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Analytical Methods Section

Polarographic determination of trace boron in foods

Guanghan Lu[a]*

[a] *Department of Chemistry, Central China Normal University, Wuhan, 430070, People's Republic of China*

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Xiaoming Li[b] **& Yufang Deng**[b]

[b] *Hubei Pharmaceutical Industrial School, Wuhan, People's Republic of China*

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A very sensitive polarographic method has been developed for the determination of trace amounts of boron in foods, based on the adsorptive characteristics of the boron complex with beryllium (III) (4-((4-diethylamino-2-hydroxypheny)-azo)-5-hydroxy-2,7-naphthalenedisulphonic acid) at the dropping mercury electrode in a solution of potassium hydrogen phthalate (pH 3·7–4·6). The peak height is directly proportional to the concentration of boron over the range 5×10^{-9} to 5×10^{-7} g ml^{-1}. The detection limit and the recovery of the method are 1×10^{-9} g ml^{-1} and 89–105%, respectively. The method has been applied to determination of trace amounts of boron in foods, with satisfactory results.

INTRODUCTION

Many analytical methods have been developed for the determination of boron, but not all are suitable for routine trace determinations. Atomic emission spectrometry (AES) can be used for boron determinations (Ecrement & Burelli, 1973; Jones & Benton, 1975; Scott & Strasheim, 1975; Hamner & Deaeth, 1980; Schramel, 1989; Novzamsky *et al.*, 1990; Wang *et al.*, 1990; Yuan *et al.*, 1990; Jia *et al.*, 1991), but requires expensive instrumentation. Another analytical method that can be used to determine boron is spectrophotometry (Chen, 1981; Cumakov, 1981; Kyoji *et al.*, 1981; Shigeya, 1983, 1985; Takeuchi & Takeyama, 1983; Aznarez & Mir, 1984; He, 1988; Perasnar *et al.*, 1989; Zenki *et al.*, 1989; Sheng *et al.*, 1991; Zhu *et al.*, 1991; Gao, 1993). However, the sensitivities of these methods are not very high. Recently, a polarographic method for the determination of boron has been reported (Zheng, 1987; Zhang, 1989), but not for the determination of boron in foods.

This paper describes a sensitive polarographic procedure for the determination of trace amounts of boron. A sensitive polarographic wave at −0·45 V (SCE) can be obtained from the stable boron complex with beryllium (III) which forms in potassium hydrogen phthalate solution (pH 4) on heating. Its peak height is proportional to the concentration of boron.

The proposed method has been used for the determination of boron in corn, soybean, rice and other foods, and the results show excellent agreement with those from inductively coupled plasma (ICP)-AES.

MATERIALS AND METHODS

Apparatus

A Model JP-1A oscillopolarograph (Chengdu Instrumental Factory), and a three-electrode system, with a dropping mercury working electrode, were used. The reference and counter electrodes were saturated calomel and platinum wire electrodes, respectively. A Model AD-3 polarograph (Jintan Analytical Instrumental Factory) and a pH meter were used.

Reagents

A standard solution of boron (200 μg ml^{-1}) was prepared by dissolving dried boric acid (0·5720 g) in HCl (1 ml) and diluting to 500 ml with water. A beryllium (III) aqueous solution (0·05%) and potassium hydrogen phthalate aqueous solution (0·1M) were used. An EDTA solution (0·1M) was prepared. Methyl Orange indicator was added and the solution was adjusted to an orange colour with HCl and NaOH solution. All solutions were prepared from double-distilled water and analytical grade reagents.

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* To whom correspondence should be addressed.

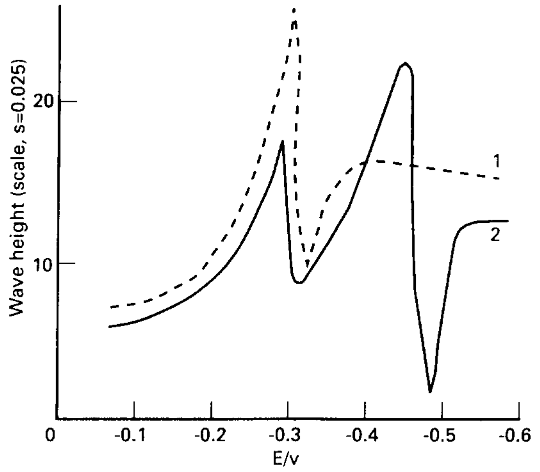

Fig. 1. Derivative polarogram of boron complex with beryllium (III). 1, 0·01M EDTA + 0·015M potassium hydrogen phthalate + 0·005% beryllium (III); 2, 1 + 0·25 μg ml^{-1} boron. S: Current sensitivity.

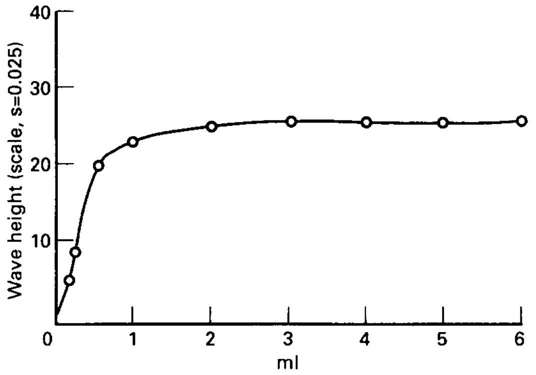

Fig. 2. Effect of the concentration of beryllium (III); 0·01M EDTA + 0·015M potassium hydrogen phthalate + 0·25 μg ml^{-1} boron. S; current sensitivity.

Procedure

An appropriate amount of standard solution of boron was transferred to a 20-ml volumetric flask and EDTA solution (2 ml), potassium hydrogen phthalate solution (3 ml) and beryllium (III) (2 ml) solution were added. The solution was diluted to 20 ml with water, heated in a boiling water-bath for 3 mins, then placed in cold water to cool to room temperature. The solution was transferred to an electrolytic cell, the initial scanning potential was set at −0·3 V (SCE) and a scan was carried out in the negative direction. The peak height was recorded at −0·45 V (see Fig. 1).

RESULTS AND DISCUSSION

Selection of experimental conditions

Effect of pH on the peak height

In the pH range 3·7–4·6, a stable polarographic wave can be obtained. If the pH value is outside this range, the peak height decreases and the peak shape deteriorates. The optimum pH was about 4·0 in our experiments.

Effect of the concentration of beryllium (III)

No boron peak appeared in the potassium hydrogen phthalate solution alone. After adding beryllium (III), a peak occurred at a potential of −0·45 V, which increased with increasing amounts of beryllium (III) and became constant when the volume of beryllium (III) was at least 2 ml in a 20 ml solution. The optimum volume of beryllium (III) was therefore 2 ml (see Fig. 2).

Effect of temperature

At room temperature, no stable peak appeared after standing, even after 24 h. On heating the solution in a boiling water-bath for 1 minute or more, a stable peak was obtained. In all the subsequent experiments, the solution was heated for 3 min in a boiling water-bath to form a stable boron complex with beryllium (III), and then cooled to room temperature in cold water before measurement.

Effect of foreign ions

In the presence of EDTA, the experimental results show that large amounts of K^+, Na^+, NH_4^+, Mg(II), Ca(II), Sr(II), Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}, 500-fold Ag^+, Fe(III), Pb(II), Zn(II), Co(II), Cd(II), Ni(II), Si(IV), Bi(III) and Al(III), and 150-fold V(V), Cu(II), Cr(VI), Te(IV) and In(III) have no effect on the determination of boron at a level of 0·25 μg ml^{-1}.

Peak height calibration

Before the addition of boron, there was only one reagent peak, at −0·35 V. After adding boron, a new peak appeared, at −0·45 V. A working curve of peak height as a function of the concentration of boron (see Fig. 3) shows that the peak height is linear for amounts of boron over the range of 0·005–0·5 μg ml^{-1}. The correlation coefficient is 0·999, and the detection limit is 0·001 μg ml^{-1}.

Formation of polarographic wave

No boron peak was observed for a solution of boron at the peak potential of −0·45 V in the absence of beryllium (III). When beryllium (III) was added to the solution containing boron and potassium hydrogen phthalate, a boron peak appeared at −0·45 V. As boron is very difficult to reduce at the dropping mercury electrode, this peak is obviously not due to

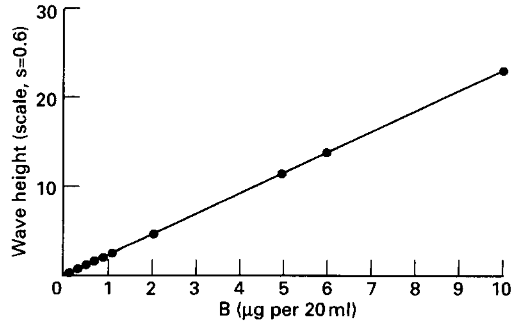

Fig. 3. Calibration graph. S; current sensitivity.

Table 1. Analytical results for boron in foods ($n = 5$)

Sample	Present method (mg kg^{-1})	Recovery (%)	ICP-AES (mg kg^{-1})
Corn	3·14 ± 0·13[a]	104	3·06
Soybean	25·40 ± 0·37	99	26·70
Rice	0·46 ± 0·08	98	0·49
Glutinous rice	0·31 ± 0·09	90	0·38
Wheat	3·61 ± 0·11	89	3·90
Peas	21·30 ± 0·41	105	22·03
Barley	2·18 ± 0·13	90	1·90

[a] ± Standard deviation.

direct reduction of boron. Therefore, this result suggests that the boron peak is the reduction peak of the boron–beryllium (III) complex adsorbed on the electrode.

Application

An appropriate amount of corn, soybean, rice or other food was ground and sieved through a 100-mesh sieve and then dried for 4 h at 65–70°C. After cooling, sample 0·5–0·6 g was impregnated with saturated $Ca(OH)_2$ solution (3 ml) in a porcelain crucible, and heated over a flame for about 10 mins until it turned black. The sample was transferred to a furnace for 6–8 h at 450°C until the ash turned white or grey. The sample was removed from the furnace and cooled, 0·1M HCl (10 ml) was added, and the sample solution was diluted to 25 ml. The solution (5·0 ml) was then transferred to the electrolytic cell, followed by addition of an appropriate amount of Methyl Orange, adjusted to orange colour with NaOH, and then peak height was recorded by the procedure described above. Table 1 summarizes the results obtained for the determination of boron and recovery studies on corn, soybean, rice and other foods. The recovery of boron in all foods was good. Table 1 also shows good agreement between the amount of boron obtained by ICP-AES and by the proposed method.

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