Fluorine Level in some City Water Supplies of Bangladesh

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Abstract

Nuclear reaction based Proton Induced Gamma Emission (PIGE) analytical method was employed for the quantitative measurement of fluorine in the city water supplies of the major cities of Bangladesh. 102 water samples collected from 14 city supplies were analyzed and these samples contain fluorine in the range of 0.03 to 1.10 mg/L with a mean of 0.33 ± 0.21 mg/L. It was also observed that except the samples of Barisal, Dinajpur and Rajshahi, all other water samples analyzed contain a much lower amount of fluorine than the maximum permissible value for Bangladesh in drinking water, which is 1 mg/L. The mean concentration of fluorine in the samples of Barisal, Dinajpur and Rajshahi are respectively 0.79±0.01, 0.71±0.13 and 0.92±0.18 mg/L. For the 55 samples of Dhaka city supply the mean fluorine concentration is 0.31±0.17 mg/L and that of 9 samples from Chittagong city supply is 0.19±0.10 mg/L, which is the lowest among the 14 city supply samples analyzed in this study.

Key words: City water supply, fluorine concentration, groundwater, proton induced gamma emission, water fluorine.

1. Introduction

Contamination of water supply and other components of the biosphere with fluoride is a human health concern in many parts of the world. The fluoride content of drinking water is a very important factor from the health point of view. Dental researchers have reported that the supplementation of fluoride in drinking water improves the resistance to dental caries [1-2]. However, recent studies by public health dentists in New Zealand, Canada, the United Kingdom, and the United States have reported no such benefit from water fluoridation [3-6]. Presently, there are reports that excessive fluoride intake causes fluorosis, cancer, arthritis, and other diseases [7-11]. It has also been observed that fluoride in excess affects human intelligence, especially in the children, who are most susceptible to fluoride toxicity [8,11]. Chronic fluoride intoxication (fluorosis) has been reported not only in humans, but also in domestic animals, such as, cattle, buffaloes, sheep, and goats [12].

The contamination of water with fluoride is a health problem in many parts of south Asia and other regions of the world. In some regions of India, water contains fluoride up to 38 mg/L, which is exceedingly high compared to the maximum permissible limit (MPL) of 1 mg/L set for India [13].

The fluoride content in groundwater scenario in India especially in the States bordering Bangladesh should make us interested about the situation in Bangladesh. As the geological formation of Bangladesh is very similar to that of the some regions of India, it is likely that the groundwater in Bangladesh might have been affected by the natural fluoride. The present research program was undertaken with a view to investigate the fluoride content in drinking water of major city supplies of Bangladesh using PIGE method.

Proton induced gamma emission (PIGE) is a nuclear reaction based analytical method, which is suitable for non-destructive analysis of low mass elements especially in environmental samples [14-15]. PIGE analysis of fluorine is based on the detection of the gamma rays emitted on proton interaction with $^{19}$F. The energy of the gamma ray identifies the isotope present in the sample and its intensity is a measure of the concentration of the isotope. Compared to other methods of fluorine
analysis in water [15-16], the PIGE method has the advantage of being isotopic in nature with virtually no interference; its sensitivity is high, and it is multielemental.

2. Materials and Method

i) Sampling and sample preparation

In total 102 water samples were collected from 14 major cities of Bangladesh. The cities are Barisal, Bogra, Chittagong, Comilla, Dhaka, Dinajpur, Gazipur, Jessore, Khulna, Mymensigh, Rajshahi, Rangpur, Sylhet, and Tangail. Most of the drinking water samples were collected from the tap of the reservoir tank. A 200 mL water sample together with 100 mg of ashless cellulose powder (Whatman) was evaporated to dryness in a porcelain dish on a steam bath and then under an infra-red lamp. The residue was cooled at room temperature in a desiccator for 1 hr. The powdered sample was then weighed and sealed in a polythene bag and stored in a desiccator.

ii) Experiment

The experiment was performed with a proton beam of 2.9 MeV from the 3MV Van de Graaff Accelerator of the Atomic Energy Centre, Dhaka (AECD). The schematic diagram for both internal/external beam PIGE setup is shown in Fig. 1.

A 50 mg sample was pressed into a 10 mm diameter pellet with 3 tons of pressure in a graduated hydraulic press. The pellet was mounted on a 35 mm slide frame with adhesive tape and preserved in a desiccator until irradiation. A 200 mL de-ionized water mixed with 100 mg of cellulose was prepared in the same way to serve as the blank and analyzed for contamination control during the sample preparation. The details of the sample preparation have been published earlier [14-15].

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Fig. 1: Schematic diagram of the external/internal beam of the PIGE experimental system.

Fig. 2: Gamma ray spectrum from water residue.
absorption at the exit window and the air between the window and the sample is estimated to be 2.3 MeV. Each sample was irradiated for a preset charge of 20 μC with a beam intensity of 15 nA. The characteristic γ-rays were detected with a high purity germanium (HPGe) detector having a resolution of 1.75 keV at 1332 keV γ-rays. A typical PIGE spectrum from a water residue sample is illustrated in Fig. 2.

iii) Data analysis
The gamma ray spectra were analyzed using a commercially available γ-ray spectrum unfolding software obtained from APTEC Nuclear Inc. USA. The software provides an analysis report of the net peak intensities including peak centroid, FWHM, background under peak, range of the peak, and their uncertainties for the different elements present in the sample. These net peak intensities were then used to calculate the concentrations of the elements in the sample.

iv) Concentration calibration
The concentration calibration curve shown in the Fig. 3. was obtained by using CaCO₃ matrix mixed with AnalaR grade NaF concentrations ranging from 10 to 100 mg·kg⁻¹ as described elsewhere [14].

The number of gamma rays emitted from the nuclear reaction \(^{19}\)F(p, p'γ)\(^{19}\)F per unit charge was used to construct the curve. The calibration curve was used to determine the fluoride concentrations in water residues on dry weight basis (mg/kg). These concentration data were then converted to mg F/L of water samples with respect to 200 mL of each analyte sample.

3. Results and Discussion
The bulk of the water residue obtained after evaporation consists mostly of carbonates and bicarbonates. The weight of the residue obtained from different samples varied from 0.01 to 0.18 g. Under these conditions, it was assumed that the matrix composition consists predominantly of H, C, and O. CaCO₃ was therefore chosen as the carrier for calibration with known amounts of NaF [14].

Some water samples were analyzed by the fluoride ion selective electrode (ISE) method,
Table 1: Concentration of Fluorine in 14 city water supplies of Bangladesh.

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Name of city</th>
<th>Number of Samples</th>
<th>Distribution of fluorine (mg.L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Range</td>
</tr>
<tr>
<td>1</td>
<td>Barisal</td>
<td>2</td>
<td>0.78 - 0.79</td>
</tr>
<tr>
<td>2</td>
<td>Bogra</td>
<td>4</td>
<td>0.19 - 0.27</td>
</tr>
<tr>
<td>3</td>
<td>Chittagong</td>
<td>9</td>
<td>0.05 - 0.34</td>
</tr>
<tr>
<td>4</td>
<td>Comilla</td>
<td>4</td>
<td>0.12 - 0.53</td>
</tr>
<tr>
<td>5</td>
<td>Dhaka</td>
<td>55</td>
<td>0.03 - 0.76</td>
</tr>
<tr>
<td>6</td>
<td>Dinajpur</td>
<td>3</td>
<td>0.60 - 0.85</td>
</tr>
<tr>
<td>7</td>
<td>Gazipur</td>
<td>2</td>
<td>0.32 - 0.33</td>
</tr>
<tr>
<td>8</td>
<td>Jessore</td>
<td>3</td>
<td>0.16 - 0.46</td>
</tr>
<tr>
<td>9</td>
<td>Kustia</td>
<td>3</td>
<td>0.19 - 0.37</td>
</tr>
<tr>
<td>10</td>
<td>Mymensingh</td>
<td>4</td>
<td>0.05 - 0.63</td>
</tr>
<tr>
<td>11</td>
<td>Rajshahi</td>
<td>3</td>
<td>0.75 - 1.10</td>
</tr>
<tr>
<td>12</td>
<td>Rajshahi</td>
<td>3</td>
<td>0.08 - 0.39</td>
</tr>
<tr>
<td>13</td>
<td>Sylhet</td>
<td>4</td>
<td>0.05 - 0.33</td>
</tr>
<tr>
<td>14</td>
<td>Tangail</td>
<td>3</td>
<td>0.21 ± 0.14</td>
</tr>
</tbody>
</table>

considered to be the most appropriate one for fluoride in water. The results are shown in Fig. 4 along with those of PIGE measurements for comparison. The results obtained from two methods are in good agreement. The concurrence between the two results indicates the validity of the PIGE methodology. The reproducibility of the results has been tested by measuring the fluoride content of the same sample several times. For 5 replicate measurements, the standard deviation was found to be ±0.03 mg.kg⁻¹ at the concentration level of 0.60 mg.kg⁻¹.

i) Minimum detection limit (MDL)

The MDL is defined as the amount of an element in mg.kg⁻¹ that yields a γ-ray intensity equal to 3σ of the background under the peak in an interval equal to the full width at half maximum (FWHM). The MDL for water residue of 200 mL water sample containing 100 mg cellulose, which was irradiated for a preset charge of 20 μC, was found to be 0.2 mg/kg on the dry weight basis of the water residue. This corresponds to approximately 0.0001 mg.L⁻¹ in the original water sample.

ii) Fluoride levels in city supply waters of Bangladesh

In cities generally chlorinated waters are supplied which has lower fluoride content. The mean fluoride distribution in water supplies of different cities is shown in Table 1. The fluoride concentration in 102 water samples analyzed from 14 major city supplies was found to be in the range of 0.03–1.10 mg.L⁻¹, with a mean of 0.33 ± 0.21 mg.L⁻¹. The results show that the fluoride levels in water of most of the city supplies are much lower than the maximum permissible limit (MPL) of 1 mg.L⁻¹ in drinking water set for Bangladesh [16].

In general, the ground water is bleached before they are distributed for drinking and other purposes. These chlorinated waters contain lower amount of fluorine and lies within the maximum permissible limit. It can be seen from Table 1 that the city supply water of all the 14 cities, except Barisal, Dinajpur and Rajshahi contains much lower amount of fluorine than the MPL. The mean of fluoride concentration of Barisal, Dinajpur, and Rajshahi are respectively 0.79±0.01, 0.71±0.13, and 0.92±0.18 mg.L⁻¹. The mean of fluoride concentration for 5-5 samples of Dhaka city supply is 0.33±0.17 mg.L⁻¹ and that of the 9 samples of the Chittagong city is 0.19±0.10 mg.L⁻¹, which is the lowest among the 14 city supply samples analyzed in this study. It therefore appears that the water of most city supplies contains fluorine lower than the maximum permissible level of 1 mg.L⁻¹ in drinking water set for Bangladesh [16].

The important feature of the results of the present study is that the fluoride content of the drinking water of 14 major city supplies of Bangladesh is well below the maximum permissible set limit of 1mg.L⁻¹ and is also lower than that of the many countries in the region. In South Asia the highest level of the concentration of fluorine is found in
India, which is 38.5 mg.L\(^{-1}\) [12, 17]. The fluorine content in water of Sri Lanka lies between 0.07 and 4.46 mg.L\(^{-1}\) [18] and that of China lies between 0.08 and 4.20 mg.L\(^{-1}\) [19].

This study suggests that the fluorine concentration in city water supplies of Bangladesh is low. However the result of this study is only indicative. To assess the extent of the dietary deficiency or excess of fluorine, more rigorous study may be undertaken. Research program in this regard has already been initiated.

4. Acknowledgement

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