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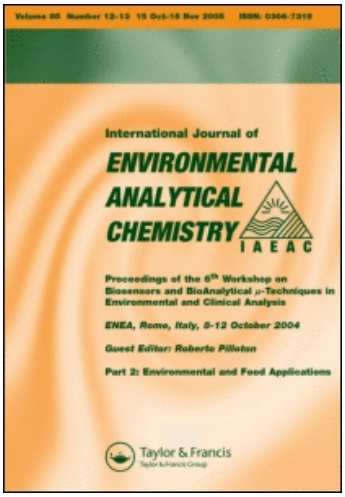

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A simple method of boron determination in mineral waters using Victoria blue 4R

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The reaction of the tetrafluoroborate anion with Victoria blue 4R (VB4R) reagent was investigated, and a new, simple, rapid and sensitive method was developed for the spectrophotometric determination of boron. The method is based on the reaction of boric acid with fluoride, which forms the tetrafluoroborate anion, and that is followed by the extraction of BF_4^- with VB4R into benzene and subsequent spectrophotometric detection. The optimum conditions for the conversion of boron to tetrafluoroborate anion as well as for complex formation and extraction of BF_4^- with VB4R were found. The molar absorptivity of the investigated complex is $9.6 \times 10^4\,L\,mol^{-1}\,cm^{-1}$ at 610 nm. The absorbance of the coloured extracts obeys Beer's law in the range 0.03–$0.55\,mg\,L^{-1}$ of B(III). The limit of detection calculated from a blank test ($n = 10$; $P = 0.95$) based on 3 s is $0.02\,mg\,L^{-1}$ of B(III). Under appropriate extraction conditions, the majority of metals (excluding probably tantalum and some others) did not form extractable fluoride complexes with VB4R. Therefore, the presence of small quantities of metals should not interfere with the determination of boron in the presence of a sufficient surplus of fluoride. Exceptions, however, are metal ions such as Sn(IV), Ti(IV), Sn(II), Zr(IV), Hg(II), Hg(I), Tl(I), etc., which strongly hydrolysed under experimental conditions. Some anions formed complexes with the cation of VB4R and are easily extractable using benzene. Examples of such ions are NO_3^-, I^-, SCN^-, Br^-, bromate, chlorate, iodate and perrhenate. These anions strongly interfere with boron determination and therefore must first be extracted with VB4R before boron determination. The boron must then be converted to BF_4^- and extracted with VB4R into benzene for determination. The Cl^-, SO_4^{2-}, HPO_4^{2-}, CH_3COO^- and $HC_4H_4O_6^-$ anions are extracted in very small amounts or not at all, and do not interfere with boron determination. The reaction mechanism was also discussed. Quantum chemical calculations were carried out for VB4R, and the optimised molecular structure and atomic net charges were calculated. The possible position of the protonation of VB4R as well as the possible position for dipole-ion interaction (associate building) between the reagent and

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the BF_4^- anion was predicted. The method was used for the determination of boron in commercial brand mineral waters.

Keywords: boron; determination; mineral waters; Victoria blue 4R; spectrophotometry

1. Introduction

Boron and its compounds are widely used in a variety of industries, such as for control rods in the nuclear energy industry, as a buffer component for the deposition of nickel in the electroplating industry, as a significant component of steel and glass, as fire retardants, laundry additives, fertilizers, herbicides and insecticides. Boron is widely distributed in nature and is naturally found in minerals, rocks, plants, coal and natural waters. Boron gets released into the environment through volcanic activity and geothermal steam. Elemental boron is not found in the environment; in nature, it is often present in combined forms. Boron compounds are present in small amounts in seawater ($5\,mg\,L^{-1}$) and in some mineral waters. The daily dose of boron for older people is approx. 3 mg, but excess boron may be toxic for humans [1,2]. According to Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, the limit of boron content in drinking water is $1.0\,mg\,L^{-1}$ [3]. The accurate determination of boron in different kinds of samples has been a difficult task until now.

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A variety of analytical methods have been previously used for boron determination, including spectrophotometry, spectrofluorimetry [4], voltammetry [5,6], ion-selective electrode [7,8], capillary electrophoresis [9], indirect AAS [10], solid sampling GF-AAS [11], ICP-AES [12] and ICP-MS [13]. Each of these techniques offers both advantages and disadvantages, though spectrophotometry is the most commonly used method. Various organic reagents have been suggested for boron determination, including carminic acid [14,15], quinalizarin [16], Alizarin Red S [17], 1,1′-dianthrimide [16,18], curcumin [19–24], azomethine-H [25–30], methylene blue [31,32] and Crystal Violet [33], but the number of such reagents is limited. Moreover, most of these methods require the separation of boric acid by distillation as methyl borate or the use of a concentrated sulfuric acid as reaction medium, and the procedures are often complicated [34], laborious and lengthy. In recent years, some new derivatives of azomethine-H have been synthesised. A comparison of the derivatives of azomethine-H as a reagent for the spectrophotometric determination of boron was given in [35]. As can be seen from this, despite having the main advantage of not requiring concentrated acidic medium, the method has a number of disadvantages, such as the fact that colour systems are also sensitive to the pH of the medium, the reaction temperature or the reagent concentration [35].

One interesting method, based on the spectrophotometric measurement of the decrease in pH produced by the reaction between boric acid and mannitol [36] or D-sorbitol [37,38] in the presence of an acid–base indicator, has been described. Another method, based on the discolouring of a Gly-NQS (1,2-naphthoquinone-4-sulfonate) system in the presence of boron in pharmaceutical and biological samples, has also been reported [39]. Boron can be extracted by benzene or chlorobenzene [40] as ion pairs of its mandelates using malachite green. Boric acid is extractable with 1,3-diols into chloroform [41,42]. Methods of boron determination have been previously discussed in a series of books and reviews [43–45].

Victoria blue 4R (VB4R) is a well-known analytical reagent and has previously been described for the spectrophotometric determination of U [46], Mo [47] and Zn [46] based on the colour reaction of analytes with thiocyanate and VB4R. In addition, methods for determination of Cd [48], Te [49] and Tl [50] have been described based on the reaction of the halide complexes of these analytes with VB4R followed by the extraction of the complexes formed and their spectrophotometric detection. Kinetic methods for the determination of various analytes such as As(III), phenylhydrazine and iodide [51] based on the inhibitory effect of analytes on the oxidation of VB4R by $KBrO_3$ have also been reported.

VB4R, immobilised on a triacetylcellulose membrane, has been used as an optode-sensing reagent for the catalytic determination of trace amounts of oxalic acid in vegetables and water samples [52]. This method is based on the strong catalytic effect of oxalic acid on reagent oxidation by dichromate in acidic media, which results in the discolouration of the membrane. The catalytic spectrophotometric determination of trace amounts of nitrite based on the oxidising discolouration reaction between VB4R–sodium dodecylbenzene sulfonate ion association and potassium iodate has been presented [53]. Determination of heparin with basic bisphenylnaphthylmethane dyes using fading spectrophotometry has also been described [54]. This method is based on the discolouration reaction between heparin and VB4R in a weakly acidic medium.

The aim of this investigation was to study the complexation and extraction of boron with VB4R reagent as well as to develop a method for the spectrophotometric determination of boron in mineral water samples. The structure of VB4R is given in Figure 1(a).

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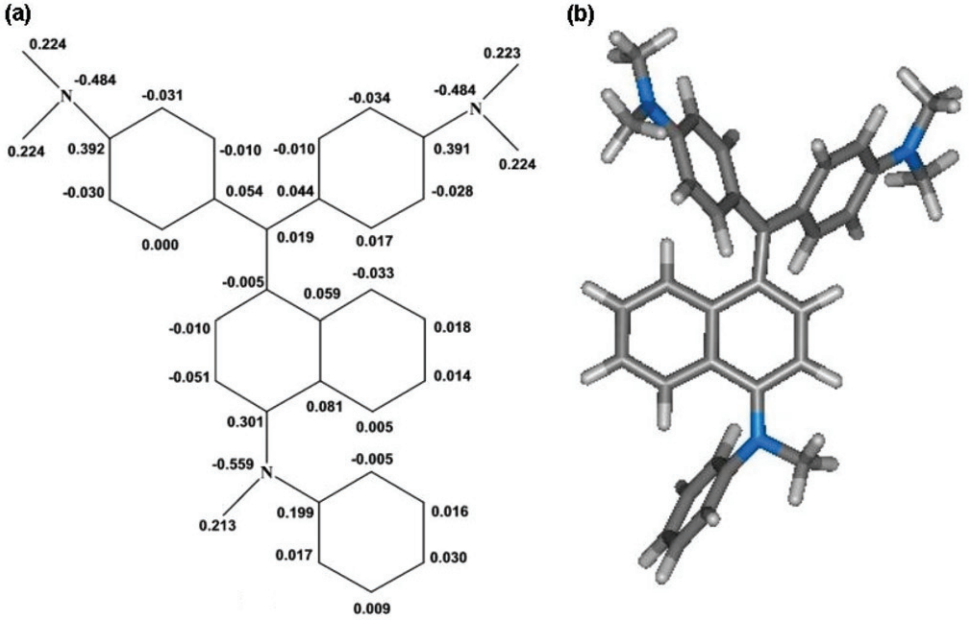

Figure 1. (a) The structure of VB4R and calculated Mulliken atomic net charges with hydrogens summed into heavy atoms. H atoms and double bonds are omitted for clarity; (b) Optimised molecular geometry of VB4R.

2. Experimental

2.1 *Reagents and apparatus*

All the chemicals and solvents used were of analytical grade quality. Double-distilled water was used throughout the experiment. The boron stock solutions (0.01 mol L^{-1}) were prepared by dissolving KBF_4 in 0.5 mol L^{-1} of H_2SO_4 or H_3BO_3 in water and were then stored in polyethylene bottles. For the basic study (the investigation of appropriate experimental conditions of the reaction of BF_4^- anion with VB4R reagent), KBF_4 was used in order to avoid any effect of the conversion of H_3BO_3 to tetrafluoroborate anion. H_3BO_3 was then used as the standard for constructing a calibration plot. Using H_3BO_3 in the Calibration Procedure section allowed for the creation of identical conditions as all of those in the analysis of real samples. A working solution containing 1×10^{-3} mol L^{-1} of boron was prepared daily prior to use from the stock solutions using the appropriate dilution with water. A 0.1% aqueous solution of dye was prepared by directly dissolving its chloride re-crystallised from methanol.

An SF-10 UV–Vis scanning spectrophotometer and a Carl Zeiss Spekol-11 spectrophotometer were used to record the absorption spectra and for routine measurements, respectively, with matched cells of 3 or 5 mm path length. The pH measurements were made using a pH-121 potentiometer with a glass electrode.

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2.2 *General procedure for investigating the complexation and extraction of BF_4^- with VB4R*

The extraction was carried out in polyethylene test tubes at room temperature (18–22°C). The volume of the phases was 3 mL. First, 0.1 mL of 10^{-3} mol L^{-1} KBF_4 was introduced into the test tubes. In this step, KBF_4 was used in order to avoid any effect of the conversion of H_3BO_3 to tetraflouroborate anion. Next, an appropriate volume of 0.1% VB4R was added, and the required acidity of the solution was reached by the addition of an H_2SO_4 solution (in the range of 4.5 mol L^{-1} H_2SO_4 to pH 2) and by the addition of a 20% solution of urotropine and water (in the range of pH 2–9). The volume was then diluted with water up to 3 mL. After the addition of each reagent, the solution was mixed thoroughly. The complex was then extracted for 1 min using 3 mL of benzene. After extraction, the organic phase was separated and centrifuged for 2 min at 3000 rpm, and the absorbance was measured against that of a blank test (or pure benzene) with cells of 3 or 5 mm path length.

2.3 *Calibration procedure*

To polyethylene test tubes containing various amounts of H_3BO_3 (ranging from 0.03 to 0.55 mg L^{-1}), 0.2 mL of 0.5 mol L^{-1} NaF, 0.3 mL of 5 mol L^{-1} H_2SO_4 and 0.3 mL of water were added. After the addition of each reagent, the solution was mixed thoroughly. The test tubes were stoppered and heated at 70°C in a water bath for 30 min. After the solution had cooled, urotropine was added to neutralise the excess H_2SO_4 in order to reach a pH value of 2–5. Next, 0.5 mL of 0.1% VB4R was added, and the volume was filled up to 3 mL with water. The complex was then extracted using 3 mL of benzene for 1 min. After the extraction, the organic phase was separated and centrifuged for 2 min at 3000 rpm, and the absorbance measured with cells of 3 mm path length against that of a blank test, which

had been prepared by following all the steps identical to those used for the sample but without the addition of boron.

2.4 *Procedure for real samples*

A 0.2–0.5 mL sample of mineral water was introduced into the polyethylene test tube and 0.3 mL of 5 mol L^{-1} H_2SO_4 was added. The solution was then heated at 40–50°C in order to eliminate any CO_2. Next, 0.2 mL of 0.5 mol L^{-1} NaF was added. The last phase of determination was the same as that described in the Calibration Procedure section. Five measurements were performed for each sample. Benzene may be replaced by toluene, which is characterised by lower toxicity in comparison with benzene. For daily measurements, the use of toluene as an extractant is strongly recommended.

3. Results and discussion

3.1 *Theoretical aspects and preliminary investigations*

The method is based on the reaction of boric acid with fluoride [55], which forms the tetrafluoroborate anion, and is followed by the extraction of BF_4^- with VB4R into benzene and subsequent spectrophotometric detection.

The tetrafluoroborate anion forms sufficiently and fully in acidic solutions, though at pH > 1 hydrolysis can occur according to the reaction:

$$BF_4^- + H_2O \rightleftharpoons BF_3OH^- + HF \quad (1)$$

Boric acid converted relatively slowly to HBF_4. For a complete conversion, the following conditions are required: sufficient acidity for the suppressing of hydrolysis as well as a sufficient surplus of fluoride anion. In addition, heating significantly accelerates the formation of HBF_4.

In order to optimise the experimental conditions for conversion, a series of experiments were carried out with a constant concentration of boric acid (1.67×10^{-5} mol L^{-1}) and varying concentrations of fluoride ions and sulfuric acid. The influence of temperature and time on conversion was also studied, and optimum conditions were found to be: pH < 0.7 (0.1 mol L^{-1} H_2SO_4); >0.02 mol L^{-1} NaF; heating time 30 min; temperature 70°C.

The acid–base properties and main spectrophotometric characteristics of VB4R were investigated [56]. The protonation constant, the hydrolysis constant, the optimum wavelength and the molar absorptivity were found to be, respectively, $pK_{pr.} = 2.3$, $pK_{h.} = 8.5$, $\lambda_{max.} = 590$ nm and $\varepsilon = 4.80 \times 10^4$ L mol^{-1} cm^{-1}. It has been shown that VB4R exists in the reactive single charged form over a relatively wide range of acidity and that the aqueous solution of the dye is intensely coloured.

Quantum chemical calculations were carried out at the computer centre of the Vienna University of Technology (Central Information Service). The Gaussian 03 program package [57] was used with the B3P86 functional and the 6-31G basis set for computing the optimised structure of the VB4R cation and its atomic net charges.

The connections of the atoms in the VB4R cation are given in Figure 1(a). Figure 1(b) shows the optimised molecular geometry. The cation is not planar. If the naphthalene plane is regarded as a reference, the three benzene rings turn away from this plane. The internal structure and two 4-dimethylamino-phenyl groups were found

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to be equivalent. Their phenyl rings form about 30° angles with the reference plane and turn in the same direction (Figure 1(b)), they are not mirror images of one another. The third phenyl group stands almost perpendicular to the reference plane (84°).

Mulliken's atomic net charges of hydrogen atoms were summed into those of the joined heavy atoms. The cation contains three nitrogen atoms, all of which have a negative net charge. The imide nitrogen connecting the benzene and naphthalene ring was found to be the most negative, with −0.559 a.ch.u (Figure 1(a)). The other two nitrogens of the dimethylamino groups are less negative, with −0.484 a.ch.u. net charges. As expected, the carbon atoms connected to the nitrogens have the highest positive atomic net charges: falling between +0.199 and +0.392 a.ch.u. Looking at Figure 1, all nitrogen atoms are enclosed by positively charged carbon atoms that shield the nitrogens. The hydrogen atoms have positive net charges, their charges are added to the connected heavy atoms. Consequently, the VB4R cation shows positive charge in all directions, i.e. an attracting positive potential.

The quantum chemical calculations yielded the equivalence of the two dimethylaminophenyl groups. This result describes a well-defined structure, with equivalent geometric parameters and atomic net charges.

The position of the BF_4^- anion in relation to the VB4R cation depends on the environment. If a cation and an anion were in a vacuum (not a real situation), the anion could be close to one of the three possible positive centres. If one of them were a 4-dimethylaminophenyl group, the equivalence of the two groups can be resolved. However, the solvent can surround both ions, and its influence can act on the structure of the ions. In terms of crystal structure the cation and the anion are well arranged, and a possible asymmetry may resolve the equivalence of the two 4-dimethylamino-phenyl groups.

The optimised molecular structure and atomic net charges of the BF_4^- anion were calculated in a manner similar to that for the VB4R cation. Its optimised structure is tetrahedral, the B–F distances are 1.406 Å, the net charges of the fluorine atoms are −0.397 a.ch.u., while the same of the boron atom is 0.587 a.ch.u. As was expected, the negative charges of the fluorine atoms shield the positive boron charge.

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3.2 *Investigation of complexation and extraction of BF_4^- with VB4R*

Various factors influencing boron determination, such as the acidity of the medium, the concentration of VB4R, the molar ratio of B(III) and VB4R and the main spectrophotometric characteristics of the extracted complexes, were studied.

3.2.1 *Acidity of the medium*

The acidity of the medium can strongly influence the equilibrium of complexation and extraction. An experiment was carried out as described in the General Procedure section. The required acidity of the solution was reached by the addition of an H_2SO_4 solution (in the range of 4.5 mol L^{-1} H_2SO_4 to pH 2) and by the addition of a 20% solution of urotropine and water (in the range of pH 2–9). As seen in Figure 2 (for H^+ concentrations higher than 1 mol L^{-1}, Hammet's function of acidity H_0 was used instead of pH [58]), the extraction of boron is highest in the range from pH 2 to pH 5. A decrease in absorbance at pH < 2 can be explained by protonation of the dye reagent and by the formation of the double-charged cation (HR^{2+}) of the reagent, which is unable to

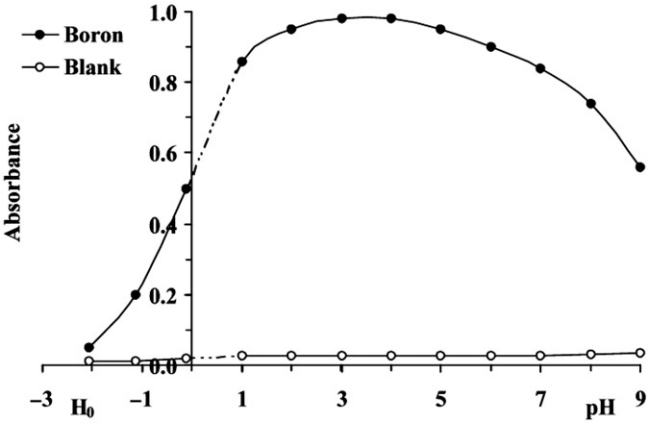

Figure 2. Effect of medium acidity on the extraction of BF_4^- complex with VB4R by benzene 0.1 mL 1×10^{-3} mol L^{-1} of B; 0.5 mL 0.1% of VB4R; $V_{(aq)} = V_{(org)} = 3$ mL; $l = 0.3$ cm; $\lambda = 610$ nm.

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extract the tetrafluoroborate anion. Therefore, after the formation of BF_4^-, the excess H_2SO_4 must be neutralised, and the medium acidity must be set at a level of pH 2–5 so that the reagent will remain in the single-charged R^+ form. The decrease in the absorbance at pH > 5 is probably caused by the formation of the non-extractable BF_3OH^- anion during the course of hydrolysis of KBF_4, according to reaction (1) above or hydrolysis of the VB4R and the formation of the inactive ROH form of the reagent. We did not conduct any experiments to confirm this. Our assumption is based on the theoretical calculations of boron distribution diagram [55] and pK values of VB4R [56].

3.2.2 *Concentration of dye reagent*

The optimum concentration of dye reagent is 0.3–0.5 mL of 0.1% of VB4R in 3 mL.

3.2.3 *Molar ratio of B(III) and VB4R*

The extraction equilibrium is established in 30–60 s, and the absorbance of the extracts does not change for several hours. The stability constant is $\beta = 3.3 \times 10^8$. The molar ratio of boron(III) and VB4R dye reagent in the extracted coloured complexes was determined under the appropriate experimental conditions for complexation and extraction by the isomolar series method and Asmus' method. It was found that the BF_4^- : VB4R molar ratio is 1 : 2.

3.2.4 *Absorption spectra*

The absorption spectra of the boron complex during extraction with benzene under optimum extraction conditions were recorded (Figure 3) and the main spectrophotometric characteristics calculated. The molar absorptivity of the investigated complex is 9.6×10^4 L mol^{-1} cm^{-1} at $\lambda_{max} = 610$ nm. This is approximately twice the molar absorptivity of VB4R, a fact that once more confirms the composition of BF_4^- : VB4R complex at a ratio of 1 : 2.

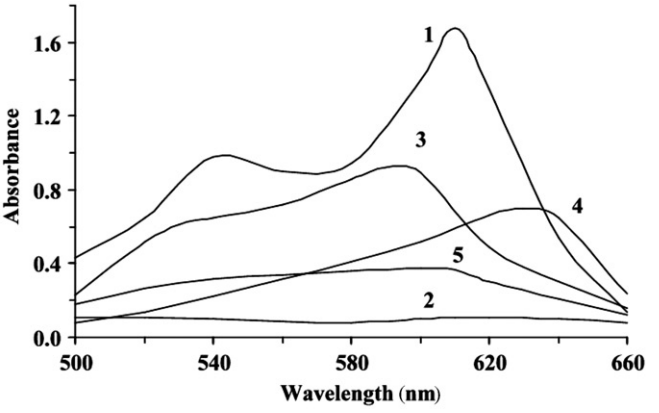

Figure 3. Absorption spectra of benzene extract of BF_4^- complex with VB4R (1) and blank test (2) as well as absorption spectra of the VB4R reagent at differing medium acidities (3–5) (1, 2): 0.1 mL 1×10^{-3} mol L^{-1} of B; 0.5 mL 0.1% of VB4R; $V_{(aq)} = V_{(org)} = 3$ mL; $l = 0.5$ cm (3–5): 4×10^{-5} mol L^{-1} VB4R; pH 7 (3); pH 0 (4); pH 13 (5); $l = 0.5$ cm.

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3.3 *Effect of extraneous ions*

The effect of diverse ions on the absorbance of coloured extract and, consequently, on the spectrophotometric determination of B was investigated. The tolerance limit was defined with a margin of error of less than ±5% in the analysis. Under appropriate extraction conditions (at pH 2–5), the majority of metals (excluding probably tantalum and some others) did not form extractable fluoride complexes with VB4R. Therefore, the presence of small quantities of metals should not interfere with the determination of boron in the presence of a sufficient surplus of fluoride. Exceptions, however, are metal ions such as Sn(IV), Ti(IV), Sn(II), Zr(IV), Hg(II), Hg(I), Tl(I), etc., which strongly hydrolysed under experimental conditions at pH 2–5. These ions thus do interfere with the determination of boron. If there is an insufficient surplus of fluoride, the following ions weaken the absorbance of the extracts: Fe(III), Al(III), Ag(I), Zn(II), Cd(II), etc. The disruption caused by these ions can be eliminated by increasing the concentration of fluoride (but the concentration of fluoride must remain lower than 0.1 mol L^{-1}).

Absorbance decreases in the presence of gram levels of alkali metals, probably caused by the fact that a NaCl molecule, at high concentrations in solution, forces from the formed tetrafluoroborate-VB4R complex one molecule of dye, which is subsequently adsorbed. Evidence of this phenomenon lies in the fact that the absorbance of extracts decreased in the presence of high concentrations of NaCl by half.

The maximum amounts, in mg, of several interfering ions which do not disturb the determination of 0.5 μg of boron were established, and are as follows: Na(40); K(5); Ni, Co(0.3); Cd, Cu, Ca, Mg, Al, Fe, Zn, Mn, Mo, W(0.2).

Some anions formed complexes with the cation of VB4R and are easily extractable using benzene (Figure 4). Such ions include, for example, NO_3^-, I^-, SCN^-, Br^-, bromate, chlorate, iodate and perrhenate. These anions strongly interfere with boron determination and therefore must first be extracted with VB4R before boron determination. The boron must then be converted to BF_4^- and extracted with VB4R by benzene for determination. The anions F^-, Cl^-, SO_4^{2-}, HPO_4^{2-}, CH_3COO^- and $HC_4H_4O_6^-$ are extracted in very small

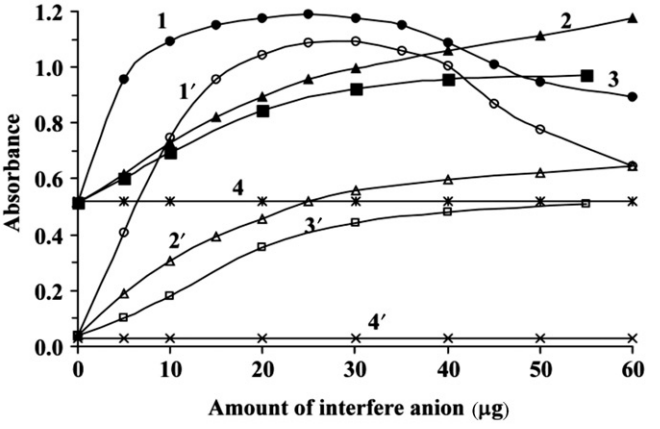

Figure 4. Effect of interfering anions. Note: Extraction of selected anions SCN^- (1,1′), I^- (2,2′), NO_3^- (3,3′) with VB4R by benzene at the optimum experimental conditions for boron determination, in the presence of 0.54 μg of B (4,4′) 1′–4′ blank tests – without B; $l = 0.3$ cm; $\lambda = 610$ nm.

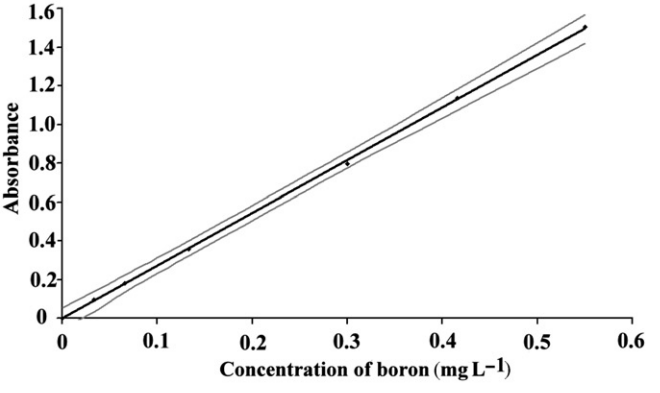

Figure 5. The calibration plot.

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amounts or not at all, and do not disturb boron determination even at concentrations 10,000 times that of boron.

3.4 *Analytical application*

Based on the obtained results, a spectrophotometric procedure for the determination of boron was developed. The absorbance of the coloured extracts obeys Beer's law in the range 0.03–0.55 mg L^{-1} of B(III) (Figure 5). The limit of detection calculated from a blank test ($n = 10$; $P = 0.95$) based on 3 s is 0.02 mg L^{-1} of B(III). The precision of the suggested method was evaluated by repeated determination of different boron concentrations. The method was used for the determination of boron in commercial brand mineral waters, with the given results shown in Table 1. As is evident, there is no significant difference between the results of the suggested method and the labelled concentrations.

Table 1. Determination of boron in mineral waters ($n = 5$, average).

Mineral water	Concentration of boron ($mg\,L^{-1}$)		S_r
	Determined	Labelled	
'Svalyavska'	1.98 ± 0.03	2.0	0.019
'Shayanska'	1.61 ± 0.02	1.6	0.022

4. Conclusion

Based on the investigated reaction of tetrafluoroborate anion with VB4R reagent, a new, simple, rapid and sensitive spectrophotometric determination of boron in commercial brand mineral waters was suggested. The method is based on the reaction of boric acid with fluoride, which forms the tetrafluoroborate anion, and is followed by the extraction of BF_4^- with VB4R into benzene and subsequent spectrophotometric detection. One of the advantages of developed procedure is that the method does not require the separation of boric acid by distillation as methyl borate nor the use of a concentrated sulfuric acid media.

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