Conductimetric detection of anions of very weak acids by incomplete suppressed ion chromatography

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Abstract

A novel method, incomplete suppressed conductimetric detection, has been developed for the determination of anions of very weak acids. The principle of the method was discussed. Theoretical considerations involved the choice of background conductance and its effect on linearity and detection limits. Results showed that for both arsenous acid and boric acid, the sensitivity was improved greatly with low background conductance, compared with the suppressed conductimetric method. With 250 mg/l boric acid, there were 261- and 1002-fold increases in peak height and peak area, respectively. Within the linear range of the detection, quantified by peak areas, the linear correlation coefficients were 0.9991 and 0.9985 for arsenous acid and boric acid, respectively. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Anions; Boric acid; Arsenous acid; Very weak acids

1. Introduction

In ion chromatography, suppressed conductimetric detection is the most popular method applied by virtue of its high sensitivity and universal properties. For anions, they are always converted into their conjugated acids. By doing this, on the one hand, the noise of the system, which is directly proportional to the background conductance, is greatly reduced. On the other hand, because of the high equivalent conductance of hydronium ion, the analyte signal is greatly enhanced [1]. For strong acids, it is an advantage, but weak acids are weakly ionized and give a lower detector response.

Several novel approaches have been reported in attempts to overcome the weak acid anion problem [2–12]. Rocklin et al. [2] used ion-exclusion chromatography. At present, many methods have been reported based on ion conversion as a means of improving the detection of weak acids in chemically suppressed ion chromatography (IC). Tanaka and Fritz [3] obtained about a ten-fold increase in sensitivity for carbon dioxide and bicarbonate using two ion-exchange 'enhancement' columns in series to convert carbonic acid first to potassium bicarbonate and then to potassium hydroxide. Berglund and Dasgupta [4,5] converted anions first to weak acids and then converted acids to salts using a laboratory-made membrane converter, obtaining a signal that was more than one order of magnitude greater. Another successful approach was first converting anions to acids and then reintroducing NaOH to convert weak acids back to a more conducting salt

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[6–9]. This novel approach provided µg/l levels of detection. Caliamanis et al. [12] obtained a great increase in the sensitivity for boric acid by first converting anions to acids and then using EDTA at pH 11 as an ion replacement reagent to convert it to the salt.

Nonsuppressed conductimetric detection can be used for the determination of weak acids, usually with some kind of basic solution as the eluent. By using an appropriate anion-exchange resin of low capacity, Fritz et al. [13] successfully separated and detected anions by nonsuppressed conductimetric detection, using sodium hydroxide and sodium phenenolate as eluents [13]. Okada and Kuwamoto [14–17] used potassium hydroxide solution as an effective eluent for nonsuppressed anion chromatography; for weak acids, detection limits can reach to 0.1 mg/l.

The usage of potassium hydroxide in nonsuppressed IC has two advantages. First, it is sensitive because of the large ion equivalent conductance of hydroxide ion and, second, weak acids, such as phenol and silicic acid, can be determined since the separation and detection are carried out in a basic solution. However, only eluents of low concentration can be used because of the noise caused by high background conductance [17].

In this paper, we report preliminary experiments and theoretical discussion on the feasibility of a novel approach for the determination of very weak acids using a commercial micromembrane suppressor and a low concentration regenerant. Relatively more concentrated hydroxide ion can be employed as the eluent with low background conductance while the analyte ions were detected as negative peaks. Compared with methods based on ion conversion, only one commercially available suppressor was used. Thus, both the dilution effect caused by post-column reaction and the band dispersion due to the employment of more than one suppressor were reduced.

2. Experimental

2.1. Chemicals

All reagents used were of analytical reagent grade unless specified otherwise. Distilled deionized water was used throughout. All solutions were filtered through a 0.45-µm membrane filter and degassed before use. An arsenous acid stock solution (1 g/l, expressed as As_2O_3) was prepared by dissolving 0.1 g of arsenous trioxide (As_2O_3, JMC 642 specpure, Johnson Mattey) in 4 g/l sodium hydroxide, and then diluting it to 100 ml. Boric acid stock solution (1 g/l) was prepared by dissolving appropriate amounts of boric acid (high purity, Beijing Xinguang Chemical Reagent Factory, China) in deionized water. Standard solutions were prepared daily by serial dilution of the stock solution prior to use. The mobile phases used were 1 and 4 mmol/l NaOH for arsenous acid and boric acid, respectively. The regenerants used were 0.1 and 0.4 mmol/l H_2SO_4 for the two acids, respectively.

2.2. Apparatus

A Dionex Model DX-500 ion chromatograph (Sunnyvale, CA, USA), equipped with a 10-µl sample loop was employed along with a Dionex PeakNet chromatography workstation for instrument control as well as data acquisition and processing. A Dionex AG11 guard column and an AS11 separation column were used. Detection was performed by a Dionex ED40 electrochemical detector in conductivity detection mode. Incomplete chemical suppression was achieved by a Dionex ASRS-I micromembrane suppressor. A Dionex Model DQP-1 pump was employed to pump the regenerant to the suppressor.

2.3. Procedures

For arsenous acid, the eluent and regenerant were 1 mmol/l NaOH and 0.1 mmol/l H_2SO_4, respectively. For boric acid, the eluent and regenerant were 4 mmol/l NaOH and 0.4 mmol/l H_2SO_4, respectively. Flow-rates of both eluents were 1.0 ml/l. The flow-rate of the regenerant was varied until the background conductance was between 35 to 40 µS, and this flow-rate was then maintained. Injection was initiated after a steady baseline was obtained.

3. Results and discussion

3.1. Theory

Incompletely suppressed IC uses NaOH as the eluent. By using regenerant of low concentration (a concentration of about one tenth of that of the eluent) in the suppressor, the background conductance is greatly reduced. However, as hydroxide ions in the sample peak are not completely neutralized by the regenerant, most of the analyte anions exist in anionic form, whose equivalent conductances are lower than that of hydroxide ion, therefore, the analyte ions are detected as negative peaks (see Fig. 1).

The relationship between conductivity responses and the concentrations of analyte can be deduced as follows. The additional assumptions are implicit in this expression [1]:

1. The Kohlrausch law of independent mobilities is applied. This is legitimate in view of the low concentrations that are common to IC ($<10^{-3}$). The use of limiting conductances is justified on the same grounds.
2. The cell constant is 1 cm^{-1}.
3. The unit of concentration is mol/l.

Considering that NaOH is used as the eluent. After being suppressed, its conductivity response, denoted as G_B, is then given as
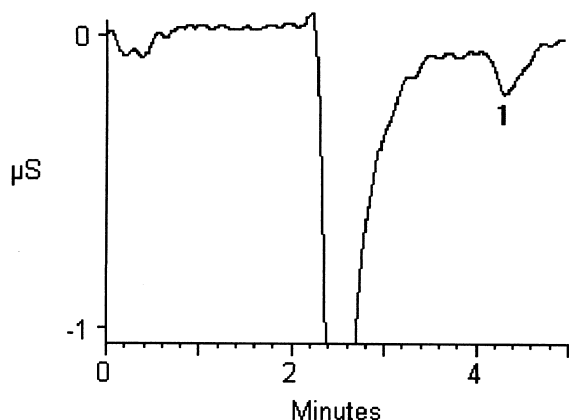

Fig. 1. Chromatograms of 5 mg/l arsenous acid by the incompletely suppressed IC method. 1, arsenous acid.

$$G_B = 1000C_E(\lambda_{Na^+} + \lambda_{OH^-})\mu S \qquad (1)$$

where C_E is the concentration of the eluent after being suppressed, λ_{Na}^+ and λ_{OH}^- are the limiting equivalent conductances of sodium and hydroxide ions, respectively.

Since the flow-rates and concentrations of both eluent and regenerant are fixed, when exchange equilibrium in the suppressor between Na$^+$ and H$^+$ is reached, the concentration of sodium ions after passing the suppressor (C_E) is also fixed. Therefore, the sum of the concentrations of analyte and eluent anions in the sample peak must likewise equal C_E, so as to obey electroneutrality demands. Consequently, if the concentration of analyte anion at its peak is $C_S I_S$, it follows that the concentration of hydroxide ion at that point is

$$[OH^-] = C_E - C_S I_S \qquad (2)$$

Therefore, the conductance at the peak of S$^-$, denoted G_S, is the sum of the contribution of all of the ions present at that point and is given by

$$G_S = 1000(C_E\lambda_{Na^+} + (C_E - C_S I_S)\lambda_{OH^-} + C_S I_S \lambda_{S^-})\mu S \qquad (3)$$

where C_S is the concentration of analyte at its peak, I_S is the fraction of anion form in analyte, which is denoted as

$$I_S = [S^-]/([S^-] + [HS]) \qquad (4)$$

where $[S^-]$ and $[HS]$ are the concentrations of analyte anion and its conjugated acid, respectively. It follows that the change in conductance at the peak, ΔG, is then

$$\Delta G = G_S - G_B = 1000C_S I_S(\lambda_{S^-} - \lambda_{OH^-})\mu S \qquad (5)$$

Under conditions where variation of the value of I_S is small enough, the magnitude of the response is therefore proportional to the concentration of the analyte.

3.2. Choice of background conductance

Choosing the proper background conductance is rather complicated. As regards the signal-to-noise ratio, the background conductance should be as low as possible to reduce the noise of the system.

However, with the decrease of the background conductance, the magnitude of the analyte signal will also decrease, which will possibly, in turn, decrease the signal-to-noise ratio of the system. In addition, if the background conductance is too low, I_S will vary considerably with C_S, which will seriously distort the linear relationship between ΔG and C_S.

In order to study the effect of C_E on the linearity and detection limits, a computer-simulated experiment was performed as follows:

From the dissociation equilibrium of HS, the concentration of HS can be given by the expression:

$$[HS] = ([S^-][H^+])/K_a \qquad (6)$$

Combining Eqs. (4) and (6), I_s is therefore given by

$$I_S = K_a/(K_a + [H^+]) \qquad (7)$$

where K_a is the dissociation constant of HS and $[H^+]$ is the concentration of hydronium ion in the sample peak. In the linear–ideal case, the peak shape can be described by a normal or Gaussian distribution function [18], thus, the concentration of analyte in the center of the sample peak can be calculated using Eq. (8)

$$C_S = M/(F\sigma_t(2\pi)^{0.5}) = V_0 C_0/(F\sigma_t(2\pi)^{0.5}) \qquad (8)$$

where M is the mass of the analyte, C_S is the concentration of analyte in the center of sample peak and σ_t is the standard variation of the peak. The volume of the injection loop is denoted as V_0 and C_0 is the injection concentration of the analyte, thus, values of C_S for different values of C_0 can be calculated using Eq. (8). The parameters are assumed to be as follows: $V_0 = 10$ µl, $\sigma_t = 25$ s, $F = 1$ ml/min and the values of C_0 are 0.1, 1.0, 2.0, 4.0, 8.0 and 10 mmol/l, respectively.

According to the dissociation equilibrium of water, we have

$$[H^+] = k_w/[OH^-] \qquad (9)$$

where k_w is the dissociation constant of water, and

$[H^+]$ and $[OH^-]$ are the concentrations of hydroxide ion and hydronium ion in the sample peak, respectively. Combining Eqs. (2) and (7) with Eq. (9), one obtains

$$K_a C_s I_S^2 - (k_w + K_a C_E + K_a C_s)I_S + K_a C_E = 0. \qquad (10)$$

From Eq. (10), I_S can be calculated by the Newton–Raphson procedure [19]. By including the value of I_S in Eq. (5), the conductance response can then be calculated. Since the dissociation constants of boric acid and arsenous acid are 9.27 and 9.29, respectively [20], K_a is assumed to have a value of 9.28. Values of C_E are assumed to be 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.10, 0.20, 0.50 and 1.00 mmol/l, respectively. The values of λ_S^-, λ_{OH}^- and λ_{Na}^+ were assumed to be 60, 198 and 50, respectively. The results of the simulated experiment are discussed in Section 3.2.1 Section 3.2.2.

3.2.1. Effect of C_E on the linearity of the conductance response

Table 1 shows the effect of C_E on the linear correlation coefficients between the conductance response and the injection concentration according to the results of the simulated experiment. It shows that only when the concentration of hydroxide, after being suppressed (C_E), is above 0.2 mmol/l, are the conductance responses proportional to the injection concentrations of the sample (with the linear coefficient reaching 1.000).

3.2.2. Effect of C_E on the detection limits of the method

Since the signal-to-noise ratio is always used to evaluate the detection limits of a system [21], and since the noise is proportional to the background conductance, the signal-to-background conductance ratio was used to study the effect of C_E on the detection limits. Fig. 2 shows the effect of C_E on the magnitude of the signal-to-background conductance ratio according to the results of the simulated

Table 1
Effect of C_E on linear correlation coefficients between the conductance response and the injection concentration (from 0.001 to 1.0 mmol/l)

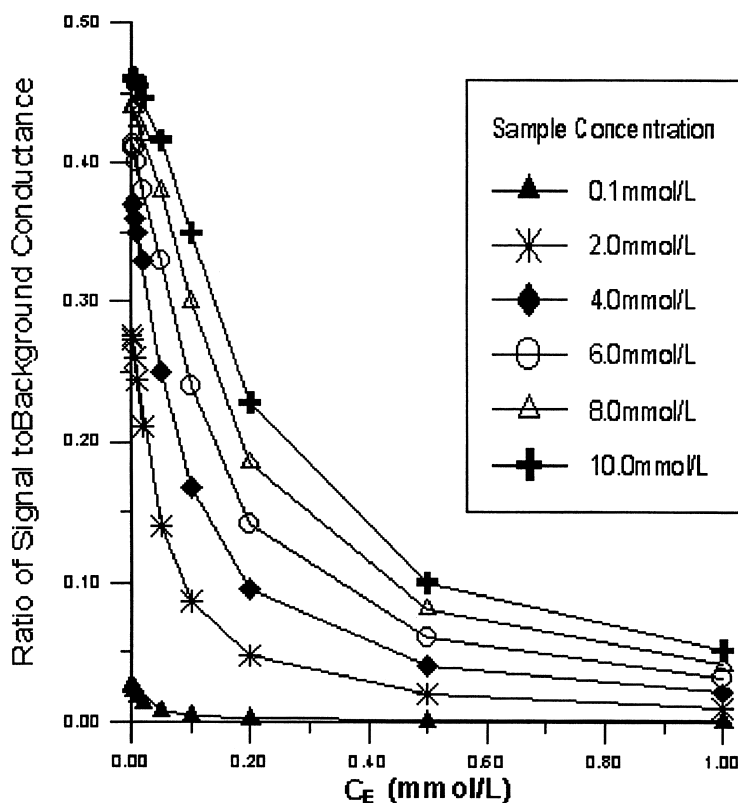| C_E (mmol/l)	0.001	0.002	0.005	0.01	0.02	0.05	0.10	0.20	0.50	1.00
Correlation coefficient	0.8889	0.8868	0.8950	0.9084	0.9708	0.9729	0.9955	1.000	1.000	1.000

Fig. 2. Effect of C_E on the magnitude of the signal-to-background conductance ratio.

experiment. It shows that the signal-to-background conductance ratio increased with decreasing values of C_E. From this, it appears that better detection limits can be obtained by reducing the background conductance indefinitely, but there are two sides to everything: Fig. 3 shows the effect of C_E on the magnitude of the signal according to the results of the simulated experiment. It was shown that the signal sharply decreased when C_E values were lower than 0.2 mmol/l. It follows that if the background conductance is too low ($C_E < 0.2$ mmol/l), there will be two results:

1. With the decrease in the background conductance, the signal of the analyte will be too weak for the detectors to detect, which will directly worsen the detection limits in a real detection system.
2. Since the signal decreased sharply with decreasing background conductance, a slight fluctuation in the background conductance will result in a

large fluctuation of the signal, which will worsen the repeatability of the method.

From the discussion above, two conclusions can be drawn:

1. Considering the effect of C_E on the signal-to-noise ratio, the background conductance should be as low as possible.
2. Considering the effect of C_E on linearity, repeatability and the magnitude of the signal, the background conductance should be higher than 0.2 mmol/l.

As in real experiments, when C_E was 0.2 mmol/l, the background conductance was about 35 μS, therefore, 35–40 μS was chosen as the background conductance for these two acids.

3.3. Comparison with suppressed IC

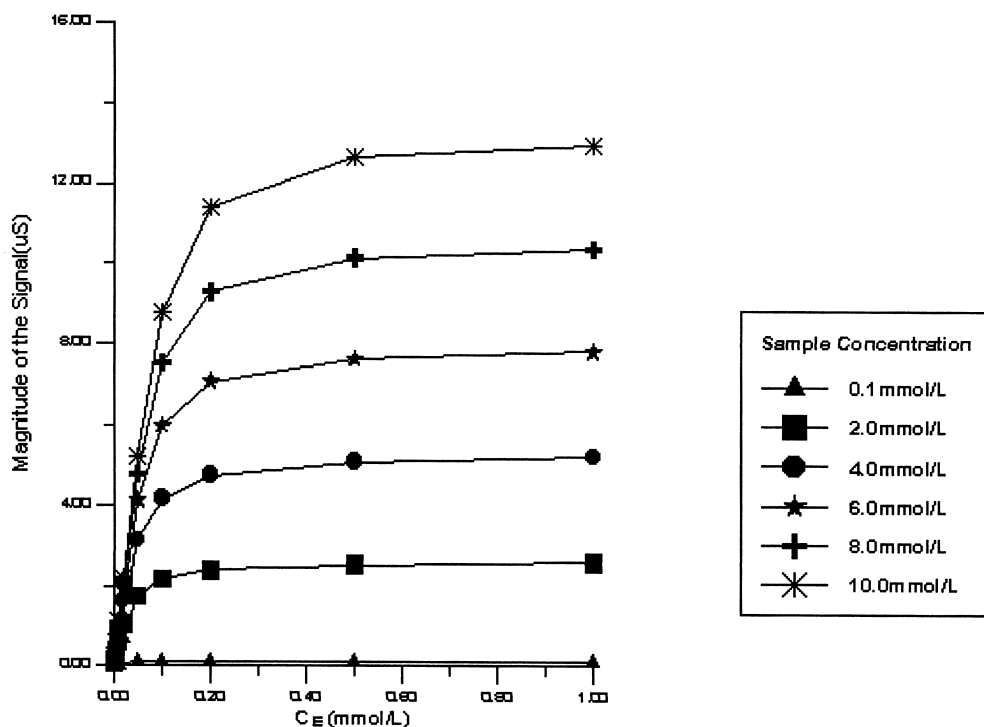Theoretically, great increases in signal can be

Fig. 3. Effect of C_E on the magnitude of the signal.

obtained by the incomplete method. In the suppressed method, because of the small amount of impurities that are inevitable in the eluent reagent and some slight leakage from the suppressor, low background conductance always exists [1]. This means that sodium cations cannot be exchanged completely by the regenerant. Assuming that the remaining concentration of sodium cations after suppression is C_E, deduction of ΔG can be discussed as follows:

(I) $C_E > C_S I_S$: In this case, eluent anions (hydroxide ions) will not be neutralized completely by regenerant in the sample peak. Therefore, the deduction of ΔG is the same as that in the incomplete mode and can also be expressed by Eq. (5). However, small values of C_E will not only lead to a narrow dynamic range for detection, but will decrease the signal, as discussed in Section 3.2.

(II) $C_E < C_S I_S$: In this case, the eluent anions (hydroxide ions) in the sample peak are neutralized completely by regenerant and some of the analyte anions are converted to their conjugated acids. Regardless of the hydronium and hydroxide ions generated by the dissociation of water, the cations at the sample peak are sodium ion and hydronium ion generated by conjugated acid, while the anion is analyte anion whose concentration at its peak is given by $C_S I_S$. To obey electroneutrality demands, the concentration of hydronium ion at the sample peak is $C_S I_S - C_E$. Therefore, the conductance at the sample peak is given by

$$G_S = 1000(C_S I_S \lambda_{S^-} + \lambda_{Na^+} C_E + (C_S I_S - C_E)\lambda_{H^+})\mu S$$

(11)

By combining Eqs. (1) and (11), one gets

$$\Delta G = 1000 C_S I_S (\lambda_{S^-} + \lambda_{H^+})$$
$$- 1000(\lambda_{OH^-} + \lambda_{H^+})C_E \mu S \qquad (12)$$

For strong acids, signals are positive peaks because of the large value of I_S, while for weak acids, the

value of I_S is so small that only when C_S is large enough, can positive peaks be observed. For boric acid, positive peaks were observed by the suppressed method in our experiment when concentrations were higher than 100 mg/l. For arsenous acid, only negative peaks were observed in the range of 10 to 200 mg/l. As the dissociation constants of the two acids are close to each other (9.27 and 9.29, respectively), the difference between negative and positive peaks might be caused by the difference in the equivalence conductance of the two anions.

(III) There is also a possibility that $C_E < C_S I_S$ and, at the same time, the dissociation of water cannot be ignored. In this situation, as the conductance of hydronium or hydroxide ion resulting from the dissociation of water cannot be ignored, and as neither of their concentrations is proportional to the concentration of analyte, the conductance response will not be proportional to the concentration of analyte and, thus, cannot be used in quantitative analysis. This is not discussed in detail in this paper.

The conductivity responses expressed as ratios of peak height and peak area obtained by incompletely suppressed IC (according to the procedures described in Section 2.3) to those obtained by suppressed IC in real experiments are shown in Table 2. It was shown that, compared with suppressed IC, great increases in both peak height and peak area were obtained for both arsenous acid and boric acid. From Table 2, it was shown that, since the magnitude of the signal obtained by the incomplete method is at least two orders of magnitude greater than that obtained by the complete method, small errors in the signal, which

are inevitable in real experiments, will cause the ratio to fluctuate wildly.

3.4. Detection limits of the method

For arsenous acid and boric acid, detection limits in our real experiments, according to the procedures described in Section 2.3, were found to be 1.5 and 1.0 mg/l, respectively. Compared to the suppressed method (for arsenous acid and boric acid, the detection limits were 10 and 100 mg/l, respectively.), the detection limits were improved. Although in the incompletely suppressed method, the background conductance is lower than that of the nonsuppressed method and, theoretically, the signal-to-noise ratio should be better than that of the nonsuppressed method, in our real experiments, the detection limits of the method were still worse than the reported results of the nonsuppressed method (for arsenite, 0.2 mg/l) [17]. We attribute it to following reasons:

1. As the experiments were performed by instruments designed for suppressed IC and no measurements were taken to keep the cell temperature stable, fluctuation of the temperature would increase the noise of the system.
2. In order to control the flow-rate of the regenerant, a DQP-1 pump, which is a pulsed pump, was applied to deliver the regenerant. The pulse of the regenerant may disturb the baseline.
3. In order to separate the peaks of arsenous acid and sodium hydroxide (see Fig. 4) as much as possible, a relatively small loop (10 μl) was used and the signals were thus reduced.

Table 2
Conductivity detector responses expressed as ratios of height and area obtained by incompletely suppressed IC compared to those obtained by suppressed IC.

(A) For arsenous acid						
Concentration (mg/l)	10.0	20.0	40.0	80.0	100	200
Ratio of area	402	295	204	230	185	198
Ratio of height	146	205	199	164	175	138

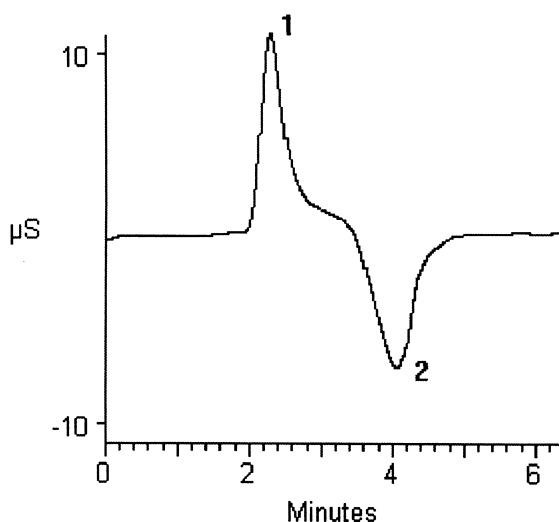| (B) For boric acid					
Concentration (mg/l)	100	250	400	800	1500
Ratio of area	779	1002	677	315	465
Ratio of height	205	261	189	105	119

Fig. 4. Chromatogram of 200 mg/l arsenous acid by the incompletely suppressed IC method. 1, sodium hydroxide and 2, arsenous acid.

3.5. Repeatability and linearity of response

Standard solutions of different concentrations were analyzed according to the procedures described in Section 2.3 (seven times for each concentration under the same conditions). The results showed that, for arsenous acid, when the concentration was varies from 5 to 200 mg/l, the R.S.D.s were found to be in the range of 1.6–6%. Correlation coefficients of peak area and peak height were 0.9991 and 0.9942, respectively. Fig. 4 shows a chromatogram of 200 mg/l arsenous acid obtained using the incompletely suppressed conductimetric method. It shows that when the concentration was above 200 mg/l, there was a positive peak that interfered with the quantitative analysis of arsenous acid. This was caused by sodium hydroxide added to the arsenous acid stock solution to dissolve arsenous trioxide. For boric acid, when the concentration was varied from 10 to 800 mg/L, the R.S.D. values were found to be in the range of 1.9–5.4%. Correlation coefficients of peak area and peak height were 0.9985 and 0.9587, respectively. When the concentration was above 1500 mg/l, the boric acid peaks split, indicating column overloading.

3.6. Application of the method

The results for carbonic acid, citric acid, glutamic

acid and malic acid showed that, for acids with a dissociation constant larger than 10^{-7}, the sensitivity of the incompletely suppressed method was lower than that of the suppressed method. Therefore, the application of this method is restrained to very weak acids whose association constants are smaller than 10^{-7}. However, as the detection limits for both boric acid and arsenous acid (association constants smaller than 10^{-7}) are still not good enough, and the time taken to reach equilibrium is too long (5 h), further work is necessary to make this method more applicable.

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