CHAPTER - III

A COLORIMETRIC METHOD FOR THE TRACE DETERMINATION OF BORON
WITH ARSENAZO-1*

SUMMARY

The method described is based on the complex formation of boron with arsena zo-1 in concentrated sulphuric acid medium. The violet colour of the dye in sulphuric acid changes to blue-violet in presence of boron. Beer's law is valid in the range of 0.05 - 0.4 ppm of boron. The molar absorptivity and Sandell's sensitivity were found to be $2.2 \times 10^4 \text{ lit mol}^{-1}\text{cm}^{-1}$ ($\lambda$ 100) and 0.0005 $\mu\text{g cm}^{-2}$ respectively. The method has been successfully applied for the determination of boron in river water, rock and soil samples.

Boron is a versatile and useful element used mainly as borax and boric acid. The largest single use of boron is in glass making where boron compounds add strength to the glass, especially above the temperatures at which ordinary glass softens (1). Significant quantities of boron compounds are also used in vitreous enamel, metal fluxing and agricultural chemicals. Boron is commercially important as a metallurgical additive, is agriculturally significant as a component of fertilizers and is commonly used for home laundry and cleaning purposes (2). However, these uses eventually may be overshadowed by the new use of boron such as in atomic energy control rods, jet and rocket fuels, heat and radiation shields, steel hardening and as the stiffening agent in extremely strong, light weight and composite structural materials (1). Elemental boron is also currently used in production-run aircraft for such components as wing flaps, tail sections and helicopter rotor blades (3). There is increasing interest in the determination of boron in several fields, such as in geochemistry and as an eligible element in the physiology of plants and in the nuclear industry owing to the large cross section neutron capture of boron (4). The main source of boron in water is through industrial waste effluents and cleaning compounds (5).
Boron is an essential micronutrient for normal plant growth, but larger amounts are toxic to plants and may cause soil sterilization (5). Boron helps in the development of cell walls, fruit development and translocation of sugars (7,8). Boron toxicity is characterized by marginal necrosis of mature leaves near the end of the growing seasons (9). Concentrations of boron above 2 mg/l in irrigation waters adversely affect citrus and other plants (10).

Boron compounds, in general, are toxic to humans and animals when ingested. Intake of large amount of boron affects the central nervous system and protracted ingestion results in a clinical syndrome known as borism (5). Boron is ingested in the normal human diet, primarily from fruits and vegetables and is excreted at the same rate with little or no accumulation in the body. The symptoms of boric acid poisoning include nausea, vomiting, weariness, renal injury and death from circulatory collapse and shock within five days (1). Hypoacidity in adults and decreased fecal entero-kinase activity in children are observed by drinking high boron water for prolonged periods (11). As regards chronic toxicity, workers engaged in the packaging of boron fertilizers complain of poor appetite and loss of weight. It also results in alterations of upper respiratory tract mucosa, arthralgia and gynecological diseases (1).

The permissible boron limit in domestic water supplies and irrigation waters is 1.0 ppm boron. Sensitive plants are black berry, lemon, cherry, grape, kidney bean,
cowpea and zinnia (1). Many varieties of fruits can tolerate not more than 0.5 mg/l of boron in irrigation water. The U.S. E.P.A. recommends limits of 0.75 mg/l for most fruits, 1 mg/l for most cereals, potatoes and tomatoes and 2 mg/l for tolerant species including sugar-beet, turnips and cabbage. The maximum permissible limit is 1 mg/l and 1 - 1.2 mg/l respectively for crop irrigation and potable water abstractions (12).

Boron though an important trace element in plant nutrition, is unusual because of the narrowness of the range of concentration between deficiency and toxicity in plants and human beings. Hence large number of methods have been developed for the determination of boron in trace quantities. Some of the reported instrumental methods for the determination of boron are ion chromatography (13), thin layer chromatography (14), mass spectrometry (15), inductively coupled plasma emission spectrometry (16), neutron activation analysis (6), argon plasma emission spectrometry (10), atomic absorption spectrometry (17), \( \gamma \)-ray spectrometry (2) and others (18-22).

Various spectrophotometric reagents cited in the literature for the determination of boron are curcumin (23-25,43), carminic acid (26,27,43), quinalizarin (29,30), azomethine-H (30-32,43), dianthrimide (30,43), methylene blue (33), ethylviolet (34), 6 amino-5-nitro-pyrimidine-2,4 diol (35), beryllion III (36), brilliant green (37), chromotropic acid (38), Nile blue A (39), crystal violet (19,40), alizarin blueS, solway purple (41), 2-methyl pentane
6,4 diol (42) and chromatrole-28 (43). The popular spectrophotometric methods of determination are based on the complex formation of boron with the dye in concentrated sulphuric acid medium (26,27,30,41,43). In the present communication a new reagent arsenazo-I has been reported for the determination of boron. The method is based on the complex formation of boron with arsenazo-I in concentrated sulphuric acid medium. The violet colour of the dye in sulphuric acid changes to blue violet in presence of boron. The method has been successfully applied for the determination of boron in river water, rock and soil samples.

**EXPERIMENTAL**

**APPARATUS** - A Carl Zeiss spekol with 1 cm matched silica cells was used for all spectral measurements.

**REAGENTS** -

**Stock boron solution** - A 1 mg/ml solution was prepared by dissolving 0.5716 g of boric acid in 100 ml of demineralised water. Working standards were prepared by appropriate dilution of the stock.

**Arsenazo-I** - 0.02% solution in 98% sulphuric acid.

**Sulphuric acid** - 98% A.R. grade.

All chemicals used were of AnalaR grade.
**PROCEDURE** - Aliquots containing 0.5 - 4 μg of boron were taken in a 100ml volumetric flask. To it 2 ml of arsenazo-I was added followed by 2 drops of concentrated hydrochloric acid (44). The volume was made up with 98% sulphuric acid. The absorbance of the blue-violet dye-boron complex was measured at 590 nm after 30 minutes against a reagent blank.

**RESULTS AND DISCUSSION**

**Spectral characteristics** - The absorbance of the blue-violet dye-boron complex was measured at 590 nm against a reagent blank (Fig. 1).

**Colour reaction** - On addition of boron solution to the purple solution of arsenazo-I in sulphuric acid, the colour of the solution changes to blue-violet. This change of colour is apparently due to the formation of an inner complex boric acid-phenolic ester involving the -OH groups in the peri position. The reagent has an esterifiable phenolic -OH group in a coordination position with respect to a N-atom of the azo group. The chelate binding responsible for the colour change would be II or III i.e. an inner complex ester of ortho or metaboric acid (45).

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{III} & \quad + \text{H}_2\text{O}
\end{align*}
\]
FIG. 1. ABSORPTION SPECTRA OF THE DYE
A. REAGENT BLANK
B. CONCENTRATION OF BORON = 1 μg / 10 ml.
EFFECT OF VARYING REACTION CONDITIONS

Effect of various acids - Different acids like acetic acid, hydrochloric acid, orthophosphoric acid and sulphuric acid were studied. The latter was found to be suitable and most sensitive. In presence of acetic acid and orthophosphoric acid the dye-boron complex decomposes. In presence of hydrochloric acid an excess of acid leads to the decomposition of the complex, but very small amounts do not show much adverse effect.

Effect of reagent concentrations - The effect of dye at varying concentrations ranging from 0.005% to 1% was studied. At lower concentrations low results were obtained but no change was observed at concentrations above 0.02% (Fig. 2). Effect of water content in sulphuric acid was studied by using various concentrations of sulphuric acid. 98% sulphuric acid was found to be most sensitive (Fig. 3).

Beer's law, molar absorptivity and Sandell's sensitivity - The colour system obeys Beer's law in the range of 0.5-4 µg of boron per 10 ml of the final solution (0.05 - 0.4 ppm) (Fig. 4). The molar absorptivity and Sandell's sensitivity were found to be $2.2 \times 10^4$ l/mol·cm$^{-1}$ (+ 100) and 0.0005 µg cm$^{-2}$ respectively.

Reproducibility of the method - The standard deviation and relative standard deviation were found to be ± 0.009 and ± 2.25% respectively for a solution containing 2 µg of boron in 10 ml analysed over a period of ten days (Table - I).
FIG. 2. EFFECT OF AMOUNT OF ARSENAZO-I ON COLOUR REACTION.
CONCENTRATION OF BORON = 1 µg / 10 ml.

FIG. 3. EFFECT OF CONCENTRATION OF SULPHURIC ACID ON THE FORMATION OF THE BORON COMPLEX.
CONCENTRATION OF BORON = 1 µg / 10 ml.
FIG. 4. CALIBRATION CURVE FOR THE DETERMINATION OF BORON
Effect of foreign species - Effect of various copollutants on the colour reaction was assessed by analysing a solution containing 1 μg/ml of boron with known amounts of copollutants. The results (Table - II) show that the method is free from most of the interfering copollutants like phosphate, iron and fluoride (35,36). Concentrated hydrochloric acid prevents the interference from nitrite and fluoride (44).

APPLICATION OF THE METHOD

River water - Since river water samples obtained were free from boron, spiked samples were analysed to check the recovery of the present method as well as reported method (27). The recovery was found to be ~99%.

Rock sample - Since the original samples were free of boron, the samples were fortified with known amounts of boron and were taken in a polyethylene beaker and digested with sulphuric acid and hydrofluoric acid as reported (43). The aliquots of the digested samples were then analysed by the proposed method and recovery was found to be ~99% (Table - III A).

Soil - The soil samples were finely powdered and digested as reported (43). The aliquots of the digested sample were then analysed by the proposed as well as the reported method (27). The results (Table - III B) show that the soil samples contained trace amount of boron.
**Table I**

**REPRODUCIBILITY OF THE METHOD**

Concentration of boron = 2 μg/10 ml (0.2 ppm)

<table>
<thead>
<tr>
<th>No. of days</th>
<th>Absorbance, 590 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.410</td>
</tr>
<tr>
<td>2</td>
<td>0.400</td>
</tr>
<tr>
<td>3</td>
<td>0.410</td>
</tr>
<tr>
<td>4</td>
<td>0.415</td>
</tr>
<tr>
<td>5</td>
<td>0.410</td>
</tr>
<tr>
<td>6</td>
<td>0.390</td>
</tr>
<tr>
<td>7</td>
<td>0.400</td>
</tr>
<tr>
<td>8</td>
<td>0.395</td>
</tr>
<tr>
<td>9</td>
<td>0.415</td>
</tr>
<tr>
<td>10</td>
<td>0.410</td>
</tr>
</tbody>
</table>

Mean = 0.400

Standard deviation = ± 0.009

Relative standard deviation = ± 2.25%

**Table II**

**EFFECT OF FOREIGN SPECIES**

Concentration of boron = 1 μg/ml (0.1 ppm)

- NO₃⁻ (5), Cr⁶⁺ (10), Fe³⁺ (20), Mg²⁺ (50), Cu²⁺, Br⁻ (50)
- PO₄³⁻, F⁻, Al³⁺, Ba²⁺, Ca²⁺, Cd²⁺, Sb³⁺, Sr²⁺, Mn²⁺, Se⁴⁺ (100), Ni²⁺, Sn²⁺ (200), As³⁺ (400), K⁺, Na⁺ (500)

* Amount may vary by ± 2%.
### TABLE - III A

**APPLICATION OF THE METHOD IN ROCK SAMPLES**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of boron added (μg)</th>
<th>Amount of boron found (μg)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock</td>
<td>4.50</td>
<td>4.45</td>
<td>98.8</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>1.48</td>
<td>98.6</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>1.97</td>
<td>98.5</td>
</tr>
</tbody>
</table>

* Mean of three replicate analyses.

### TABLE - III B

**APPLICATION OF THE METHOD IN SOIL SAMPLES**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of boron added (μg)</th>
<th>Amount found (μg)*</th>
<th>Proposed method</th>
<th>Reported method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-</td>
<td>33.12</td>
<td>33.10</td>
<td></td>
</tr>
<tr>
<td>Soil**</td>
<td>-</td>
<td>31.25</td>
<td>31.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>28.92</td>
<td>28.91</td>
<td></td>
</tr>
</tbody>
</table>

* Mean of three replicate analyses.

** Samples were collected from different points.
Comparison with other methods - The present method can be compared with other methods (Table - IV) and has been found to be more sensitive than the various reported spectrophotometric methods.

CONCLUSION

The method is sensitive, rapid and is free from the interference of most of the copollutants (35, 46). Boron can be analysed satisfactorily in polluted waters without prior treatments. The method is also applicable to rock and soil samples.
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Method</th>
<th>$\lambda_{\text{max}}$, nm</th>
<th>Range of determination (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cianthrimide-3</td>
<td>620</td>
<td>80 – 1000</td>
<td>47</td>
</tr>
<tr>
<td>2.</td>
<td>Chromotrope 2B-3</td>
<td>620</td>
<td>10 – 50</td>
<td>43</td>
</tr>
<tr>
<td>3.</td>
<td>6-aminonitroso-pyrimidine-2,4 diol-8</td>
<td>500</td>
<td>1 – 9</td>
<td>35</td>
</tr>
<tr>
<td>4.</td>
<td>2 methyl pentane 2,4 diol - B</td>
<td>460</td>
<td>1 – 10</td>
<td>42</td>
</tr>
<tr>
<td>5.</td>
<td>Alizarin blueS - B</td>
<td>601</td>
<td>1 – 10</td>
<td>41</td>
</tr>
<tr>
<td>6.</td>
<td>Carminic acid - B</td>
<td>585</td>
<td>0.1 – 0.8</td>
<td>27</td>
</tr>
<tr>
<td>7.</td>
<td>Curcumin - B</td>
<td>550</td>
<td>0.1 – 0.5</td>
<td>25</td>
</tr>
<tr>
<td>8.</td>
<td>Crystal violet - B</td>
<td>590</td>
<td>0.05 – 0.5</td>
<td>19</td>
</tr>
<tr>
<td>9.</td>
<td>Methylene blue - B</td>
<td>659</td>
<td>0.87 – 7</td>
<td>33</td>
</tr>
<tr>
<td>10.</td>
<td>Ethyl violet - B</td>
<td>610</td>
<td>0.06 – 0.43</td>
<td>34</td>
</tr>
<tr>
<td>11.</td>
<td>Arsenazo-I - B</td>
<td>590</td>
<td>0.05 – 0.4</td>
<td>Present method</td>
</tr>
</tbody>
</table>
REFERENCES


3. R. Thompson, Chem. in Britain, 7 (1971) 140.


41. N. Trinder, Analyst, 73 (1948) 494.


