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Determination of inorganic and small organic anions in pure boric acid using capillary zone electrophoresis

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Abstract

Inorganic and small organic anions were determined in pure boric acid using an on-line process for removal of the boric acid matrix from the capillary by adjusting the pH of the electrolyte and the electroosmotic flow. Employing this procedure, the matrix has no further influence on the separation and the analytes can be detected up to analyte-to-matrix ratios (ATMR) of $1:5 \cdot 10^5$ to $1:4 \cdot 10^5$ using hydrostatic injection. The limits of detection of the analytes were improved by on-line preconcentration procedures such as electrokinetic injection and sample stacking, resulting in an increased ATMR of $1:1 \cdot 10^7$ to $1:3 \cdot 10^7$ for sample stacking. These optimized conditions were applied to analyse two different batches of boric acid for impurities.

1. Introduction

The determination of inorganic anions in real samples containing a large excess of a matrix component is a fundamental analytical problem, which is becoming more and more important also for capillary zone electrophoretic (CZE) applications [1–3]. Recently, it has been shown that a matrix effect can be an advantage in comparison with a common CZE separation because a stacking process can occur, resulting in increased plate numbers for the analytes [3–6]. Thus, the matrix ion can act as the leading or the terminating species in an initial isotachophoretic state. The co-ion of the electrolyte has to be chosen in such a way that the mobilities of the analyte ions are between those of the electrolyte and the matrix ion.

Using this method, the inorganic anions can be determined in the presence of a fluoride matrix up to an analyte-to-matrix ratio (ATMR) of $1:6 \cdot 10^4$ [3]. Above this value, overlapping of the analyte peaks by the matrix peak occurs. With a non-ionic matrix, the matrix cannot co-migrate with the analyte ions and, further, it is not able to influence the isotachophoretic initial state.

Another difference between a non-ionic matrix and an ionic matrix is the possibility of using preconcentration methods for the analyte ions such as electrokinetic injection or sample stacking because the matrix does not contribute to the conductivity of the sample. Thus, the limit of detection (LOD) and the ATMR can be improved.

A disturbance of the CZE separation could happen only if the matrix component is moved by the electroosmotic flow (EOF) in the same direction as the analytes. Then, the different viscosity between the sample zone and the electrolyte, memory effects at the capillary wall and increased diffusion effects due to the high con-

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centration gradient could influence the baseline and the migration times.

Therefore, with a non-ionic matrix the EOF should be adjusted in the opposite direction to the analyte ions. Hence the matrix will be removed from the capillary at the beginning of the separation and the analytes can be detected without matrix effects (see Fig. 1).

The dissociation of a number of matrices is strongly dependent on the pH of the solution. By choosing the pH of the electrolyte in such a way that the dissociation of the compound is decreased, the above-mentioned procedure is applicable to the determination of the ionic impurities in the substance. The purpose of this paper is to demonstrate the determination of inorganic and small organic anions in non-ionic matrices, e.g., in industrial chemical boric acids as matrix.

2. Experimental

The separations were carried out using a laboratory made CZE system and conventional untreated fused-silica capillaries (CS Chromatographie Service, Langerwehe, Germany). For detection the separation capillary passed through a Dionex (Sunnyvale, CA, USA) variable-wavelength UV detector and its outlets were placed in two 10-ml electrolyte vials. The high voltage from a 30 kV power supply (F.u.G. Electronic, Rosenheim, Germany) was applied with Pr–Ir electrodes dipping into the electrolyte. The positive electrode was placed in the outlet vessel.

Data were processed by an A/D board from ERC (Alteglofsheim, Germany) using APEX chromatography software (Autochrom, Milford, MA, USA). The absorbance units (AU) of the detector were transformed by the A/D board into μV, and therefore the output of the data was in the voltage mode (19 V = 1 AU).

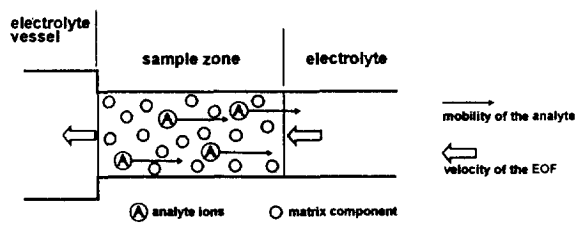

Fig. 1. Schematic illustration of the on-line matrix removal process.

2.1. Chemicals

All solutions, electrolytes and standards were prepared with ultra-pure water obtained from a Milli-Q system (Millipore, Eschborn, Germany). For the preparation of the electrolyte, sodium chromate and tetradecyltrimethylammonium bromide (TTAB) was used (Aldrich-Chemie, Steinheim, Germany). Boric acid was obtained from different companies in several purity grades. All other reagents were of analytical-reagent grade from Merck (Darmstadt, Germany).

3. Results and discussion

3.1. Optimization of electrolyte composition

In order to detect UV-inactive ions, the indirect detection mode [7–10] using a UV-active background electrolyte should be applied. To measure several inorganic and organic anions in the presence of boric acid, the pH of the electrolyte and the EOF additionally have to be optimized.

Depending on the pH of the electrolyte, boric acid exists as different dissociated species. As boric acid behaves as a weak acid in aqueous solutions (pK_a 9.14, 12.74 and 13.80 [11]), at pH > 9 it is strong dissociated and can cause the above-mentioned matrix effects. At pH < 9 boric acid is not sufficiently dissociated and it can move only by the EOF. Therefore, the pH of the electrolyte should be <9.

To shorten the analysis time for the determination of anions by reversing the EOF, a modifier (e.g., TTAB or CTAB) [12–14] is commonly applied as an additive to the electrolyte. Fig. 2a shows an electropherogram obtained using a chromate electrolyte at pH 8.1 with 0.2 mmol/l TTAB. It can be seen that the analyte peaks can

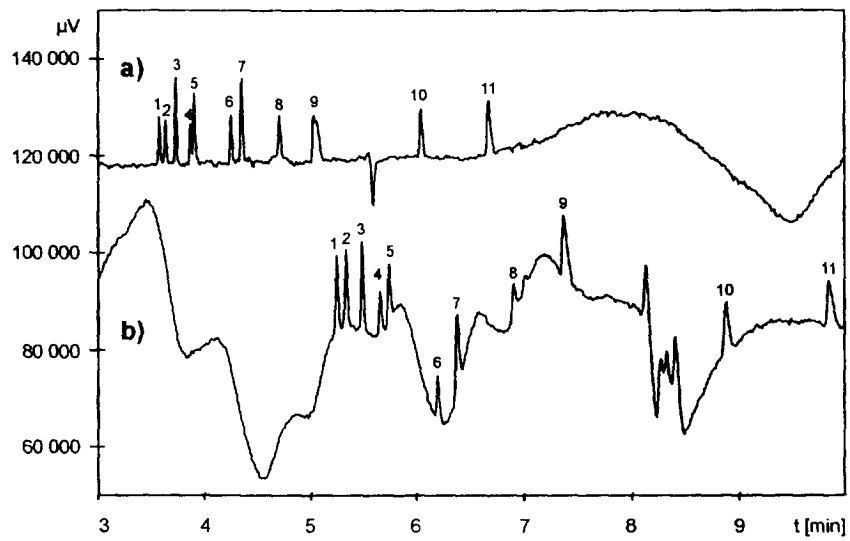

Fig. 2. Electropherograms of an anion mixture. (a) Anionic mixture without boric acid. (b) Anionic mixture with a 0.9 mol/l boric acid matrix. Electrolyte, 5 mmol/l sodium chromate–0.2 mmol/l TTAB (pH 8.1); samples: 1 = bromide; 2 = chloride; 3 = sulfate; 4 = nitrate; 5 = oxalate; 6 = chlorate; 7 = malonate; 8 = fluoride; 9 = phosphate; 10 = acetate; 11 = propionate; sample concentration, each 25 μmol/l; injection, hydrostatic (10 cm, 30 s); capillary, 70 cm to the detector, 85 cm total length, 75 μm I.D.; detection, indirect UV, 254 nm; EOF, in the same direction as the analytes, $v_{EOF} = -0.05$ cm/s.

be determined in short times and with a stable baseline. On the other hand, for a boric acid sample (0.9 mol/l) to which an anionic standard was added (see Fig. 2b), baseline interferences and longer migration times resulted using the same experimental conditions as in Fig. 2a. The reason for this effect is that for this modifier concentration the EOF and, therefore, also the matrix are moving in the same direction as the anions and so matrix effects can occur.

Therefore, it is necessary to adjust the EOF in the opposite direction to that of the analytes. Optimizing the electrolyte system by changing the concentration of the TTAB modifier, a reversal of the EOF takes place at a TTAB concentration of 0.07 mmol/l. Without the modifier the migration times of the analytes would be longer than 15 min. At a TTAB concentration of 0.01 m*M* the EOF is directed opposite to the anions but slowed down to obtain acceptable analysis times.

Fig. 3 shows two electropherograms of anions, (a) without and (b) with a matrix of boric acid, obtained using these optimized conditions. no difference concerning the baseline and migration times can be seen between the two electropherograms because the matrix is removed from the capillary by the EOF and no matrix effect can occur.

It can be seen that the peak heights are comparable in both electropherograms, except for the chloride peak. This can be explained by chloride contamination of the boric acid used. A disadvantage of these experimental conditions is that acetate and propionate cannot be detected because of their slow mobility.

3.2. Determination of the blank value of boric acid using different injection techniques

Fig. 4 shows the electropherograms of 0.9 mol/l boric acid obtained using three different injection methods. Owing to the small injection volume and the low concentration of the sample, the LOD for the hydrostatic injection is relatively high. As can be seen in Fig. 4a, only chloride can be determined using hydrostatic injection. It is therefore not recommended to use this method for trace analysis.

In order to decrease the LOD, the sample had

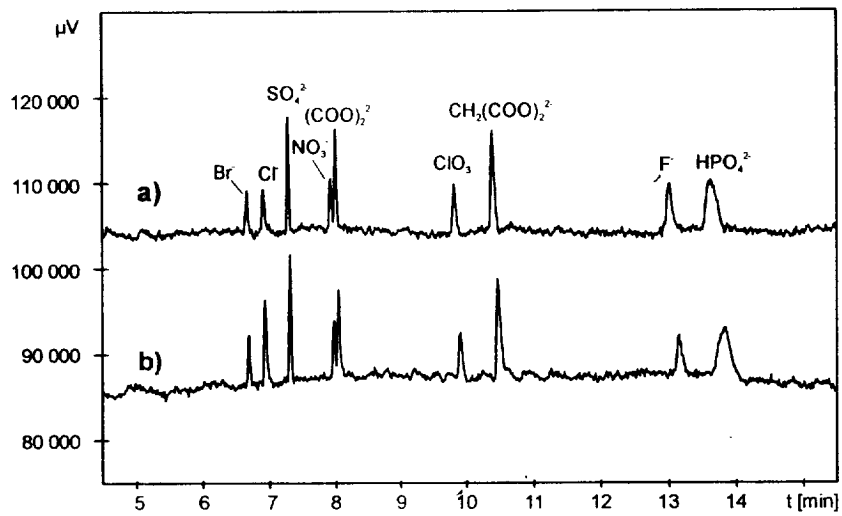

Fig. 3. Electropherograms of an anion mixture. (a) Anionic mixture without boric acid. (b) Anionic mixture with a 0.9 mol/l boric acid matrix. Electrolyte, 5 mmol/l sodium chromate–0.01 mmol/l TTAB (pH 8.1); EOF, in the opposite direction to the analytes, $v_{EOF} = +0.12$ cm/s; all other conditions as in Fig. 2.

to be enriched by electrokinetic injection or by sample stacking [15,16]. Electrokinetic injection as a preconcentration method (see Fig. 4b) allows an improvement of the LOD of the fast analyte ions by a factor of 15. Thus, additionally to chloride also other analytes such as sulfate, nitrate, oxalate and hydrogenphosphate can be detected. Disadvantages of this method are the discrimination of ions having a low mobility, the dependence of the enrichment factor on the conductivity of the sample and the necessity for a correcting calculation using two internal standards [17] to quantity the results.

Another on-line preconcentration method by which the LOD can be improved is sample stacking. Sample stacking was performed by filling the capillary with the sample up to the detector, resulting in a sample volume of 2.6 μl. After applying the high voltage, the analyte ions migrate rapidly toward the boundary between the sample and electrolyte. Simultaneously, the reverse-directed EOF removes the stacked cations and the water plug from the capillary. When the water plug leaves the capillary, a uniform field strength is reached and the current increases from zero to the common separation level. Then the CZE separation begins without switching the polarity. The results of sample stacking are shown in Fig. 4c.

The main advantage is the very low LOD for all analyte ions. The amount of sample is increased by a factor of nearly 200 compared with hydrostatic injection, allowing an improvement of the LOD by a factor of 200 also, and also bromide can be determined. Further, there are no discriminating effects for slow analyte ions as observed in the electrokinetic injection method. A disadvantage of the stacking process with a boric acid sample is that the EOF takes 10.5 min to remove the boric acid from the capillary, whereas a water plug of a sample without matrix is removed after 5.3 min (not shown). Therefore, long analysis times and peak broadening occur, especially for the slow analytes fluoride and hydrogenphosphate in the presence of a boric acid matrix. The explanation of this effect is the high viscosity and the low pH (pH 3.5 of 0.9 *M* boric acid) of the boric acid solution. Both parameters decrease the EOF in the part of the capillary filled with the boric acid solution. In spite of these disadvantages, sample stacking is preferred because analyte discrimination does not take place and peak correction is not necessary.

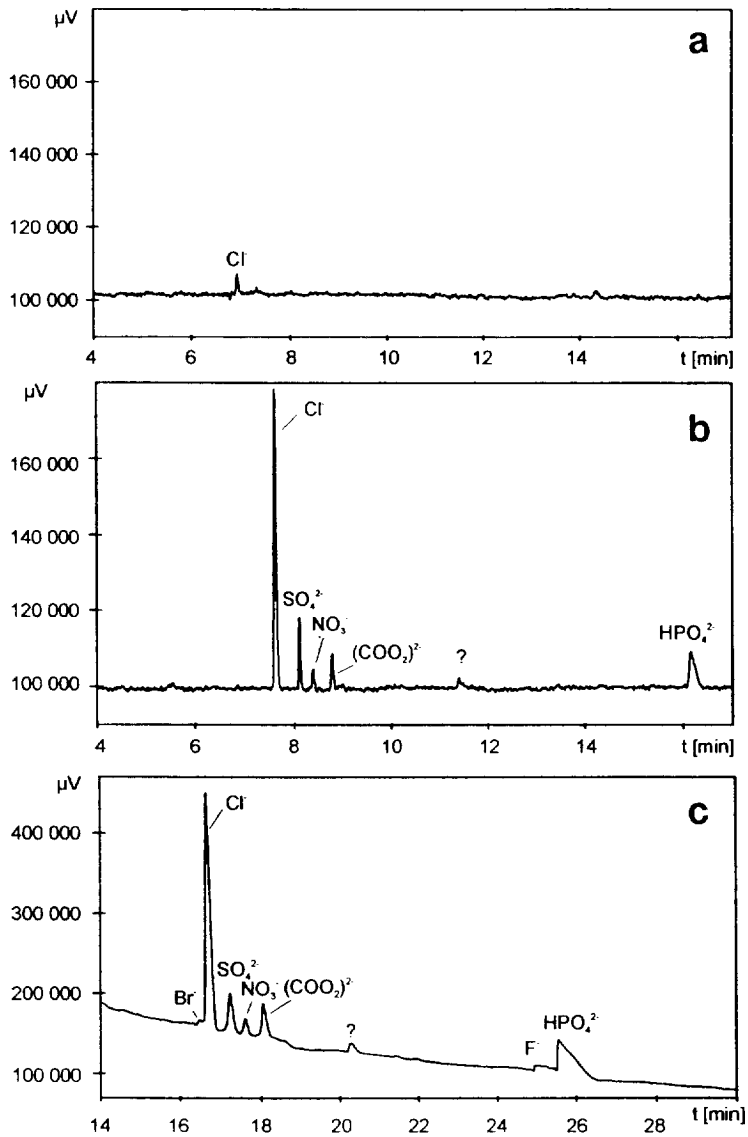

Fig. 4. Determination of the blank value of a commercially available boric acid of technical grade using different injection techniques. (a) Boric acid 2 using hydrostatic injection (10 cm, 30 s); (b) boric acid 2 using electrokinetic injection (3 kV, 10 s); (c) boric acid 2 using sample stacking (hydrodynamic injection up to the detector, sample volume 2.6 μl, duration of the stacking process 10.5 min). Electrolyte, 5 mmol/l sodium chromate–0.01 mmol/l TTAB (pH 8.1); sample, 0.9 mol/l boric acid 1 without addition of anions; all other conditions as in Fig. 3.

In Table 1, the LOD and the ATMR for the different injection methods are summarized. The values with sample stacking are better than those for hydrostatic injection and electrokinetic injection. With sample stacking an LOD in the low nmol/l region is achieved.

To apply the developed CZE method, the blank values of two boric acids from different companies were measured. For this purpose the boric acid was dissolved in pure water. According to its solubility, a maximum concentration of 0.9 mol/l was achieved. To determine the impurities, the standard addition method was carried out. In this way, systematic errors caused by

Table 1
Comparison of different injection techniques for samples with boric acid matrix

Anion	Hydrostatic injection		Electrokinetic injection		Sample stacking	
	LOD[a] (μmol/l)	ATMR	LOD[a] (μmol/l)	ATMR	LOD[a] (μmol/l)	ATMR
Bromide	8	$1:1.1\cdot10^5$	0.3	$1:2.7\cdot10^6$	0.07	$1:1.2\cdot10^7$
Chloride	7	$1:1.3\cdot10^5$	0.5	$1:1.7\cdot10^6$	0.04	$1:2.1\cdot10^7$
Sulfate	5	$1:1.8\cdot10^5$	0.2	$1:3.8\cdot10^6$	0.02	$1:3.5\cdot10^7$
Nitrate	7	$1:1.3\cdot10^5$	0.3	$1:2.8\cdot10^6$	0.04	$1:2.2\cdot10^7$
Oxalate	5	$1:1.8\cdot10^5$	0.4	$1:2.1\cdot10^6$	0.03	$1:2.8\cdot10^7$
Chlorate	7	$1:1.3\cdot10^5$	0.4	$1:2.2\cdot10^6$	0.05	$1:1.5\cdot10^7$
Malonate	5	$1:1.8\cdot10^5$	0.4	$1:2.0\cdot10^6$	0.05	$1:1.7\cdot10^7$
Fluoride	10	$1:0.9\cdot10^5$	0.7	$1:1.2\cdot10^6$	0.89	$1:9.0\cdot10^5$

Experimental conditions as in Fig. 4c.
[a] The LOD was defined as three times the signal-to-noise ratio.

different migration times of samples with and without a matrix of boric acid can be prevented. The results are summarized in Table 2. It can be seen that the results achieved conform to the specified purities (boric acid 1 = analytical-reagent grade, boric acid 2 = technical grade).

4. Conclusion

It has been shown that the combination of an electrophoretic separation with an on-line process for the removal of a non-ionic matrix is a very effective approach for improving the detectability of the anions. Using ion chromatography as separation method, an automated sample preparation step can be applied to prevent baseline disturbances due to the boric acid matrix. In this case, removal of the matrix in addition to preconcentration of the analytes [18] takes place.

In the described CZE method a similar result occurs, because the matrix is removed by the reverse-directed EOF and, simultaneously, the analytes are concentrated by the stacking procedure. An advantage of the latter method is the on-line procedure without variation of the CZE device. Using the CZE method, the anionic impurities in two different boric acids were determined. For the anions in a 0.9 mol/l solution of boric acid an LOD of 5–10 μmol/l is obtained with hydrostatic injection. On enriching the analytes by electrokinetic injection or sample stacking, the LOD is improved by a factor 15 or 200, respectively, in comparison with hydrostatic injection. It can be assumed that the described

Table 2
Blank values (μmol/l) for two different boric acids

Sample	Bromide ($r^2 = 0.9885$)	Chloride ($r^2 = 0.9427$)	Sulfate ($r^2 = 0.9980$)	Nitrate ($r^2 = 0.9909$)	Oxalate ($r^2 = 0.9872$)
Boric acid 1 (analytical-reagent grade)	1.1	4.2	0.9	1.5	0.4
Boric acid 2 (technical grade)	0.9	23.1	2.2	1.4	2.3

r^2 = Regression coefficient of the calibration line. For the electropherogram of boric acid 2, see Fig. 4c; for boric acid 1, no electropherogram shown.

method is applicable to all samples with neutral matrices and to matrices with low mobility. In the latter case, the matrix can influence the isotachophoretic state. Then, in addition to the pH of the electrolyte and the EOF, the mobility of the co-ion of the electrolyte also has to be considered.

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