deal with the suitability of the groundwater of the area in respect of Fe content. The iron content in the groundwater samples ranged between 0.05 and 6.06 ppm. The iron content in the sample nos. 1, 2, 4, 6, 7, 8, 11, 13, 14, 15, 18 was within the recommended limit of 0.3 ppm (USEPA, 1979). However, iron content in the rest of the samples was high and beyond acceptable limits, which suggests that these samples are not suitable for drinking purpose, even not for industrial purposes.

The gross average iron concentration in the area determined by the three separate methods, namely, spectrophotometric, atomic absorption spectrophotometric, and titrimetric methods was found to be 1.29, 1.34 and 1.29 ppm, respectively. It is evident from the present results that the groundwater bodies

of this area contain a higher amount of Fe, in general. Specifically the Fe contents of water from 11 tubewells (nos. 1, 2, 4, 6, 7, 8, 11, 13, 14, 15 and 18) were within the permissible limit of 0.3 ppm and suitable for drinking purposes. The water of remaining 9 tubewells was not potable in terms of Fe contents and hence should not be used for the purpose. Moreover, water with high concentration of iron is not recommended for industrial purposes also.

Conclusion

It may be concluded from the present observations, that the three methods, spectrophotometric, atomic absorption spectrophotometric and titrimetric methods are all applicable for the determination of Fe in water samples. However, spectrophotometric, atomic absorption spectrophotometric methods give more precise results. Regarding titrimetric method, one can observe that in few cases it may be somewhat difficult to indicate sharp end point of the titration, hence variations in comparison with the other two methods were noted.

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