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Note

Determination of borate at trace levels in environmental samples by ion-exclusion chromatography

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Boron can be toxic to higher plants when present in soil solution at levels (0.5–5.0 $\mu g\ ml^{-1}$) not much greater than trace amounts needed for normal growth[1]. Minerals containing boron are found in naturally occurring igneous, metamorphic and sedimentary rocks. Chemical weathering of these minerals releases soluble boron that is readily available for plant uptake. Boron is probably the most troublesome microelement in managing saline and alkaline soils[2]. While boron is essential for plant growth at low concentrations, most crops are extremely sensitive to this element. Boron toxicities are more prevalent than are boron deficiencies among crops grown on saline soils[1].

Boron in drinking water in many regions of the world has been reported to be 100 $\mu g\ l^{-1}$ or less[1]. The recommended maximum concentration for boron in irrigation water is 750 $\mu g\ l^{-1}$ (ref. 3).

Ion-exclusion chromatography has wide applications for the separation of ionic species[4–6]. It is an accepted technique for organic acid analysis and is increasingly being used for weakly ionized inorganic solutes. In this paper, we have applied ion-exlusion chromatography for the trace determination of borate in soils, sediments and water samples using D-sorbitol in the mobile phase. This method also has applications in the determination of bicarbonate. Two ion-exclusion columns were evaluated for their efficiencies in separation of borate. This ion-exclusion chromatography technique enables separation, detection and quantification of borate from various matrices obtained from several environmental problem sites. Results obtained by ion-exclusion chromatography were compared with a standard spectrophotometric method for determination of borate.

EXPERIMENTAL

Chromatographic instrumentation

The high-performance liquid chromatographic (HPLC) assembly consisted of a Beckman Model 332 liquid chromatograph equipped with a Model 110A pump and a Model 210 sample injector. Conductometric detection was carried out with a Wescan (San Jose, CA, U.S.A.) Model 213 detector. The ion-exclusion chromatography

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system was composed of the following: a Wescan ion-exclusion column (No. 269-006) (300 mm × 7.8 mm I.D.), particle size 10 μm, connected to a Wescan ion guard anion-exclusion column (No. 269-007); Interaction (Mountain View, CA, U.S.A.) ORH-801 anion-exclusion column (No. 25310) (300 mm × 6.5 mm I.D.), particle size 8 μm, and an Elden (Elden Labs., Menlo Park, CA, U.S.A.) Model III thermostatic column heater. A Hewlett-Packard (Avondale, CA, U.S.A.) Model 3390A printer–plotter integrator with variable input voltage was used to monitor the signal output with a chart speed of 0.5 cm min^{-1}. Sample injection loops of 100, 200, 500 and 1000 μl were employed to establish detection limits.

Reagents

The mobile phase consisting of D-sorbitol (Sigma, St. Louis, MO, U.S.A.) was prepared as 0.025–0.4 *M* solutions. The flow-rate was 2 ml min^{-1} for the Wescan column and 1.0 ml min^{-1} for the Interaction column. The column inlet pressure was approximately 1200 p.s.i. (Wescan) or 1500 p.s.i. (Interaction). The detector output was 10 mV. The eluent was passed through an LC-SCX tube (5-8997M) (Supelco, Bellefonte, PA, U.S.A.) to remove ionic impurities, filtered through a 0.22-μm GS membrane filter (Millipore, Bedford, MA, U.S.A.) and degassed under vacuum prior to conditioning the column.

Solutions were made by dissolving sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) (Mallinckrodt, Paris, KY, U.S.A.) and sodium bicarbonate ($NaHCO_3$) (Mallinckrodt) in HPLC-grade water. HPLC-grade water was obtained by filtering deionized water through an HN organic removal resin (Barnstead, Boston, MA, U.S.A.), then HN Ultrapure DI exchange column (Barnstead) and finally a 0.22-μm Millipore GS filter.

Field samples and preparation

Sediment samples were collected from an evaporation pond facility at the Sumner Peck Ranch and from the San Luis Drain near Fresno, CA, U.S.A., containing agricultural drainage water that had percolated through boron-rich soils.

Saline surface soil samples (Traver and Twisselman) were collected from Kern County, CA, U.S.A. and San Bernardino, CA, U.S.A. The soil samples were allowed to air-dry, passed through a 2-mm-mesh screen and homogenized.

Water samples from local lakes (Riverside, CA, U.S.A.) were also analyzed for borate. No sample preparation was needed for the water samples except diluting with deionized water and then passing through a 0.22-μm Millipore GS filter before analysis.

Air-dry soil or sediment (10 g) was boiled under reflux with 30 ml of water for 10 min. The samples were then subjected to shaking for 2 h and filtered through Whatman No. 3 filter paper. Organic impurities were removed by passing the extract through a Supelcosil LC-Si tube (5-8974M) (Supelco). The extract was then passed through a 0.22-μm Millipore GS membrane filter before the ion-exclusion chromatographic analysis.

To check the reproducibility of the ion-exclusion chromatography method, a minimum of ten injections of combined standards containing borate and a bicarbonate mixture were used. The detection limits for borate and bicarbonate with various sample sizes were calculated as the three-fold signal-to-noise ratio of the baseline ($S/N = 3$).

Spectrophotometry

Determination of the borate content in soils, sediments and water samples was also carried out by the method of John *et al.*[7]. This method involves the spectrophotometric determination of a borate azomethine–H (Pierce, Rockford, IL, U.S.A.) complex stable at pH 5.1 and measuring the absorbance at 420 nm.

RESULTS AND DISCUSSION

Ion-exclusion chromatography was chosen because of the high pK_a value of borate (9.2). With ion-exclusion chromatography, retention is due primarily to an exclusion–partition mechanism on a polymeric cation-exchange resin although non-polar interactions may also affect retention. The basis for separation of borate by ion-exclusion chromatography involves the use of a polyalcohol in the mobile phase which forms a polyborate complex[6,8–10].

$$B(OH)_3 + 2LH_2 \rightleftarrows H^+ + L_2B^- + 3H_2O$$

The formation of such a complex is dependent upon the concentration, pH and nature of the polyol[8]. A mannitol–boric acid complex has been previously studied with 0.1 *M* mannitol – 0.001 *M* hydrochloric acid in the mobile phase for borate determination by ion-exclusion chromatography with suppresed ion chromatography (IC)[6]. The suppressed IC system was inherently non-linear and had unavoidable deposition of halides on the suppressor column.

In this study, D-sorbitol in the mobile phase forms a stable and detectable complex with borate. The retenion time of this complex was only 3.5 min compared to approximately 12 min reported in the suppressed IC system[6].

Optimization parameters for ion-exclusion chromatography

Studies were carried out to determine the optimum concentration of D-sorbitol for separation and detection of borate. An increasing concentration of D-sorbitol up to 0.4 *M* did not cause an increase in background conductance. Higher sensitivity of borate detection was observed in the range 0.2–0.3 *M versus* <0.2 *M* D-sorbitol (Fig. 1). The response of borate was not affected by a change in the pH (5–10) of the

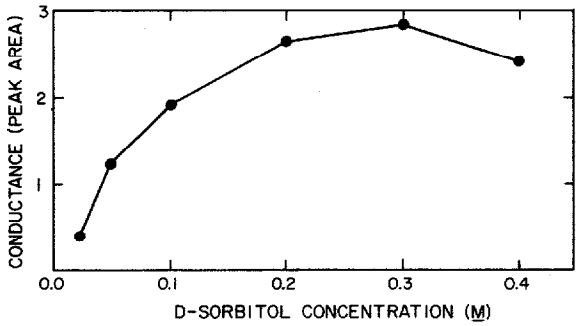

Fig. 1. Dependence of signal response of borate on the concentration of D-sorbitol in the mobile phase (other chromatographic conditions as in Table I).

mobile phase, while bicarbonate decreased with increasing pH (5–7) of 0.3 *M* D-sorbitol. There was no effect on retention times of borate and bicarbonate (100–1000 mg l^{-1}) with variations in sample pH (5–10) and injection volume (100–1000 μl). The optimum concentration of D-sorbitol for borate determination was 0.3 *M* (pH 5.3). Broader peaks were observed at concentrations lower than 0.2 *M*. At higher D-sorbitol concentrations (>0.4 *M*), the solubility of D-sorbitol was limited.

Comparison of D-sorbitol (0.3 *M*) with D-mannitol (0.3 *M*) showed that retention times were considerably less with D-sorbitol when used in the mobile phase with the Wescan column. Borate and bicarbonate eluted at 3.45 and 5.60 min, respectively, with D-sorbitol, and 4.04 and 6.22 min, respectively, with D-mannitol. D-Sorbitol was preferred over mannitol because of its higher solubility in water, its lower cost and lower detection limits. The effect of column temperature was studied with maximum sensitivity observed in the temperature range 25–30°C. Higher temperatures resulted in decreased sensitivity, possibly due to the decomposition of the borate–sorbitol complex.

Comparison of columns

Two columns were evaluated for borate determination. Both columns were composed of functionalized polystyrene–divinylbenzene with ionic groups. The difference in their behavior could be due to their degree of cross-linkages. Each was compared in terms of retention time, number of theoretical plates (*N*) and height equivalent to a theoretical plate (HETP). The retention time for borate was 3.45 min with the Wescan column compared to 5.06 min with the Interaction column. The *N* and HETP for borate were 2055 (0.15 mm) and 1592 (0.19 mm) with the Wescan and Interaction columns, respectively. It was on the basis of these comparative parameters that the Wescan column was selected for further studies in the separation of borate.

Precision, linearity of response and detection limits

The precision of this ion-exclusion chromatography method for the analysis of borate as determined by repeated injections made of standards is given in Table I. The results show that the relative standard deviations (R.S.D.) of borate ranged from 0.68 to 1.42% with a 500-μl loop. A calibration plot was obtained by plotting peak area against the borate concentration. The plot was linear within the range 0.10–

TABLE I

PRECISION OF THE ION-EXCLUSION CHOMATOGRAPHY METHOD IN THE DETERMINATION OF BORATE AND BICARBONATE (n = 10)

Column, Wescan (300 mm × 7.8 mm I.D.); mobile phase, 0.3 *M* D-sorbitol; detection, conductometric; temperature, 25°C. Values in parentheses are R.S.D. values (%).

Sample volume (μl)	*Concentration (mg l^{-1})*	
	Borate	*Bicarbonate*
100	7.4 (1.04)	28.0 (2.26)
200	4.2 (0.72)	14.5 (2.90)
500	1.1 (0.48)	6.4 (1.42)
1000	0.6 (0.68)	7.0 (1.52)

9.60 mg l^{-1}. The minimum detection limit for borate was 0.05 ng obtained by injecting 500 μl of a 0.1 μg ml^{-1} sample. For bicarbonate, the calibration curve was linear from 1 to 100 mg l^{-1} with the limit of detection being 1.25 ng.

Interferences

One of the major concerns in the analysis of environmental samples is the accurate determination of the ion of interest in the presence of other inherent ions. The response due to such ions when present in large amounts could easily mask the signal of the target analyte, particularly with conductometric detection. With ion exclusion, strong mineral acid anions such as Cl^-, NO_3^- and SO_4^{2-} eluted rapidly giving an early single peak before the borate complex was detected. Further tests with weak anions (AsO_3^{3-}, F^-, $H_2PO_4^-$, HCO_3^-, SO_3^{2-}, TeO_4^{2-}, TeO_3^{2-} and SiO_3^{2-}) under the conditions described (500-μl sample) cause no interferences in the determination of borate.

Comparison of methods

A close relationship was observed by the proposed ion-exclusion chromatography method and the colorimetric azomethine–H procedure in determination of borate in soil, sediment and lake water samples (Table II). The relationship can be expressed as follows: $y_{\text{azomethine}} = 1.06x_{\text{ion exclusion}} - 0.43, r^2 = 0.997 (P < 0.001)$. The unity in slope indicates excellent agreement between the two methods.

Determination of borate by ion-exclusion chromatography

A typical chromatogram of a hot water soil extract is shown in Fig. 2. The solutes (borate and bicarbonate) were separated into well defined peaks with a total time of analysis of 7 min. Calculation with external standards indicated that this soil extract contained 3.4 mg borate per kg soil.

TABLE II

COMPARISON OF ION-EXCLUSION CHROMATOGRAPHY AND AZOMETHINE-H METHODS FOR BORATE DETERMINATION IN ENVIRONMENTAL SAMPLES (n = 3)

Values in parentheses are R.S.D. values (%).

Sample type	*Borate concentration*	
	Ion-exclusion chromatography	*Azomethine–H*
Evaporation pond sediments (mg kg^{-1})		
Peck	6.7 (0.81)	6.5 (0.92)
San Luis Drain	14.4 (1.02)	15.3 (1.42)
Saline soils from Kern County, CA, U.S.A. (mg kg^{-1})		
Traver silt loam	0.8 (0.56)	0.8 (2.44)
Traver II loam	7.5 (1.14)	7.3 (1.55)
Twisselman clay loam	3.4 (0.84)	3.2 (0.78)
Lake water (mg l^{-1})		
Sample I	2.1 (0.55)	2.0 (1.31)
Sample II	3.2 (0.76)	3.3 (1.12)

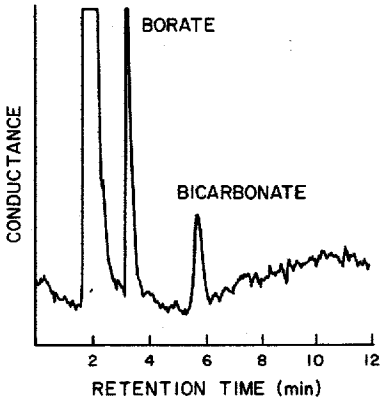

Fig. 2. Chromatogram of a soil extract (chromatographic conditions as in Table I).

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