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1-(2-hydroxy-3-methoxybenzylideneamino)-8-hydroxynaphthalene-3,6-disulfonic acid as a reagent for the spectrophotometric determination of boron in ceramic materials

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A sensitive and selective spectrophotometric method for the determination of boron is described. The method is based on the colour reaction between boron and the reagent 1-(2-hydroxy-3-methoxybenzylideneamino)-8-hydroxynaphthalene-3,6-disulfonic acid (HMOA). In a HOAc–NH_4OAc buffer of pH 5.5, HMOA reacts with boron to form a 1:2 yellow complex with a maximum absorption at 423 nm. The absorbance (λ_{max} = 423 nm) is linear up to 1.2 μg ml^{-1} boron in aqueous solution with a repeatability (RSD) of 1.12%. The molar absorptivity and Sandell's sensitivity are 7.19×10^3 l mol^{-1} cm^{-1} and 0.0015 μg cm^{-2}, respectively. The limit of quantification and limit of detection were found to be 17.1 and 5.2 ng ml^{-1}, respectively. The interference of various ions was examined in detail. All the metal ions studied can be tolerated in considerable amounts; in particular, the tolerance limits of Fe, Al, Zn, Ca and Mg are superior to those of other reagents such as Azomethine-H and Azomethine-HR. The proposed method was applied to the determination of boron in ceramic materials with satisfactory results.

Borate chemicals and boric acid have a wide variety of industrial applications. Borax, ulexite and colemanite are principally used in the ceramics industry for manufacturing borosilicate and similar glasses. The presence of boric oxide in these glasses facilitates the dissolution of metallic oxides and produces a decrease in the melting-point of the frit. Boric oxide influences both the refractive index and the coefficient of expansion. The control of impurities of boron in other materials is also important.[1]

Boron is an element that is difficult to determine. Sah and Brown have reviewed analytical methods for the determination of boron.[2] Atomic absorption/emission spectrometric methods (AAS/AES) have remained limited because they have poor sensitivity and suffer from serious memory effects and interferences. The prompt gamma-ray method can determine boron concentrations in intact samples, but is time-consuming and not suitable for the detection of low levels of boron. 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[3–10] (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.

Capelle first suggested the use of Azomethine-H as a reagent for the determination of boron,[11] because it can be directly applied in aqueous acidic medium. The reagent has since found wide application.[12–16] However, its selectivity and stability are not ideal. Ions such as Al(III), Cu(II), Fe(III), Ti(IV) and Zr(IV) interfere with the determination of boron, and the temperature, reagent concentration and pH of the medium affect the absorbance of the boron complex.

In order to develop the merits of Azomethine-H and overcome its drawbacks, a series of derivatives of Azomethine-H were designed and synthesized in our laboratory. It was found that 1-(2-hydroxy-3-methoxybenzylideneamino)-8-hydroxynaphthalene-3,6-disulfonic acid (HMOA) (Fig. 1) has excellent analytical characteristics for the spectrophotometric determination of boron. On the one hand, the reaction of boron with HMOA occurs in an aqueous acidic solution; the other reaction conditions are also simple and stable. On the other hand, most metals do not interfere with the determination of trace amounts of boron even when present in considerable amounts. The proposed method offers the advantages of simplicity, high selectivity and sensitivity for the spectrophotometric determination of boron.[3–10]

Experimental

Apparatus

All absorbance measurements and absorption spectra were obtained with a Beckman DU-7HS spectrophotometer (Beckman, Fullerton, CA, USA). The pH value of solutions was

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measured with a Model pH-29A pH-meter (Shanghai Third Analytical Instrument Factory, Shanghai, China).

Reagents

All reagents were of analytical-reagent grade and distilled, deionized water was used throughout. All solutions, including samples and standards, were stored in polyethylene bottles to avoid boron contamination.

A stock standard boron solution (1.00 mg ml^{-1}) was prepared by dissolving 0.5720 g of boric acid in an appropriate volume of water. Working standard boron solutions (10 μg ml^{-1}) were prepared by appropriate dilution of the stock standard solution with water.

HMOA was synthesized in a similar manner to that described by Edwards[17] and Basson *et al.*,[18] except that 2-hydroxy-3-methoxybenzaldehyde was used instead of salicylaldehyde. The reagent solution (0.9%) was prepared by dissolving 0.9 g of HMOA and 2.0 g of ascorbic acid in 100 ml of water and was stored in a polyethylene bottle.

A buffer solution (pH 5.5) was prepared by dissolving 500 g of ammonium acetate in about 700 ml of water, adjusting the pH with dilute hydrochloric acid by using a pH-meter.

General procedure for the determination of boron

An aliquot containing not more than 30 μg of boron was transferred into a 25 ml calibrated flask. Then, 5 ml of buffer solution, 2.5 ml of 2% EDTA, 2.5 ml of 2% citric acid and 5 ml of 0.9% HMOA were added sequentially and the solution was diluted to the mark with water. After standing for 30 min in an ice-bath, the absorbance was measured at 423 nm in a 1 cm quartz cell against a reagent blank prepared in a similar manner but without boron. All measurements were carried out at room temperature.

Results and discussion

Physico-chemical properties of HMOA

HMOA is a yellow powder; it is less soluble in water than Azomethine-H. As HMOA solution does not have an absorption maximum in the visible region, the determination of the acid dissociation constants was carried out in the ultraviolet region. Absorbance–pH curves of the aqueous solution were obtained at 362 nm from which the acid dissociation constants were calculated in the usual way. The pK_a values are given in Table 2. It appears that the sulfonic acid groups are ionized first, then the *o*-hydroxy group is ionized, as the *o*-hydroxy proton is hydrogen-bonded to the azomethine group.

Absorption spectra

The absorption curves of HMOA and the boron–HMOA complex are shown in Fig. 2. It can be seen that the absorption spectrum of the complex has a maximum absorption peak at 423 nm; the reagent has no absorption maximum in the visible region. In order to obtain the highest sensitivity, a wavelength of 423 nm was selected for the spectrophotometric determination of boron in all subsequent work.

Effect of medium and acidity

The effect of the acidity of the solution on the colour reaction was tested (see Fig. 3). Unlike Azomethine-H and Azomethine-HR, the absorbance of the boron complex remains constant and maximum in a NH_4OAc–HOAc buffer of pH 5.0–6.8; a buffer of pH 5.5 was used for the following experiments to control the pH value. Different media were also examined such as HOAc–NaOAc, NH_4OAc-HOAc and citric acid. It was found that NH_4OAc–HOAc was the best, as it gave the highest sensitivity. In addition, a high buffer concentration enhanced the colour intensity of the boron complex; this may be due to the formation of ion associates and the hydration of the borate ion. When the volume of the buffer was varied from 0.5 to 12 ml, the absorbance remained constant and maximum. Thus, the addition of 5.0 ml of NH_4OAc–HOAc buffer of pH 5.5 is recommended.

Effect of volume of masking agents

Although HMOA has excellent selectivity, the effect of the concentrations of EDTA and citric acid on the colour reaction was also investigated, as a further improvment to the selectivity of the reagent is beneficial to the determination of boron in complex samples. It was found that EDTA and citric acid addition to the reaction system was very effective in masking

Table 1 Spectrophotometric methods for the determination of boron

Reagent	Reaction conditions	Remarks	Ref.
Ethyl Violet	pH = 3.1–4.9	1: Benzene extraction 2: Ag, Au, Re, Sb and Ti interfere	3
Crystal Violet	pH = 1–2 (H_2SO_4)	1: Fe, Hg, W, V and Bi interfere seriously	4
Carminic Acid	93% H_2SO_4	1: Concentrated medium 2: Fe, Al, Cu, *etc.*, metal ions interfere	5
1-Hydroxyl-4-*p*-methylanilino-anthraquinone	Concentrated H_2SO_4	1: Concentrated medium 2: F^-, Fe, SO_3^{2-}, Mn, Cr and V interfere	3
Quinalizarin	Concentrated H_2SO_4	1: Concentrated medium 2: Ge, SO_4^{2-}, Se and Sb interfere seriously	6
Arsenazo I	Concentrated H_2SO_4	1: Concentrated medium 2: Light-sensitive 3: Mg, Fe and Ca interfere seriously	3
Arsenazo III	pH = 10	1: Light-sensitive 2: Metal ions interfere seriously	3
Curcumin	Concentrated H_2SO_4	1: Concentrated medium 2: Dichloroethylene extraction	7
D-Sorbitol		1: F^-, Mo, Ge and H_3PO_4 interfere 2: Light-sensitive	8
Azomethine-H	pH = 6.4–7.0 (HOAc–NH_4OAc buffer solution)	1: Narrow range of pH 2: Reagent concentration influences sensitivity seriously 3: Fe, Al, Cu, Ti and Zr interfere	9
Azomethine-HR	pH = 7.0 (HOAc–NH_4OAc buffer solution)	1: Narrow range of pH 2: Reagent concentration influences sensitivity seriously 3: Fe, Al, Cu, Ti and Zr interfere	10

Ca, Mg and Fe ions and greatly improved the selectivity. When the volume of EDTA was varied from 2.0 to 8.0 ml and the volume of citric acid from 0.0 to 4.0 ml, the absorbance remained constant and maximum. Thus, the addition of 2.5 ml of 2% EDTA and 2.5 ml of 2% citric acid was adopted.

Effect of concentration of HMOA

Unlike Azomethine-H and Azomethine-HR, with other concentrations fixed, for a boron concentration of 10 μg per 25 ml, the absorbance of the complex initially increased rapidly with an increase in HMOA concentration, then levelled off with a maximum in the range 4.0–9.0 ml of 0.9% HMOA, followed by a slight decrease with further increase in HMOA concentration. In subsequent experiments the concentration of HMOA was fixed at 5.0 ml of 0.9% HMOA.

Effect of temperature and time

The colour reaction temperature influences the sensitivity slightly. When the temperature is < 20 °C, the reaction of HMOA with boron is complete within 30 min and the colour remains stable for at least 12 h; when the temperature is > 20 °C, the absorbance of the complex decreases obviously, which may be due to the formation of different complexes at different temperatures. Therefore, it is better to carry out the chromogenic reaction in ice-water in order to maintain reproducible results for colour development.

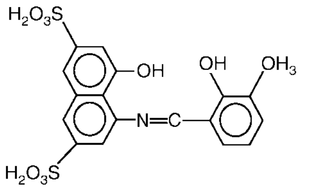

Fig. 1 Structure of HMOA.

Table 2 Acid constants of HMOA at 20 °C

pH	p*K*a value of HMOA	Remarks
0.00–1.00	0.692	Dissociation of –SO_3H group
1.00–2.00	1.623	Dissociation of –SO_3H group
3.00–5.00	4.19	Dissociation of *o*-hydroxy group of phenyl group
6.00–8.00	7.2	Dissociation of hydroxy group of naphthalene ring

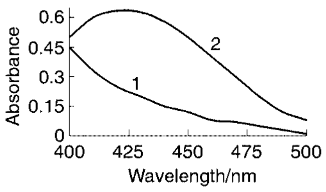

Fig. 2 Absorption spectra: 1, absorption spectrum of the reagent against water; 2, absorption spectrum of the complex against the reagent blank.

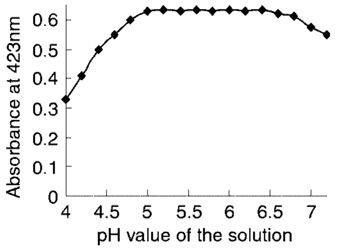

Fig. 3 Effect of pH on the colour reaction.

Calibration graph, sensitivity and precision

A calibration graph prepared by plotting the absorbance *versus* boron concentration was linear over the range 0–30 μg in 25 ml of solution. The molar absorptivity of the complex of boron and Sandell's sensitivity calculated from the slope of the calibration graph were 7.19×10^3 l mol^{-1} cm^{-1} and 0.0015 μg cm^{-2}, respectively; the limit of quantification[19,20] and the limit of detection, as defined by IUPAC,[21] were found to be 17.1 and 5.2 ng ml^{-1}, respectively. Ten replicate analyses of a test solution containing 10 μg of boron using the general procedure gave a relative standard deviation of 1.12%.

Composition of HMOA–boron complex

The composition of the complex was determined by Job's method of continuous variation and the slope-ratio method. The results showed that the stoichiometry of the HMOA–boron complex was 1 : 2 (boron : HMOA). The structure is suggested in Fig. 4.

Effect of interfering ions

Under the optimum conditions, the effect of various foreign ions on the determination of 10 μg of boron was examined separately. With a relative error of ±5%, the tolerance limits for various foreign ions are listed in Table 3. It was found that all of the foreign ions studied can be tolerated in considerable amounts; in particular, the tolerance limits for Fe, Al, Zn, Ca and Mg are superior to those of other spectrophotometric methods such as the Azomethine-H and Azomethine-HR based methods. Hence, the proposed method can be used to determine boron in ceramic materials directly.

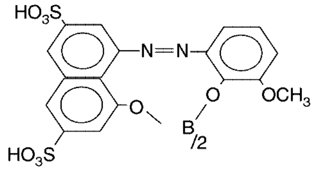

Fig. 4 Proposed structure of the boron complex.

Table 3 Tolerance limits of foreign ions

Foreign ion	Tolerance limit/mg	Foreign ion	Tolerance limit/mg
K(I)	200	Mo(VI)	1.5
Na(I)	200	Cr(III)	1.0
Ca(II)	30	AI(III)	1.5
Mg(II)	20	W(VI)	1.0
Zn(II)	20	V(V)	0.5
Ni(II)	2.5	Ti(IV)	1.0
Fe(III)	5.0	CI$^-$	200
Co(II)	1.5	I$^-$	30
Pb(II)	2.5	NO_3^-	40
Mn(II)	1.0	SO_4^{2-}	100
Cu(II)	2.5	PO_4^{3-}	30
Cd(II)	1.7	SiO_3^{2-}	15

Table 4 Results of determination in samples expressed as % B_2O_3

Sample	Proposed method[a]	Curcumin method[a]
1	4.51 ± 0.02	4.52 ± 0.08
2	1.33 ± 0.07	1.31 ± 0.05
3	1.55 ± 0.10	1.55 ± 0.11
4	2.65 ± 0.02	2.62 ± 0.04
5	5.64 ± 0.12	5.59 ± 0.17
6	2.74 ± 0.05	2.77 ± 0.07
7	3.91 ± 0.02	3.94 ± 0.03
8	1.11 ± 0.01	1.12 ± 0.02

[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.

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 min, then left in a thermostatically controlled bath for 1 h at 70–80 °C. Subsequently, the sample solution was filtered through a Whatman No. 40 filter-paper and neutralized with 1.0 mol l^{-1} 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 mol l^{-1} 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 μg 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 4.

Conclusions

It has been demonstrated that HMOA is an excellent analytical reagent for the spectrophotometric determination of boron in ceramic materials. Compared with other reported methods, the proposed method offers several notable advantages:

(i) High sensitivity. The molar absorptivity is 7.19×10^3 l mol^{-1} cm^{-1}; the sensitivity is higher than that of AAS and ICP-AES.

(ii) Excellent selectivity. All the metal ions studied can be tolerated in considerable amounts; in particular, the tolerance limits for Fe, Al, Zn, Ca and Mg are superior to those of other spectrophotometric methods such as the Azomethine-H and Azomethine HR based methods. Thus it can be used to determine boron in complex samples such as water, biological materials and alloys without the need for a separation procedure.

(iii) A simple and stable reaction system. An aqueous acidic medium is used and the reagent can be used over a wide concentration range. Therefore, the results are very reliable and accurate.

(iv) Rapidity. The reaction time is 30 min, which is five times faster than that of the Azomethine-HR based method.

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