ABSTRACT

For sustainable development, to assure health care services and for the protection of the human environment to ensure a quality of life, the knowledge of concentration on the environmental constituents is very much essential. In recent years the study of elements, both major and traces, especially related to environment has assumed increasing importance because of their vital role in human health and diseases. Fluorine is an essential element for both plant and animal life. A high incidence of caries has been shown by many investigators to be correlated with low fluorine intake. Excess intake of fluorine results in toxic symptoms described as fluorosis that causes many diseases like arthritis, lameness, pain on movement, etc. Therefore the concentration of fluorine in drinking water is very important for human health.

Nuclear analytical technique Proton Induced Gamma Emission (PIGE) method developed in the Van de Graaff Accelerator Laboratory of Atomic Energy Centre, Dhaka (AECD) was employed for the quantitative determination of fluorine in some water of Dhaka and its adjacent areas. Ion beam analysis technique PIGE was employed for the measurement of fluorine because it is suitable and reliable for the analysis of fluorine content in water, because the determination of Fluorine is very difficult by non-ion beam techniques. The fluorine concentration in the drinking water of Dhaka ranges from 0.01 ppm to 0.46 ppm. The study indicates that the inhabitants of Dhaka have low intake of fluorine from their drinking water supplies.

INTRODUCTION AND ARTICULATION OF THE PROBLEM

To ascertain human health and a quality life, monitoring of environmental pollution and identification of pollution sources is of much importance. Such studies will help thorough understanding of the environment and its effect on human life. In recent years the study of elements, both major and traces, in Environmental constituents has assumed increasing importance because of their vital role in human health and diseases. The major pathway of the elements to the human body is the food, drinks, and air. So from the point of view of environmental safety
assessment it is necessary to have the information on the levels of both toxic and essential elements in environmental ingredients such as air, water, food, etc. Moreover, the possibility that contamination of the water supply and food items with trace elements, arising from geological bearing minerals, modern agriculture and industrial practices may have detrimental effects on the long term health and welfare of human population. This has stimulated increasing interest in the study on concentrations and movements of these elements in the environment and in the intakes by man.

Fluorine, one of the 15 generally accepted essential elements, has long been recognized as a constituent of bones, teeth, soft tissues and body fluids. Criteria of adequacy and tolerance present particular problems with fluorine. Fluorine confers improved resistance to dental caries and is also necessary to assist in the maintenance of a normal skeleton and in the reduction of osteoporosis in the mature adult population. On the other hand, excessive fluoride intake causes fluorosis which is a more common condition than the deficiency state. Therefore, Fluorine is recognized as an essential trace element, but toxic when the intake is sufficiently high and for long enough period.

Drinking water is one of the major sources of fluorine for human population. In general surface waters used for drinking and cooking purposes in most communities has comparatively lower fluorine content. However, in some parts of the World the population is dependent on water from deep wells or artesian bores which could have higher fluorine content because the earth’s crust in many regions of the world has fluoride bearing minerals. Therefore, it is observed that in many countries of the world drinking water is contaminated with fluorine. For example in India an estimated 62 million people are sick due to fluorosis of which 6 million are children below the age of 14 years. It is for these reasons, the Central Ground Water Authority (CGWA) of India has warned the people not to consume water from shallow water bearing zones (up to 30 metres) in six blocks of the National Capital Territory of Delhi.

The fluorine content in ground water scenario in India especially in the States bordering Bangladesh may make some one curious about the situation in Bangladesh. There is a possibility to have the fluorine bearing minerals in the ground water in Bangladesh too. The geological aspect of Bangladesh is very similar to India. Therefore, it is likely that the ground water of Bangladesh could be affected by unintentional natural fluorine.

The knowledge of concentration of fluorine in drinking water and other foodstuffs is therefore very important from the point of view of human health and human environment. Such knowledge will help to estimate the fluorine intakes of the people and to evaluate any toxicity or deficiency. Similar studies could provide the better quantification of the effects of human environmental constituents that will help the detailed understanding of the environment and better management of the human environment. This will also help to evaluate and implement future
action plans on dental health services in the country. Under the circumstances the present research program was undertaken with a view to investigating the fluorine content in drinking water of Dhaka.

**EXPERIMENTAL METHOD**

Simplicity, non-destructiveness, multi-elemental capability, rapidity of analysis and accuracy are the main features of the PIGE technique, which make it an attractive analytical tool. Multielement PIGE technique is very much suitable for the measurement of fluorine content in water and it is a reliable analytical tool for the analysis of fluorine where chemical method is not suitable and does not give reliable results\(^5,18\). Large scale measurements using Proton Induced Gamma Emission (PIGE) method is also possible. PIGE methodology has been developed in the Van de Graaff Accelerator Laboratory of AECD for the analysis of light elements in environmental related samples.

**SAMPLING AND SAMPLE PREPARATION**

PIGE methodology was used to analyze the fluorine concentration in drinking water supplies of Dhaka city and its surrounding areas. The ground waters are usually bleached before they are distributed for drinking purpose. Most of the drinking water samples were collected from the tap of the reservoir tank. Some tube well waters (both deep and shallow) were also collected from the adjacent areas of Dhaka city. Some samples were also collected from Chittagong city.

In the present research work water samples were prepared utilizing the cellulose matrix following the methodology described in the literature\(^1\). 200 ml of water sample together with 0.1 g of ashless cellulose powder (Whatman) was evaporated to dryness on a steam bath in a porcelain dish in a stepwise way and afterwards completely evaporated under an infra-red lamp. After weighing a portion of the powder material was pressed into 10 mm diameter pellets with a graduated hydraulic press of 3 tons pressure. The blank values of the cellulose matrix were separately measured to check any possible contamination introduced during the sample preparation process.

**METHOD OF ANALYSIS EXPERIMENT**

The experiment was performed using the beam of protons provided by the 3MeV Van de Graaff Accelerator of the Atomic Energy Centre, Dhaka. A schematic diagram of the internal/external beam PIGE experimental set up is shown in Fig.1. The samples were bombarded in the air outside the chamber at atmospheric pressure with 2.9 MeV protons after extracting through 1.12 mg/cm\(^2\) Kapton window. Each of the target was irradiated for a preset charge of 10 μC of charge with a beam intensity of 10 nA. The characteristic γ-rays were detected with a 47 mm diameter and 38 mm long Princeton Gamma-Tech (PGT) high purity Germanium (HPGe)
detector having the resolution FWHM (full width at half maximum) of 1.75 keV and relative efficiency of 12.3% at 1332 keV γ-rays. A typical γ-ray spectrum obtained from a water sample is shown in Fig.2.

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

Fig. 2. A typical gamma ray spectrum from water sample.

DATA ANALYSIS

Data acquisition and data analysis is being done using a spectrum unfolding software from APTEC. The γ-ray spectrum unfolding software provides an analysis report of the net peak intensities including peak centroid, FWHM, background under peak,
range of the peak, and uncertainties of the different elements analyzed. These net peak intensities are then used to convert them into concentrations.

CONCENTRATION CALIBRATION

In order to determine concentration of fluorine in water samples, a calibration curve, shown in Fig.3, was constructed for CaCO$_3$ matrix where fluorine of different known concentrations were added. Calibration samples were made for fluorine concentration of 10, 50 and 100 mg/kg.

![Fig. 3 : Concentration Calibration Curve for Fluorine in Water](image)

Using this curve, the concentration of fluorine in mg/kg in a water sample is obtained from the relationship:

$$\text{Fluorine in water} = (\text{slope of the curve}) \times (\gamma\text{-ray yield per } \mu\text{C of charge})$$

As mentioned earlier, CaCO$_3$ matrix after the addition of known amount of fluorine was homogeneously dispersed with methanol and dried under an infrared lamp. This treatment did not change its composition as tested in terms of weight loss or gain. The blank values of the CaCO$_3$ matrix were separately measured to make appropriate corrections in constructing the calibration curve.

The bulk of the water residues obtained after the evaporation of water mostly consists of carbonates and bicarbonates. In the present case, the weight of the water residue from different samples varies from 0.01 – 0.20 g for 200 ml of water. To each of these residues, 0.1 g of cellulose powder was added. Under these conditions, it is assumed that the matrix composition is predominantly of H, C, and O. It has been shown that for light element matrix, the use of any standard with organic matrix for concentration calibration is valid to obtain results with ~10% accuracy$^{10-11}$.
In the present study PIGE methodology is utilized to analyze the fluorine content of drinking water. The results are summarized in Table-1, which shows that the fluorine level ranges from 0.01 to 0.46 µg/ml in the drinking water of Dhaka.

### Table – 1: The concentration of Fluorine in the Drinking water of Dhaka.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Sample</th>
<th>Water Type</th>
<th>Location</th>
<th>Concentration (µg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>W-8</td>
<td>WASA Supply Water</td>
<td>Old Zigatola</td>
<td>0.25</td>
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<td>2</td>
<td>W-9</td>
<td>WASA Supply Water</td>
<td>TB Gate, Mohakhali</td>
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<tr>
<td>3</td>
<td>W-10</td>
<td>WASA Supply Water</td>
<td>Gulsan – 4</td>
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<tr>
<td>4</td>
<td>W-13</td>
<td>WASA Supply Water</td>
<td>Nababgonj</td>
<td>0.31</td>
</tr>
<tr>
<td>5</td>
<td>W-15</td>
<td>WASA Supply Water</td>
<td>Green Road</td>
<td>0.11</td>
</tr>
<tr>
<td>6</td>
<td>W-16</td>
<td>WASA Supply Water</td>
<td>Shahidullah Hall</td>
<td>0.08</td>
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<tr>
<td>7</td>
<td>W-17</td>
<td>WASA Supply Water</td>
<td>Mirpur Section – 1</td>
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<td>8</td>
<td>W-14</td>
<td>WASA Supply Water</td>
<td>Mirpur, Section – 10</td>
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<td>9</td>
<td>W-26</td>
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<td>Mirpur Section – 2</td>
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<tr>
<td>10</td>
<td>W-27</td>
<td>WASA Supply Water</td>
<td>Middle Monipur</td>
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<td>11</td>
<td>W-28</td>
<td>WASA Supply Water</td>
<td>Wari</td>
<td>0.15</td>
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<tr>
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<td>W-30</td>
<td>WASA Supply Water</td>
<td>Sheker Tek</td>
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<td>W-32</td>
<td>WASA Supply Water</td>
<td>Ashkona</td>
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<tr>
<td>14</td>
<td>W-33</td>
<td>WASA Supply Water</td>
<td>Khilgaon</td>
<td>0.17</td>
</tr>
<tr>
<td>15</td>
<td>W-34</td>
<td>WASA Supply Water</td>
<td>Patra Bag</td>
<td>0.16</td>
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<tr>
<td>16</td>
<td>W-35</td>
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<td>0.11</td>
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<tr>
<td>17</td>
<td>W-36</td>
<td>WASA Supply Water</td>
<td>Makki Mosque</td>
<td>0.14</td>
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<tr>
<td>18</td>
<td>W-315</td>
<td>DU Supply</td>
<td>Jagannath Hall</td>
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<td>W-325</td>
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<td>W-6</td>
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<tr>
<td>24</td>
<td>W-11</td>
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<td>Lalkhan Bazar, Chittagong</td>
<td>0.77</td>
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<tr>
<td>25</td>
<td>W-24</td>
<td>WASA Supply Water</td>
<td>Small poll, Chittagong</td>
<td>0.04</td>
</tr>
<tr>
<td>26</td>
<td>W-25</td>
<td>WASA Supply Water</td>
<td>Large Poll, Chittagong</td>
<td>0.01</td>
</tr>
<tr>
<td>27</td>
<td>W-37</td>
<td>WASA Supply Water</td>
<td>Lalkhan Bazar, Chittagong</td>
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<tr>
<td>28</td>
<td>W-31</td>
<td>Deep Tube Well</td>
<td>AERE, Savar</td>
<td>0.25</td>
</tr>
<tr>
<td>29</td>
<td>W-12</td>
<td>Tube Well</td>
<td>Konapara</td>
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<tr>
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<td>W-20</td>
<td>Tube Well</td>
<td>Bolivadra Bazar</td>
<td>0.05</td>
</tr>
<tr>
<td>31</td>
<td>W-21</td>
<td>Tube Well</td>
<td>Nordapara, Dakhin Khan</td>
<td>0.14</td>
</tr>
<tr>
<td>32</td>
<td>W-22</td>
<td>Tube Well</td>
<td>Taltala</td>
<td>0.05</td>
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<tr>
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<td>W-39</td>
<td>Tube Well</td>
<td>Shanir Akhra</td>
<td>0.32</td>
</tr>
<tr>
<td>34</td>
<td>W-19</td>
<td>Pond</td>
<td>Shahidullah Hall</td>
<td>0.03</td>
</tr>
<tr>
<td>35</td>
<td>W-29</td>
<td>Pond</td>
<td>AERE, Savar</td>
<td>0.21</td>
</tr>
</tbody>
</table>

The redeeming feature of the results of this study is that the fluorine content of the drinking water of Dhaka is low and well below the acceptable limit.
DISCUSSION AND CONCLUSION

The present study of the fluorine concentration in the drinking water of Dhaka city and its adjacent area lies between 0.01 - 0.46 µg/ml which is very low. Therefore, fluorine intake of the people of Dhaka from their drinking water supply is low to prevent dental caries. Tube well waters also shows the similar results (0.05- 0.32 µg/ml). The fluorine concentration in the drinking water of Chittagong City shows somewhat higher amount (0.01- 1.86 µg/ml) of fluorine.

The values obtained for water in Dhaka is found to be lower than that of many countries. Surface waters used for drinking and cooking purposes in most communities, generally contain less than 1 or even 0.1 µg/ml or less. Most British water are low in fluorine, which contents usually between 0.1 and 0.5 ppm, with occasional rise to 1 ppm in case well waters and Maldon, Essex has 5 ppm. The fluorine content of Sri Lanka waters range between 0.07 and 4.46 ppm. The fluorine concentration in endemic fluorosis areas of Southern India is as high as 20-40 ppm. For the USA, the extensive results have been presented in the form of a distribution map and some considerations have been given to the causes of variations. Wide variations occur and frequently the fluorine content is below 1 ppm but figures as high as 7 ppm have been reported for S. Carolina, N. Dakota and Alabama. The relationship between fluoride concentration in water and dental caries are reported in the literature. Fluorine concentration of about 1 mg/litre in drinking water effectively prevents dental caries while fluoride level exceeding the recommended values cause fluorosis. This implies that the intake of fluorine needs to be controlled within a narrow range.

For taking an objective decision on fluoridation programme, the fluorine content in national foodstuffs, drinking water supplies and related environment needs to be analyzed. For these purposes, large scale measurements using Proton Induced Gamma Emission (PIGE) method may be considered as an appropriate methodology because PIGE is an instrumental multielement technique and it is more precise, more accurate, less time consuming, more convenient and efficient economically. The existing facilities at AECD and expertise grown so far may be utilized for this purpose.

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