Ion chromatographic determination of borate in aqueous samples together with other common anions

Andrea Tapparo, Paolo Pastore and G. Giorgio Bombi

Università degli Studi di Padova, Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Via Marzolo 1, 35131 Padova, Italy

The conversion of boric acid (pK_a ≈ 9) in a more acidic complex, using mannitol or sorbitol as ligands, has been exploited to obtain a sensitive and accurate method for the determination of boric acid by ion chromatography. Both separation and detection conditions have been selected on the basis of available thermodynamic data on the relevant equilibria, and then experimentally optimised on a conventional ion cromatograph equipped with a suppressed conductivity detector. The performances of the method are practically identical for the two eluent solutions adopted, containing mannitol or sorbitol: the detection limit is about 1 μmol dm^{-3}, the linear response range extends up to 200 μmol dm^{-3}, the repeatability is better than 5% and the analysis time is less than 6 min. Moreover, other common anions (*i.e.*, acetate, fluoride, and chloride) can be determined together with borate. The comparison of results with those obtained by conventional analytical techniques applied to real samples at known concentration of borate allows the estimation of a negligible bias for the ion chromatographic method.

Keywords: *Boric acid determination; ion chromatography; mannitol; sorbitol; pharmaceutical samples*

Boric acid plays a relevant role both in animal and vegetal physiology and is widely used as a preservative or bacteriostatic agent by food and pharmaceutical industries. Nevertheless quite few and inconvenient analytical methods for its determination are available. They are mainly based on spectrophotometric techniques and volumetric titrations.

The spectrophotometric analysis provides reactions between boric acid and various chromophoric compounds such as carminic acid, curcumin or azomethine-H.[1–4] These procedures may be affected by the presence of various interfering compounds[4,5] and they are, in general, time consuming. Improved methodologies have been recently proposed[6] often based on specific flow techniques.[7]

The second method is an acid–base titration in which the titrated species is a complex of boric acid with a polyhydroxylated species. The formed complex exhibits a markedly lower value of the pK_a, 3.7 and 6.0 for the two main protonated complexes of the mannitol–boric acid system,[8] compared with that of boric acid so that it can be titrated by strong base solutions. In other words boric acid becomes a stronger acid owing to the complex formation reaction.

Starting from this consideration, this work reports a new analytical method for the determination of boric acid by ion chromatography coupled with conductimetric detection, taking advantage of the complex formation between boric acid and polyhydroxy compounds such as sorbitol or mannitol. The use of a chromatographic technique avoids the problems arising from matrix interferences and allows the simultaneous determination of other anionic analytes present in the sample solution.

Experimental

Reagents

All the reagents employed were of analytical grade. Standard solutions of boric acid (Prolabo, Fontenay, France, > 99.5%), sodium chloride (Prolabo, > 99.8%), sodium acetate (Prolabo, > 99%), sodium fluoride (Carlo Erba, Milan, Italy, > 99.8%) were prepared by dissolving the suitable amount in high purity water produced with a Milli-Q Plus apparatus (Millipore, Bedford, MA, USA). The eluent was a 0.8 mol dm^{-3} solution of mannitol (Fluka, Buchs, Switzerland, > 99%), or sorbitol (Fluka, > 99.5 %), plus sodium hydroxide (Fluka, > 98%), 5 mmol dm^{-3}. A 25 mmol dm^{-3} solution of sulfuric acid (Prolabo) was used as regenerant solution for the suppressor membrane.

Ion chromatographic system

All the chromatograms were performed with a chromatograph Waters Act-ION Analyzer (Millipore, Milford, MA, USA) equipped with a conductivity detector Waters model 431. Chromatograms were recorded either with a Carlo Erba Integrator model SP4270 or with a HP model 7040 A X-Y recorder (Hewelett-Packard, Boeblingen, Germany). Separations were done by a Dionex IonPac AS4A-SC, 4.6 × 250 mm, analytical column (Dionex, Sunnyvale, CA, USA) equipped with a Dionex IonPac AG4A-SC, 4.6 × 50 mm, guard column. The conductivity of the eluent was suppressed by a Dionex AMMS-1 suppressor. A laboratory-made 4.6 × 250 mm purification column, packed with Amberlite IRA-458, 1.2 meq ml^{-1} (Supelco, Bellefonte, PA, USA), and inserted before the injection valve, was used to eliminate the presence of sulfates, carbonates and other anions present in the eluent at trace concentration affecting the elution time of the analyte anions. Regeneration of this column with 0.1 mol dm^{-3} sodium hydroxide were performed every week. An injection valve with a 20 μl sample loop and a flow rate of 1 ml min^{-1} was used.

Results and discussion

Mannitol–borate system

The reaction between boric acid and polyhydroxy compounds (known since 1842[9]) produces a class of complexes characterised by pK_a values markedly lower than that of boric acid. From the chromatographic point of view a lower pK_a value is very useful since a higher amount of the anion species present in solution allows its stronger retention on an anionic chromatographic column. Moreover the anionic complexes can be detected by means of the classic suppressed conductivity detector.

By considering mannitol as the representative polyhydroxy compound, the following equilibria can be considered together with the acid dissociation of boric acid.[8,10]

$B(OH)_3 + L \rightleftarrows HB(OH)_2 (H_{-2}L) + H_2O$ $\log\beta_{1,1} = 0$

$B(OH)_3 + 2L \rightleftarrows HB(H_{-2}L)_2 + H_2O$ $\log\beta_{1,2} = -0.21$

$HB(OH)_2(H_{-2}L) \rightleftarrows B(OH)_2(H_{-2}L)^- + H^+$ $pK_{a\,1,1} = 6.0$

$HB(H_{-2}L)_2 \rightleftarrows B(H_2L)_2^- + H^+$ $pK_{a1,2} = 3.7$

$B(OH)_3 \rightleftarrows H_2BO_3^- + H^+$ $pK_{a1,0} = 8.98$

Actually a simplification of the system has been introduced because the formation of dinuclear boron(III) complexes[8,10] can be neglected when a large excess of mannitol is used. Owing to the relatively low value of the formation constants of the complexes their quantitative formation can be achieved only by using a large excess of mannitol and with suitable pH conditions. A graphical representation of the distribution of the species for a H_3BO_3–mannitol system at the equilibrium in aqueous solution, as a function of pH, is given in Fig. 1. The diagram shows that for 0.5 mmol dm^{-3} boric acid and 0.8 mol dm^{-3} mannitol for pH values greater than 4.1 the species mainly present in solution is $B(H_{-2}L)_2^-$, *i.e.*, the 1 : 2 complex with charge −1. An analogous result is obtained by running the simulation again with 0.8 mol dm^{-3} mannitol and 1 μmol dm^{-3} boric acid concentration (a value close to the detection limit found with the proposed method; see below). Also in this second case $B(H_{-2}L)_2^-$ is the predominant species for pH ≥ 4.1 (Fig. 2). The very high mannitol–boric acid ratio keeps the equilibrium position of complex formation practically unchanged on changing the concentration values of the analyte.

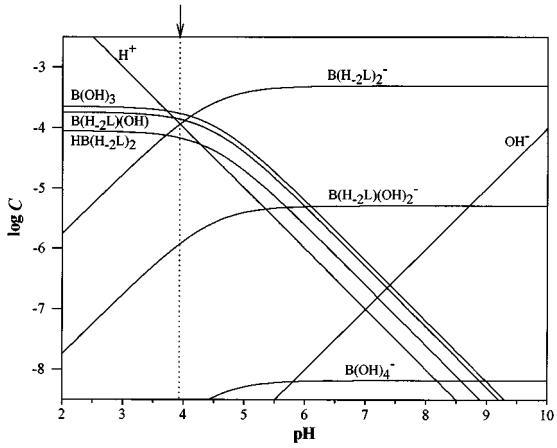

Fig. 1 Distribution diagram for a solution of 0.5 mmol dm^{-3} boric acid and 0.8 mol dm^{-3} mannitol. The arrow indicates the pH of the solution after the suppression treatment.

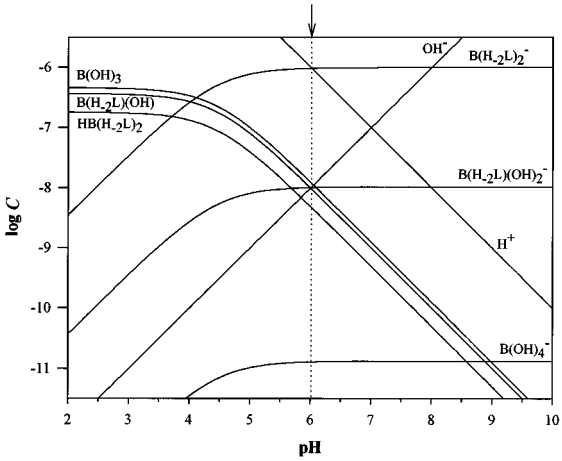

Fig. 2 Distribution diagram for a solution of 1 μmol dm^{-3} boric acid and 0.8 mol dm^{-3} mannitol. The arrow indicates the pH of the solution after the suppression treatment.

From the ion chromatographic point of view $B(H_{-2}L)_2^-$ is the most desirable species both for the separation and the conductimetric detection. This species is quantitatively present in solution at pH ≫ pK_a (= 3.70) so that an eluent characterised by a pH value greater than 5.7 after suppression of its conductivity has to be chosen.

Optimisation of chromatographic conditions

Starting from the considerations reported above, an OH^--based eluent has been chosen both for its ability to separate weakly retained anion species on conventional anionic columns and for the necessity to maintain the pH of the suppressed eluent at the optimal value to detect the analyte. The use of a sodium hydroxide solution as the eluent furnishes (i) an alkaline pH during the elution so ensuring the quantitative presence of the anion species $B(H_{-2}L)_2^-$ and (ii) a neutral pH (pH = 7) after the suppression which remains an optimal value for the detection. However, the weak acid formed by the suppression of the analyte, $HB(H_{-2}L)_2$, produces a localised acidic condition characterised by a pH value which depends on the borate concentration in the effluent. For a 0.5 mmol dm^{-3} analytical concentration of borate in the detection cell (which represents a much higher concentration in the injected sample solution), the calculated concentration of $B(H_{-2}L)_2^-$ and the pH value are 0.11 mmol dm^{-3} and 3.95 respectively (Fig. 1). Therefore the fraction of deprotonated complex (α) is 0.22, markedly lower than that in the elution condition (pH = 11.7 for the 5 mmol dm^{-3} NaOH eluent solution, α = 1). For this reason at high borate concentration levels a theoretical lower sensitivity has to be expected and a curvature of the calibration graph has to be observed. At 1 μmol dm^{-3} boric acid concentration the resulting pH value, after suppression, is 6.01 so that in this case the borate complex is quantitatively in the anionic form (α = 1, Fig. 2). Therefore, at micromolar levels of borate, the chromatographic signal has to be linear with its concentration.

The composition of the mobile phase, 5 mmol dm^{-3} NaOH and 0.8 mol dm^{-3} mannitol (see Experimental), has been formulated on the basis of the considerations above reported and the eluent has been tested for the chromatographic resolution of the borate complex with respect to other anionic compounds possibly present in the sample solution such as chloride, fluoride and acetate having k' values comparable with that of the $B(H_{-2}L)_2^-$ complex. By using the above mentioned eluent, the obtained retention times of $B(H_2L)_2^-$, fluoride, acetate and chloride are 3.7, 4.1, 4.7 and 12.0 min, respectively.

The weak elution strength of OH^- suffers from the presence of anionic impurities contained in the eluent. Typically, traces of sulfates (mainly present in the mannitol) and CO_2 absorption produce a progressive decrease of the retention times. This problem has been overcome by inserting a high capacity anionic column, loaded with OH^-, before the injection valve.

The analytical technique has been calibrated in the 10^{-5}–10^{-3} mol dm^{-3} concentration range by means of boric acid standard solutions. As expected the calibration function contains a second order term which rises from the weak acid $HB(H_{-2}L)_2$ partially formed in the suppression system. However a linear calibration function is significant (with respect to the quadratic one, $F_{8,7} = 2.62$, critical value $F_{0.05,\,8,\,7} = 3.73$) for borate concentrations lower than 200 μmol dm^{-3}. Within the calibration range, the precision of the method, measured by the repeatability standard deviation,[11] is always better than 5%.

According to IUPAC suggestions,[11,12] the detection limit of the proposed method is about 1 μmol dm^{-3} (α = β = 0.05;

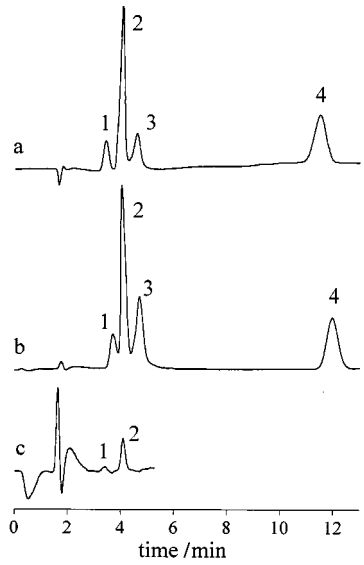

Fig. 3 Chromatograms of a synthetic sample solution containing 83 μmol dm^{-3} borate (1), 166 μmol dm^{-3} fluoride (2), 2 mmol dm^{-3} acetate (3) and 56 μmol dm^{-3} chloride (4), obtained with different eluent solutions: (a) 5 mmol dm^{-3} NaOH, 0.8 mol dm^{-3} sorbitol solution. (b) 5 mmol dm^{-3} NaOH, 0.8 mol dm^{-3} mannitol solution. (c) Synthetic sample containing 1 μmol dm^{-3} borate (1), corresponding to the detection limit, and fluoride impurity (2). Signal attenuation: (a) and (b), 1024; (c), 128.

sampling loop = 20 μl). This is a slightly better value then those reported for the azomethine-H based spectrophotometric procedures (1.5–2 μmol dm^{-3}).[4,6] Nevertheless these latter limits are computed considering only the standard deviation of blank samples signals and a direct comparison with the detection limit proposed for the chromatographic method is not possible.

The chemical behaviour of sorbitol toward boric acid is probably very similar to that described above for mannitol, though the minor availability of thermodynamic data does not allow detailed information to be obtained. Using a 5 mmol dm^{-3} NaOH and 0.8 mol dm^{-3} sorbitol solution as the eluent, identical analytical performances have been obtained, in terms of calibration parameters, precision and detection limit. This fact is reasonably related to the close values of thermodynamic constants both for the complexes formation and for the hydrolysis (pK_a) equilibria. Nevertheless the lower retention time observed for the sorbitol–borate complex $B(H_{-2}L)_2^-$ (3.5 min *vs.* 3.7 min obtained with mannitol, Fig. 3) reveals the different chromatographic behaviour of the two complexes on the specific column probably induced by non-ionic interactions. As a practical consequence, the sorbitol-based eluent gives a better chromatographic resolution with respect to fluoride and acetate.

Analysis of real samples

The method has been applied to the simultaneous determination of borate and chloride or fluoride in three different aqueous samples of pharmaceutical relevance, with declared composition. The results, reported in Table 1, are compared with those obtained by the standard volumetric methods. The very good agreement between the results, stated by the *t*-test and *F*-test used for the comparison between the different experimental results, suggests absence of bias in the proposed method.

Conclusions

The proposed analytical method allows a rapid and accurate determination of borate and other anions in aqueous matrices with a conventional chromatographic instrumentation. The described method is characterised by the high quality of the results in terms of low detection limit and accuracy as demonstrated by the comparison with the values of known composition samples. Finally, the possibility to easily automate the procedure makes it a good proposal for routine analysis.

Table 1 Comparison of experimental results obtained by ion chromatographic method*

Contact lens solution Ciba Vision SoftWear—

	$[B(OH)_3]$/mol dm^{-3}	$[Cl^-]$/mol dm^{-3}
Declared value	0.084	0.114
Chromatographic method	0.084 ± 0.003	0.114 ± 0.002
Volumetric method	0.082 ± 0.001	0.114 ± 0.003
t_1 (n = 10)	0.43 (2.23)	0.00 (2.23)
t_2 (n = 8)	0.00 (2.31)	0.00 (2.31)
F	9.00 (39.37)	2.25 (6.06)

Contact lens solution Clerz—

	$[B(OH)_3]$/mol dm^{-3}	$[Cl^-]$/mol dm^{-3}
Declared value	0.023	0.171
Chromatographic method	0.027 ± 0.001	0.177 ± 0.003
Volumetric method	0.028 ± 0.001	0.176 ± 0.003
t_1 (n = 10)	0.60 (2.23)	0.30 (2.23)
t_2 (n = 8)	4.00 (2.31)	2.00 (2.31)
F	1.00 (39.37)	1.00 (6.06)

Thermal spring water, 'Acqua di Sirmione' Terme di Sirmione SpA—

	$[B(OH)_3]$/mmol dm^{-3}	$[F^-]$/mmol dm^{-3}
Declared value	0.47	0.226
Chromatographic method	0.45 ± 0.01	0.222 ± 0.003
t_2 (n = 8)	2.00 (2.31)	1.31 (2.31)

* Uncertainty reported as standard deviation. $t_1 : t_{0.05/2}$, ion chromatographic results/volumetric results. $t_2 : t_{0.05/2}$, ion chromatographic results/declared values. $F_{0.05/2}$, ion chromatographic method/volumetric method. Critical $t_{0.05/2}$ and $F_{0.05/2}$ values in parenthesis.

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