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# Optimized solid phase extraction methodology for separation, and spectrophotometric determination of boron using amberlite XAD-16 resin modified with 2-(2-benzothiazolylazo)-4-methoxyphenol

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A highly selective and sensitive spectrophotometric method has been developed to determine trace amount of boron in various biological and water samples. The method is based on adsorption B(III) after complexation with 2-(2-benzothiazolylazo)-4-methoxy-phenol (BTAMP) at HOAc–NH$_4$OAc buffer of pH 5.5, on amberlite XAD-16 resin in the presence of Triton X-114. The retained analyte on the resin recovered with 4.0 ml of 2.0 M sulfuric acid and boron is determined spectrophotometrically at $\lambda_{max}$ 622 nm. Beer's law is obeyed in the concentration range of 0.05–125 ng mL$^{-1}$ of B(III) in the measured solution. For more accurate results, Ringbom optimum concentration range was found to be 0.2–110 ng mL$^{-1}$. The linear regression equation obtained was A = 0.413 C ($\mu$g mL$^{-1}$) + 0.003 (r = 0.9994). The molar absorptivity was calculated to be 4.46 × 10$^5$ L mol$^{-1}$ cm$^{-1}$ at 622 nm, whereas Sandell sensitivity was found as 2.42 ng cm$^{-2}$. Various parameters such as the effect of pH, reagent concentration, surfactant, and flow rate were studied. Interference of number of metal ions on the determination of boron has been studied in detail. The proposed method was successfully applied to determine boron concentration in biological materials, water and ceramic samples. In addition, excellent agreement was observed between the proposed and the reference methods.

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## Introduction

The essentiality of boron to animals and human beings has not been identified, but it is essential for plants. Boron deficiency affects plant growth and yield, but substantial amounts of boron are toxic to plants and reduce plant yield. Boron has been classified to be hazardous by the Agency for Toxic Substances and Disease Registry (ATSDR), and minimal risk level for boron was given as 0.01 mg/kg/day for oral exposure.[1] Therefore, it is suggested that excess boron is toxic for all living organisms,[1–3] and, therefore, its determination is important in water, soil, food and some industrial fields, such as metallurgy, electronics, glass manufacture and the nuclear industry.

Boron is an element that is difficult to determine. Sah and Brown have reviewed analytical methods for the determination of boron.[3] Various spectrometric methods, including atomic absorption spectrometry,[3,4] atomic emission spectrometry,[3,5] inductively coupled plasma-atomic emission spectrometry,[3,6,7] inductively coupled plasma-mass spectrometry,[8–12] and X-Ray fluorescence spectrometry[13] have been reported to determine boron in various samples. Advantages and disadvantages of these methods have been well-discussed by Sah and Brown.[3] Inductively coupled plasma atomic emission spectrometry (ICP–AES) created a new dimension in boron determination because of its simplicity, sensitivity and multi-element capability. However, ICP-AES suffers from interferences and is not adequately sensitive for some nutritional and medical applications involving animal tissues that are low in boron. Inductively coupled plasma mass spectrometry (ICP–MS) not only overcomes most of the drawbacks of earlier methods, but is also capable of

measuring boron isotopes. However, it is time consuming and expensive, and is difficult to use in the routine determination of boron.

In general, the most common methods for the determination of boron concentration are spectrophotometric methods based on various organic colour reagents. However, reagents for the spectrophotometric determination of boron are not ideal[14–25] (see Table 1). Most of the reagents require a concentrated $H_2SO_4$ medium, so that their application to routine boron determination is not satisfactory. The ideal colour reagent would be one that reacts with boron sensitively and selectively in dilute acidic medium.

Amberlite XAD adsorption resins have good physical properties such as porosity, uniform pore size distribution, and high surface area as chemically homogeneous non-ionic structures for large amounts of uncharged compounds, and they have been used as solid sorbents for the enrichment/ separation of metal.[26–29] In this work a solid phase extraction followed by spectrophotometric determination of boron is described. The method is simple, sensitive, and selective and it allows the determination of B(III) as low as 0.1 ng mL$^{-1}$ in water samples.

## Experimental

### Apparatus

A Perkin-Elmer Lambda 12 UV–vis spectrophotometer (Waltham, MA, USA) with a 10 mm quartz cell was used for all spectral measurements. A funnel tipped glass tube (60 mm × 6 mm) was used as a column for preconcentration. The laboratory glassware (Superior, Germany) and column was kept overnight in a 5.0 % nitric acid solution. A Perkin Elmer model 5300 DV; ICP-AES (Waltham, MA, USA) was used for all ICP-AES measurements. An Orion research model 601 A/digital ionalyzer pH meter (Tokyo, Japan) was used for checking the pH of solutions.

## Reagents

All reagents used were of analytical grade and all solutions were prepared with distilled water. All solutions were prepared in polypropylene volumetric flasks. Stock boron solution (1000 µg mL$^{-1}$) was prepared by dissolving 0.5636 g boric acid (Merck, Darmstadt, Germany) in water and diluting to 100 mL in a volumetric flask. A 2.0 M sulfuric acid solution was prepared by dissolving an appropriate amount of concentrated acid (Merck, Darmstadt, Germany) in distilled water. 2-(2-benzothiazolylazo)-4-methoxy-phenol (BTAMP) was synthesized according to the method described previously.[30] Stock solution of 5 × 10$^{-3}$ M was prepared by dissolving an appropriate weight of the pure reagent in least amount of ethanol (15 mL) and then diluted to the mark in a 100-mL measuring flask with ethanol (Merck, Darmstadt, Germany).

Solutions of alkali metal salts (1.0 %) and various metal salts (0.1 %) (Sigma, St Louis, MO, USA) were used to study the interference of anions and cations, respectively. Acetate buffer solutions (HOAc–NH$_4$OAc buffer) of pH 2.75 – 6.11 were prepared as recommended.[31]

## Preparation of the amberlite XAD-16 column loaded with BTAMP

Amberlite XAD-16 (Merck, Darmstadt, Germany) was treated with an ethanol–sulfuric acid–water (2:1:1) solution overnight. Later, the resin was rinsed with deionized water until supernant water (5.0 mL pH 5.5 solution). The packing of the column must be done using ethanol as eluent since water makes resin beads float. The resin was saturated with the reagent by passing 2.5 mL of 5 × 10$^{-3}$ M BTAMP solution in ethanol and 2.0 mL of 5.0 % Triton X-114 solution (Sigma, St Louis, MO, USA) at a flow rate of 0.5 mL min$^{-1}$. Later it was washed with water until reagent excess was eliminated from the resin. All experiments were done in a funnel-tipped glass tube (60 mm × 6 mm) and were used as a column for preconcentration. It was plugged with glass wool and then filled with the

XAD-16 to the height of 1.0–1.5 cm. Before sample loading the column must be preconditioned by passing a sulfuric acid solution.

**Procedure for the sorption of boron on the column**

An aliquot of boron solution (containing 0.25–625 ng) was placed in a 50 mL beaker contained 5.0 mL of acetate buffer solution of pH 5.5 acid, and then diluted to 25 mL with bidistilled water. This solution was passed through the column at a flow rate of 2.0 mL min$^{-1}$. After passing this solution, the column was eluted with 5.0 mL of deionized water. The adsorbed boron complex on the column was eluted with 4.0 mL of 2.0 M sulfuric acid solution at a flow rate of 1.0 mL min$^{-1}$. The eluted was collected in a 5.0 mL measuring flask and completed to the mark with 2.0 M sulfuric acid and boron was determined spectrophotometrically at $\lambda_{max}$ 622 nm against a reagent blank similarly treated.

**Reference method (ICP-AES method)**

The measurements were carried out with an ICP-AES Perkin Elmer model 5300 DV. The operation conditions for ICP-AES were as follows: emission line: B(I) 249.773 nm (other lines, 208.893, 208.959, 249.678 nm were also used to confirm the results in analyses), plasma power supply: 1.0 kW, observation height: 6.0 mm, plasma gas flow: 10 L min$^{-1}$, auxiliary gas flow: 0.5 L min$^{-1}$, nebuliser gas flow: 0.6 L min$^{-1}$, photomultiplier voltage: 600 V, sample uptake rate: 1.7 mL min$^{-1}$, integration time: 1.0 s and replicates: 3.

# Results and discussion

**Absorption spectra**

The absorption bands of BTAMP and its complex in acidic media are located at 498 nm and at 622 nm, respectively.

## Reaction conditions

The reaction conditions were investigated with 100 ng mL$^{-1}$ of boron. Adsorption was carried out at different buffer media, and other variables were kept constant. It was found that the boron complex was quantitatively adsorbed on amberlite XAD-16 resin in acetate buffer solution of pH 5.5. Addition of 4.0–6.0 mL of pH 5.5 not affect the retention of boron and the use of 5.0 mL is recommended.

The effects of surfactants on the B(III)–BTAMP system were investigated. The results showed that, in the absence of surfactants, anionic or cationic surfactants, the B(III)– BTAMP chromogenic system gives a low absorption, whereas in the presence of nonionic surfactants, the absorption of the chromogenic system increases markedly. Various nonionic surfactants enhance the absorbance in the following sequence: Triton X-114 > Triton X-100 >Tween-80 > Tween-60 > Tween-20 > emulsifier-OP. Accordingly, the Triton X-114 was the best additive, and the use of 1.5–2.5 mL of 5.0 % Triton X-114 solution gave a constant and maximum absorbance (Fig. 1). Consequently, the use of 2.0 mL was recommended.

For up to 100 ng of B(III), the use of 2.5 mL of 5 x 10$^{-3}$ M of BTAMP solution was found to be sufficient for a complete reaction. Accordingly, 2.5 mL of 5 x 10$^{-3}$ M BTAMP solution was added in all further measurements.

The flow rate was varied from 0.1 to 5 mL min$^{-1}$. It was found that a flow rate of 0.1–3.0 mL min$^{-1}$ did not affect adsorption. A flow rate of 2.0 mL min$^{-1}$ was recommended in all experiments.

The volume of the aqueous phase was varied in the range of 2.0–100 mL under the optimum conditions, keeping the other variables constant. It was observed that the highest absorbance value was almost constant up to 25 mL. However, for convenience, all the experiments were carried out with 25 mL of the aqueous phase.

Preliminary observations indicated that boron complex was desorbed completely with 4.0 mL of 2.0 M sulfuric acid. Therefore, 4.0 mL of 2.0 M sulfuric acid was used in the present work.

**Sorption capacity of resin for ligand and boron**

The sorption capacity of the amberlite XAD-16 resin for ligand and bismuth was also evaluated using Langmuir model.[32] The resin has a sorption capacity of 1.2 and 0.5 mg g$^{-1}$ of XAD-16 resin for ligand and boron, respectively.

**Stoichiometric ratio**

The nature of the complex was established at the optimum conditions described above using the molar ratio and continuous variation methods. The plot of absorbance versus the molar ratio of BTAMP to B(III), obtained by varying the BTAMP concentration, showed inflection at molar ratio 2.0, indicating presence of two BTAMP molecules in the formed complex. Moreover, the Job method showed a ratio of BTAMP to B(III) = 2.0. Consequently, the results indicated that the stoichiometric ratio was (2:1) [BTAMP : B(III)]. The conditional formation constant (log K), calculated using Harvey and Manning equation applying the data obtained from the above two methods, was found to be 5.78, whereas the true constant was 5.55.

**Effect of foreign ions**

Various salts and metal ions were added individually to a solution containing 100 µg of boron and the general procedure was applied. The tolerance limit was set as the concentration of the diverse ion required to cause ± 5.0 % error in the determination of boron. The tolerance limit (error < 5.0 %) is given in Table 2. Among the salts examined, most did not interfere at the gram or milligram level except EDTA which may be due to the high formation constant of the B-EDTA complex over the boron-BTAMP complex. Thus, the method is highly selective

and therefore, has been applied successfully to the trace determination of boron in various biological and water samples without any prior separations.

## Calibration curve and sensitivity

The calibration curve showed that the system obeys Beer's law in the concentration range of 0.5–125 ng B(III) per mL in the measured solution. For more Accurate results, Ringbom optimum concentration ranges was found to be 0.2–110 ng B(III) per mL in the measured solution. The linear regression equation obtained was $A = 0.413$ C ($\mu g$ $mL^{-1}$) $+ 0.003$ (r = 0.9994). The molar absorptivity was calculated to be $4.46 \times 10^5$ $L$ $mol^{-1}$ $cm^{-1}$ at 622 nm, whereas Sandell sensitivity was found as 2.42 ng $cm^{-2}$. The standard deviations of the absorbance measurements were calculated from a series of 13 blank solutions. The limits of detection (K = 3) and of quantification (K = 10) of the method were established[33] and recorded in Table 3, according to the IUPAC definitions (C1 = $KS_o$/s where C1 is the limit of detection, $S_o$ is the standard error of blank, s is the slope of the standard curve and K is the constant related to the confidence interval. The relative standard deviation was 1.73 % obtained from a series of 10 standards each containing 100 ng $mL^{-1}$ of B(III).

The sensitivity expressed as molar absorptivity of the proposed method is compared with those of published spectrophotometric methods. The higher sensitivity of the proposed method is notable, greater even than that of other methods,[14–25] that based on spectrophotometry. Although the measurable concentration range is from approximately 5.0-150 ng $L^{-1}$ with ICP-AES, the proposed method was very simple and accurate.

## Analysis of boron in biological materials and water samples

The accuracy and applicability of the proposed method has been applied to the determination of boron in National Institute for Environmental Studies (NIES) No. 5 human hair; and NIES No. 7 tea leaves. A 0.1 g sample was taken in a

beaker and dissolved in concentrated nitric acid (~5.0 mL) with heating. The solution was cooled, diluted and filtered. Since no standard biological sample containing boron was available, experiment was conducted by adding a known amount of boron to the standard biological sample. The filtrate was made to 50 ml with water in a calibrated flask. An aliquot (5.0–25 mL) of the sample solution was taken individually and boron was determined by the general procedure. The results are given in Table 4.

In order to confirm the applicability of the proposed method, it has been applied to the determination of microgram amounts of boron in real water samples. For water samples, the samples were acidified with sulfuric acid and filtrated through a 0.45 μm filter. The boron contents were analyzed according to the general procedure. An ICP-AES method was used as a reference method and the results are also shown in Table 5.

The performance of the proposed method was assessed by calculation of the t-value (for accuracy) and F-test (for precision) compared with ICP-AES method.[7] The mean values were obtained in a Student's t- and F-tests at 95% confidence limits for five degrees of freedom.[34] The results showed that the calculated values (Table 5) did not exceed the theoretical values. A wider range of determination, higher accuracy, more stability and less time consuming, shows the advantage of the proposed method over other method.

**Application to determination of boron in ceramic materials**

Ceramic raw materials were dried at 40 °C for 12 h and finely ground to pass completely through a 200 mesh. A total of 0.1 g of sample was weighed and transferred into a 250 mL vessel, and 20 mL of 10% HCl were added. The mixture was boiled for 1.0 min, then left in a thermostatically controlled bath for 1.0 h at 70–80 °C. Subsequently, the sample solution was filtered through a Whatman No. 40 filter-paper and neutralized with 1.0 M NaOH to a pH of about 7.0 (using a pH-meter). Finally, the solution was diluted to 100 mL with de-

ionized water. Ceramic frits and pigments were dried at 110 °C and finely ground to pass completely through a 200 mesh. A total of 0.1 g of sample was mixed in a platinum crucible with a 7-fold amount of $Na_2CO_3$–ZnO (2 + 1). The mixture was heated and placed in a muffle furnace at 900 °C for 10 min. The sintered samples were transferred into a porcelain capsule and 50 ml of hot de-ionized water were added. The mixture was filtered through a Whatman No. 40 filter-paper and centrifuged if necessary. The resulting solution was neutralised with 1.0 M NaOH to a pH of about 7.0 (using a pH-meter), then diluted to 100 mL with de-ionized water. The sample solution, containing not more than 30 mg of boron was transferred into a 25 mL calibrated flask and the boron concentration was determined as described in the general procedure. The results are shown in Table 6.

## Conclusions

The proposed method has several advantages. Firstly, BTAMP is one of the most easily prepared high purity, sensitive, and selective spectrophotometric reagent for boron determination. Molar absorptivity was found to be up to $4.46 \times 10^5$ L $mol^{-1}$ $cm^{-1}$ at 622 nm in the measured solution. The higher sensitivity of the proposed method is notable, greater even than other methods, based on spectrophotometry. Secondly, the detection and quantification limits, are 15 and 49.5 ng $mL^{-1}$ in the original sample. Thirdly, most common ions do not interfere with the determination suggesting the highly selectivity of the proposed method. Fourthly, successful application of the proposed method to the determination of low levels of boron in biological and water samples was carried out with good results. Finally, the proposed method is simple and more sensitive at the nanogram level than other methods commonly used, in addition to lower tolerance limits.

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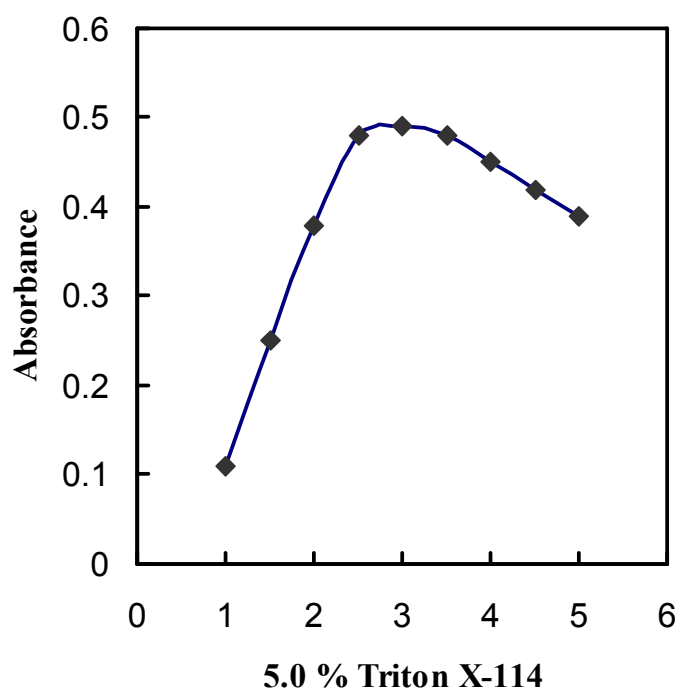
**Fig. 1** Effect of Triton X-114 on the complexation of 100 ng mL$^{-1}$ B(III) with 5.0 x 10$^{-4}$ M BTAMP at the optimum experimental conditions

**Table 1** Spectrophotometric methods for the determination of boron

| Reagent | Reaction conditions | Remarks | Ref. |
|---|---|---|---|
| Ethyl Violet | pH = 3.1–4.9 | 1: Benzene extraction<br>2: Ag, Au, Re, Sb and Ti interfere | 14 |
| Crystal Violet | pH = 1–2 ($H_2SO_4$) | 1: Fe, Hg, W, V and Bi interfere seriously | 14 |
| Carminic Acid | 93% $H_2SO_4$ | 1: Concentrated medium<br>2: Fe, Al, Cu, *etc.*, metal ions interfere | 16 |
| 1-Hydroxyl-4-*p*-methylanilino anthraquinone | Concentrated $H_2SO_4$ | 1: Concentrated medium<br>2: $F^-$, Fe, $SO_3^{2-}$, Mn, Cr and V interfere | 14 |
| Quinalizarin | Concentrated $H_2SO_4$ | 1: Concentrated medium<br>2: Ge, $SO_4^{2-}$, Se and Sb interfere | 17 |
| Arsenazo I | Concentrated $H_2SO_4$ | 1: Concentrated medium<br>2: Light-sensitive<br>3: Mg, Fe and Ca interfere seriously | 14 |
| Arsenazo III | pH = 10 | 1: Light-sensitive<br>2: Metal ions interfere seriously | 14 |
| Curcumin | Concentrated $H_2SO_4$ | 1: Concentrated medium<br>2: Dichloroethylene extraction | 18 |
| D-Sorbitol | | 1: $F^-$, Mo, Ge and $H_3PO_4$ interfere<br>2: Light-sensitive | 19 |
| Azomethine-H | pH = 6.4–7.0(HOAc–$NH_4OAc$) | 1: Narrow range of pH<br>2: Reagent concentration influences sensitivity seriously<br>3: Fe, Al, Cu, Ti and Zr interfere | 20 |
| Azomethine-HR | pH = 7.0 (HOAc–$NH_4OAc$) | 1: Narrow range of pH<br>2: Reagent concentration influences sensitivity seriously<br>3: Fe, Al, Cu, Ti and Zr interfere | 21 |

**Table 2** Tolerance limits of foreign ions

| Foreign ion | Tolerance limit/mg | Foreign ion | Tolerance limit/mg |
|---|---|---|---|
| $CH_3COO^-$ | 750 | Tartrate | 300 |
| Citrate | 225 | Oxalate | 175 |
| K(I) | 500 | Benzoate | 125 |
| Na(I) | 500 | Mo(VI) | 150 |
| Ca(II) | 100 | Cr(III) | 100 |
| Mg(II) | 75 | Al(III) | 75 |
| Zn(II) | 60 | W(VI) | 50 |
| Fe(III) | 50 | V(V) | 30 |
| Ni(II) | 35 | $Cl_2$ | 20 |
| Co(II) | 15 | Ti(IV) | 10 |
| Pb(II) | 25 | $I_2$ | 7.5 |
| Cu(II) | 15 | $NO_3^{2-}$ | 40 |
| Mn(II) | 10 | $SO_4^{2-}$ | 100 |
| Cd(II) | 7.5 | $SiO_3^{2-}$ | 15 |
| Bi(III) | 5.0 | $PO_4^{2-}$ | 30 |

**Table 3** Analytical parameters.

| Parameter | Value | Parameter | Value |
|---|---|---|---|
| Beer's law limit (ng mL$^{-1}$) | 0.5–125 | Regression equation[a] | |
| Ringbom optimum range (ng mL$^{-1}$) | 0.10–110 | Slope (b) | 0.413 |
| Molar absorptivity (L mol$^{-1}$ cm$^{-1}$) | 4.46×10$^5$ | Intercept (a) | 0.03 |
| Sandell sensitivity (ng cm$^{-2}$) | 2.42 | Correlation coefficient (r) | 0.9994 |
| Detection limit (ng mL$^{-1}$) | 0.15 | RSD (%) | 1.73 |
| Quantification limit (ng mL$^{-1}$) | 0.49 | Stoichiometric ratio (L:M) | 2:1 |

[a] $A = a + bC$, where C is the concentration of iron in ng mL$^{-1}$.

**Table 4** Determination of B(III) in biological samples

| sample,[a] | Certified composition of the boron added (μg) to reference samples | Found [b] after addition of boron |
|---|---|---|
| NIE, No. 5 human hair | Pb, 6.0; Cd, 0.20; K, 34; Rb, 0.19; Sb, 0.07; Zn, 169; Al, 240; Fe, 225; Mg, 208; Hg, 4.4; Sc, 0.05; Se, 1.4; Na, 26; Sr, 2.3; Ti, 2.3; Ca, 728; Cr, 104; Ba, 2.2; Co, 0.1; Mn, 5.2; Cu, 16.3; Ni, 1.8 μg g$^{-1}$; B[c] added 1.0 μg | 0.997 ± 0.02 |
| NIES, No. 7 tea leaves | Pb, 0.80; Cd, 0.030; Sb, 0.014; Zn, 33; Cr, 0.15; Al, 775; Mg, 1530; Ba, 5.7; K, 18600; Sc, 0.011; Na, 15.5; Sr, 3.7; Ca, 3200; Cs, 0.22; Co, 0.12; Mn, 7.0; Ni, 6.5; Cu, 7.0 μg g$^{-1}$; B[c] added 0.75 μg | 0.745 ± 0.07 |

[a] NIES: National Institute of Environmental studies reference materials.

[b] Average of five determinations ± standard deviation.

[c] No boron was present in these standard samples. Therefore, boron was added from the standard solution in each case.

**Table 5** Determination of boron in water samples by the proposed method

| Sample | Boron (ng mL$^{-1}$) | | T- test [b] | F- value[b] | ICP-AES |
| --- | --- | --- | --- | --- | --- |
| | Added | Found[a] | | | (ng mL$^{-1}$) |
| Potable | -- | 41.1 ± 2.1 | | - - | 40.0 ± 1.2 |
| water | 50 | 145.9 ± 1.9 | 1.38 | | |
| | 100 | 142.4 ± 2.1 | | 2.76 | |
| Well | | 280.3 ± 2.1 | | | 267 ± 2.5 |
| water - | 150 | 431.2 ± 1.4 | | 3.23 | |
| | 300 | 583.8 ± 0.8 | 1.56 | | |
| River Nile | -- | 133.5 ± 1.4 | | | 136.2 ± 2.2 |
| water | 175 | 304.3 ± 1.1 | 1.63 | | |
| | 350 | 482.6 ± 1.5 | | 2.87 | |
| Rain water | -- | 28.7 ±1.3 | | | 30.1 ± 2.1 |
| | 75 | 104.4 ± 1.1 | | 3.11 | |
| | 150 | 177.6 ± 0.8 | 1.52 | | |
| Mineral | - | 33.0 ± 1.4 | | | 34.5 ± 1.7 |
| water | 50 | 84.1 ± 1.3 | 1.47 | | |
| | 100 | 134.8 ± 2.6 | | 2.93 | |
| Tap water | -- | 88.5 ± 1.6 | | | 90.4 ± 2.1 |
| | 200 | 287.4 ± 1.0 | 1.72 | | |
| | 400 | 488.2 ± 1.3 | | 3.48 | |
| Sea water | -- | 247.8 ± 0.7 | | | 242.8 ± 1.8 |
| | 125 | 273.7 ± 0.9 | | 2.74 | |
| | 250 | 499.4 ± 1.0 | 1.34 | | |

[a] Average of four determinations ± standard deviation

[b] Theoretical values for t and F at 95% confidence limit (n = 5) were

   2.57 and 5.05, respectively

**Table 6** Results of determination in samples expressed as % $B_2O_3$

| Sample | Proposed method [a] | ICP-AES (ng mL$^{-1}$)[a] |
|---|---|---|
| 1 | $1.17 \pm 0.01$ | $1.14 \pm 0.02$ |
| 2 | $1.35 \pm 0.07$ | $1.39 \pm 0.05$ |
| 3 | $1.52 \pm 0.10$ | $1.58 \pm 0.11$ |
| 4 | $2.75 \pm 0.02$ | $2.72 \pm 0.04$ |
| 5 | $2.94 \pm 0.05$ | $2.99 \pm 0.07$ |
| 6 | $3.71 \pm 0.02$ | $3.76 \pm 0.03$ |
| 7 | $4.41 \pm 0.02$ | $4.43 \pm 0.08$ |
| 8 | $5.34 \pm 0.12$ | $5.29 \pm 0.17$ |

*a* Results expressed as $X \pm st/n^{1/2}$, where $X$ is the mean of $n$ observations of $x$, $s$ is the standard deviation and $t$ is the distribution value chosen for the desired confidence level.

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