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Conductometric Determination of Boric Acid by Reversed-phase High Performance Liquid Chromatography Using Sorbitol as a Complexing Agent

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Separation and determination of boric acid by reversed-phase liquid chromatography with conductivity detection have been demonstrated. D-Sorbitol was used as a precolumn complexing agent for boric acid and water as the mobile phase. The detection limit was 20 ng ml^{-1}.

Boron is one of the elements that are difficult to determine quantitatively because of its low reactivity. Many analytical methods have been reported for the determination of boron. Atomic absorption spectrometry,[1] flame spectrophotometry[2] and inductively coupled plasma emission spectrometry[3] are useful, but they are less sensitive. In contrast, spectrophotometry such as curcumin or methylene blue extraction method[4] is sensitive and widely used in the field of trace analysis. However, these methods often suffer from the following limitations; troublesome handling, time-consuming procedure and relatively low precision. In recent years, high performance liquid chromatographic analysis (HPLC) of boron has been investigated by several workers for both separation and determination. Motomizu et al.[5,6] have reported the ion-pair chromatography of boric acid with spectrophotometric detection using chromotropic acid as a complexing agent. Other chromatographic methods are concerned with ion chromatography including the conductivity detection. Hill and Lash[7] first reported the conductometric determination of boric acid as tetrafluoroborate using an anion exchange column and NaOH eluent. Wilshire and Brown[8] also reported on ion chromatography of tetrafluoroborate using carbonate eluent. At the same time, they presented on ion chromatographic exclusion technique using a cation exchange column and mannitol as an eluent. Recently, Okada and Kuwata[9] have reported the simultaneous determination of boric acid and germanic acid by the same method using fructose as an eluent. In such cases, since polyols were used both as an eluent and a complexing agent for boric acid, fairly large quantities {0.1 M(= mol dm^{-3})} of polyol had to be

delivered to the separation column. Although polyol has low conductivity, the use of concentrated eluent is neither advantageous nor economical.

The purpose of the present work is to examine the use of polyols as a precolumn complexing agent for the conductometric determination of boric acid, and to separate the acidic boron complexes by reversed-phase high performance liquid chromatography. This method is simple and sensitive and tolerates the presence of common ions.

The HPLC system consisted of a Tosoh CCPD pump and CM 8000 conductivity detector and a Rheodyne 7125 injector. A TSKgel ODS 120A column (250 mm x 4.6 mm I.D.) was used and kept in an air-oven (Tosoh CO 8000) thermostated at 35 °C. The flow rate of mobile phase (water) was 0.85 ml min^{-1}.

All reagents used were of analytical reagent grade. D-Sorbitol was obtained from Wako Pure Chemical Co. and used without further purification. Boron standard solution(100 μg ml^{-1}) was prepared by dissolving 0.2860 g of boric acid in deionized water and diluted to 500 ml. All solutions were filtered through a Millipore filter (0.45 μm) and stored in polyethylene bottle. Test-tubes made from polypropylene were used for the reaction of boric acid and sorbitol.

Recommended procedure is as follows. Five ml of the sample solutions containing boric acid was taken in a 10 ml test-tube and 5 ml of 1.6 M sorbitol solution was added and then mixed thoroughly. The solution was allowed to stand for 5 min. An aliquot (usually 100 μl) of this solution was injected into the chromatographic system.

The important factors in the separation of boric acid by HPLC are the selection of column, choice of complexing agent and composition of eluent. In this work, deionized water was used as the mobile phase and aqueous boron-sorbitol complex was directly injected onto the column. A number of separation columns including silica gel, cation and anion exchange resin and octadecyl bonded column (silica or polymer-bonded) were examined from the

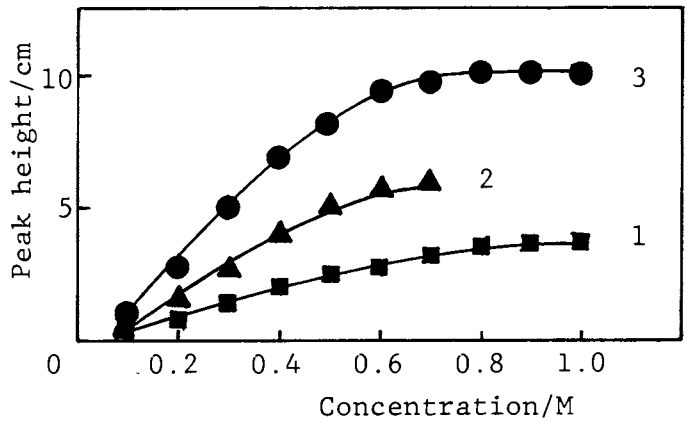

Fig. 1. Effect of polyol concentration on peak height.
1: D-Fructose; 2: D-Mannitol;
3: D-Sorbitol,
Boron: 2 μg ml^{-1}(100 μl).

viewpoint of resolution and sensitivity. As a result, a packed column, TSKgel ODS 120A (5 μm) was the best among them.

The reactivity of polyols with boric acid was also investigated. A previous paper[10] has revealed that fructose, mannitol and sorbitol yield strongly acidic complexes with boric acid. Figure 1 shows the variation of peak heights of boric acid and the comparison of sensitivity with polyol concentration. A large amount of polyol is necessary for the formation of acidic complexes with boric acid. The peak height of the boron complex became larger, with an increase in the concentration of polyols. The retention times of boron complex were independent of the variety and concentration of polyols. Sorbitol was preferable for obtaining high sensitivity, and at a concentration above 0.8 M in the sample solution, the peak height was highest and also constant.

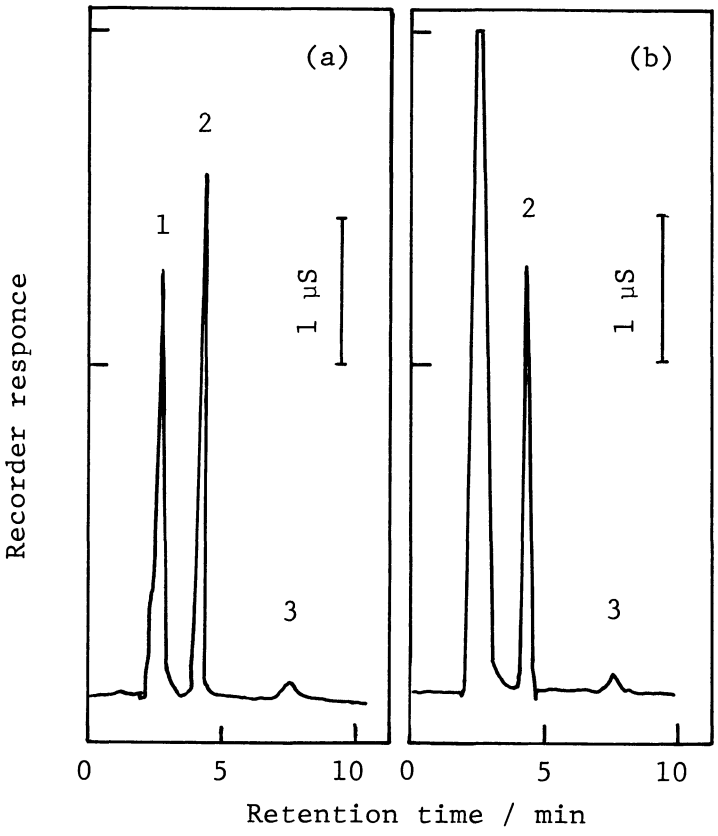

Fig. 2. Typical Chromatograms of boron-sorbitol complex.
(a): Boron standard solution (1 μg ml^{-1}); (b): Eye lotion;
1: Sorbitol;
2: Boron-sorbitol complex;
3: Carbonate.

Figure 2 (a) shows a typical chromatogram of the boron-sorbitol complex in this work. A large excess of sorbitol was eluted first together with common ions such as chloride. Because sorbitol is a non-electrolyte, the shape of its peak was not so large. The peak of the boron-sorbitol complex was well resolved and observed after approximately 4 min. This method was free from the diverse ions. Only fluoride interfered if present in a ten-fold excess.

The peak height calibration curves obtained were linear over the range

of 0.1-2.0 μg ml^{-1} for boron. The detection limit was 20 ng ml^{-1} (S/N=2). The relative standard deviation in the five replicate determinations of 0.5 and 1.0 μg ml^{-1} for boron were 1.7 and 0.91%, respectively.

Boron contents in commercially available eye lotions were analyzed by the present method. One of the chromatograms obtained is shown in Figure 2 (b). The analytical results are summarized in Table 1. The results obtained by the proposed method and azomethine HR[11] method (spectrophotometry) were in good agreement with each other. Another applications such as biological materials and natural waters will be reported elsewhere.

Table 1. Analytical results for boric acid in eye lotion

Sample	Dilution	Boron content(μg ml^{-1})	
		This method	Azomethine HR
A	1/2500	0.83±0.01	0.81±0.03
B	1/2500	0.41±0.02	0.38±0.03
C	1/2500	0.82±0.01	0.81±0.02

References

1) G. I. Spielholtz, G. C. Toralballa, and J. J. Willsen, Mikrochim. Acta, 4, 649 (1974).
2) E. J. Agazzi, Anal. Chem., 39, 233 (1967).
3) N. R. McQuaker, P. D. Kluckner, and G. N. Chang, Anal. Chem., 51, 888 (1979).
4) W. J. Williams, "Handbook of Anion Determination," Butterworths, London (1979), p. 23.
5) S. Motomizu, I. Sawatani, M. Oshima, and K. Tôei, Anal. Chem., 55, 1629 (1983).
6) Z. Jun, M. Oshima, and S. Motomizu, Analyst (London), 113, 1631 (1988).
7) C. J. Hill and R. P. Lash, Anal. Chem., 52, 24 (1980).
8) J. P. Wilshire and W. A. Brown, Anal. Chem., 54, 1647 (1982).
9) T. Okada and T. Kuwamoto, Fresenius' Z. Anal. Chem., 325, 683 (1986).
10) J. Boeseken, Adv. Carbohydr. Chem., 4, 189 (1949).
11) M. Zenki, K. Nose, and K. Tôei, Fresenius' Z. Anal. Chem., 334, 238 (1989).

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