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Enhancement of conductometric detection of weak acids in ion chromatography

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Abstract

Anions of weak acids can represent a problem when determined via chemically suppressed ion chromatography as the acids can be weakly ionised, giving low conductivity and hence low sensitivity. Previous work showed that converting some weak acids back to their sodium salts, using a second micromembrane suppressor, greatly enhanced conductivity and thus sensitivity. This paper will discuss further work in optimising the conversion for boric acid by using sodium salts of EDTA and the mechanisms involved. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Conductometric detection; Detection, LC; Mobile phase composition; Boric acid; Weak acids

1. Introduction

Ion chromatography (IC) is the most common method for determining anion concentrations in solution [1]. In chemically suppressed IC, the ions are chromatographically separated, then converted to their conjugate acids, often in a micromembrane suppressor, and then detected conductometrically [2]. Theoretically, sensitivity of some weak acids can be increased by converting them to more highly conducting ions and several approaches have been used [3–13]. A novel approach was use of a second micromembrane suppressor [12,13], as an ion-exchange reactor (IER), which allows exchange of cations but not analyte anions across the membrane. The work showed that converting 10 μM boric and 10 mM carbonic acids to their sodium salts increased conductivity and thus sensitivity [12,13]. The most effective of several ion replacement reagents investi-

gated was ethylenediaminetetraacetic acid (EDTA) at pH 11 which, for a 5.0 mM borate standard, gave 250- and 1400-fold increases in peak height and area, respectively compared to normal suppressed IC (Fig. 1). For such an increase to occur the concentration of the weak acid has to be above the critical point concentration (CPC), defined [12,14] as the concentration of the weak acid at which the solution conductance is unchanged by the conversion. Recently we developed a simple theoretical model for the calculation of CPCs for weak acid/conjugate salt pairs [14]. The CPC was found to be a function of the molar ionic conductivity of hydrogen ions, the conjugate cation (i.e., sodium) and the K_a of the acid:

$$C = K_a \left[1 - \frac{(\lambda_{M^+} + \lambda_{A^-})}{(\lambda_{H^+} + \lambda_{A^-})} \right] / \left[\frac{(\lambda_{M^+} + \lambda_{A^-})}{(\lambda_{H^+} + \lambda_{A^-})} \right]^2$$

In this paper we have further investigated parameters such as EDTA pH and concentration, and eluent flow-rate on the efficiency of conversion of boric

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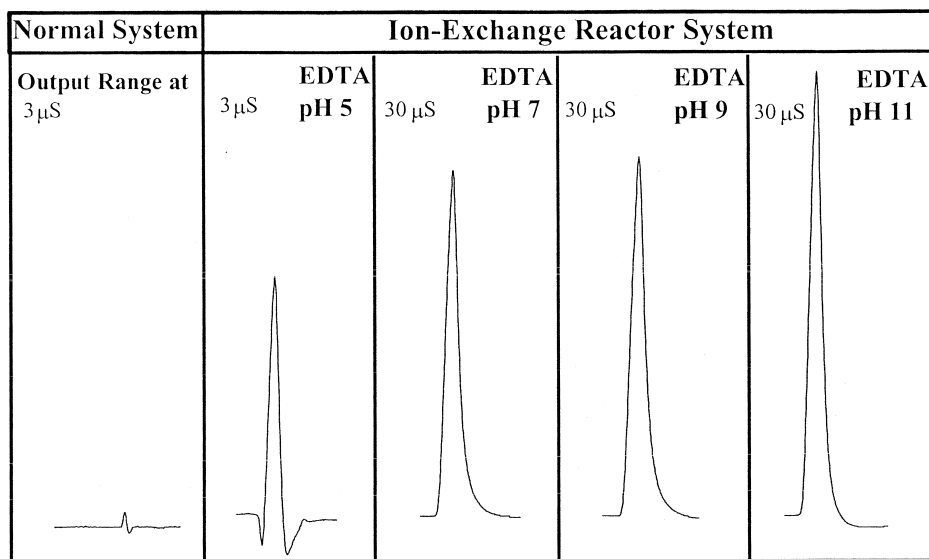


Fig. 1. Comparison of chromatographic peak obtained for 5.0 mM borate using a normal suppressed IC system (left panel) with those obtained using a second membrane suppressor as an IER for the conversion of boric acid to sodium borate. The conversion was done using 10 mM EDTA at pH of 5 to 11. From Caliamanis [13] with permission.

acid (pK_a 9.2) to sodium borate in a micromembrane suppressor, as a model for other weak acids. Some insights into the conversion process are also discussed.

2. Experimental

2.1. Chemicals

Reagent grade water was obtained from a Milli-Q system (Millipore). All chemicals were BDH analytical-reagent grade, unless otherwise specified and all glassware was A grade.

2.2. Equipment

A Dionex 4500i ion chromatograph, a Dionex GP40 programmable-gradient pump, a Dionex IonPac AG11, 4 mm (P/N 4478) guard column in series with a Dionex IonPac AS11, 4 mm (P/N 44076), followed by two Dionex Anion MicroMembrane Suppressors (AMMS-II, P/N 043074) placed in series just before the conductivity detector. The detector was operated with a default factor of 1.7 for the auto temperature compensation mode. Delta

Chromatography Computer software (Version 5.0) was used to acquire peak heights and peak areas. Regenerant solution and IER reagent were forced through the micromembrane suppressors, under 5 p.s.i. pressure (1.2 ml/min) (1 p.s.i. = 6894.76 Pa). A Metrohm 650 pH meter (calibrated over the pH range of 4–7, using Activon capsule buffers), a Pt 100 temperature probe, and a combined glass/silver, silver chloride electrode were utilised to measure the pH of solutions.

2.3. Solutions preparation

All standard solutions, eluents, regenerants and reagents were prepared with Milli-Q water, degassed under vacuum and filtered through 0.2- μ m membrane filters (PTFE), prior to use. Eluent was sodium hydroxide (5 mM). The first suppressor was regenerated by sulphuric acid (50 mM). The second suppressor was flushed with EDTA solution, 1 to 100 mM, adjusted to pH 5, 7, 9 or 11 by the addition of sodium hydroxide solution. Stock solutions of boric acid were 1 to 10 mM. Solutions of boric acid (10–1000 μ M) were prepared by dilution of the stocks with 5 mM NaOH. Solutions were injected into the IC system via a 20- μ l injection loop. Three

replicate injections of each sample were made and the results averaged. An eluent flow-rate of 1.0 ml/min was used, unless otherwise stated. The second suppressor was flushed with Milli-Q water after the use of the EDTA reagent to avoid crystallization and damage to the suppressor membrane.

3. Results and discussion

3.1. EDTA solution concentration and pH variation

Preliminary work [12,13] with an older Dionex 2010i IC system indicated that the optimum concentration and pH for EDTA solutions as IER reagent was 10 mM at pH 11. This work was repeated since a newer Dionex 4500i IC system with a more sensitive conductivity cell would be used for all future work. A set of standard borate solutions (10–1000 μM) was chromatographed using 10 mM EDTA solutions with pH being varied from 5 to 11 as the IER reagent. Again pH 11 gave the highest responses, consistent with previous work [12,13], and confirming that the analysis is reproducible on a different system. For a 5.0 mM standard of borate, 850- and 3400-fold increases in peak height and area, respectively (compared to normal suppressed IC) was achieved, compared to the 250- and 1400-fold increases in peak height and area, respectively, obtained previously [12,13].

To further optimise the EDTA IER solution, the EDTA concentration was varied from 10 to 100 mM, while keeping the pH constant at 11. At this pH the EDTA is calculated to be 85% present as the tetrasodium salt and 15% as the trisodium salt [15]. Thus there is an increase in the calculated sodium ion concentration available for ion replacement from 39 to 385 mM. The effect of these concentration variations was monitored by average area and height responses given by a set of borate standards (10–1000 μM). The area results (Fig. 2a) show that 20 mM EDTA gave the highest sensitivity for the borate standards and also produced the most linear response when compared to the other EDTA concentrations used. Similar results were obtained for the height responses. Chromatograms obtained for the borate standards showed a negative peak (dip) coinciding

with the borate peak (Fig. 3). This dip was observed to increase with increasing concentration of EDTA and was more pronounced with the higher concentrations of borate analysed. Due to this, accurate quantification of the borate peaks was difficult to achieve, which could explain the lack of linearity and sensitivity of the borate responses obtained at the higher concentrations of EDTA (Fig. 2a). The background conductivity also increased from 5.3 to 19.1 $\mu\text{S}/\text{cm}$ as the EDTA concentration was increased (Table 1), coinciding with the increase in magnitude of the dip. This background increase was likely due to increasing leakage of Na^+ and OH^- ions across the membrane, as the EDTA anions should be too large to cross. This increase in background could have contributed to the lack of linearity observed in the low borate concentration results when the higher EDTA concentrations were used (Fig. 2a). The increase in background was similar to that observed previously [12,13], using NaOH as IER reagent.

The chromatograms also show a baseline ripple which increased as EDTA concentration was increased from 20 to 100 mM (Fig. 3A–C). The ripple was traced to the eluent proportionating system in the pump, which was mixing 25 mM NaOH with water to produce 5 mM eluent and can be eliminated by premixing the required eluent. The increase in ripple with EDTA concentration is discussed later.

To investigate whether the age of the suppressors contribute to the amount of leakage across the membrane, the experiments were repeated with two new micromembrane suppressors. The results (Fig. 2b) show that 10 mM EDTA at pH 11 gave the most sensitive borate responses, but they were still 13% less than the response for 20 mM EDTA found earlier (Fig. 2a) with the older suppressors. Interestingly, the responses for 10 mM EDTA found with both sets of suppressors were not significantly different. The lowest responses were again obtained using 100 mM EDTA; the borate peaks were once again in the dip, making quantification difficult. The background conductivity followed the same trend as for the older suppressors, and increased from 3.7 to 15.8 $\mu\text{S}/\text{cm}$ as the EDTA concentration was increased (Table 1), again coinciding with the increase in the magnitude of the dip. Thus the new suppressors reduced the amount of NaOH leakage across the membrane by about 15%.

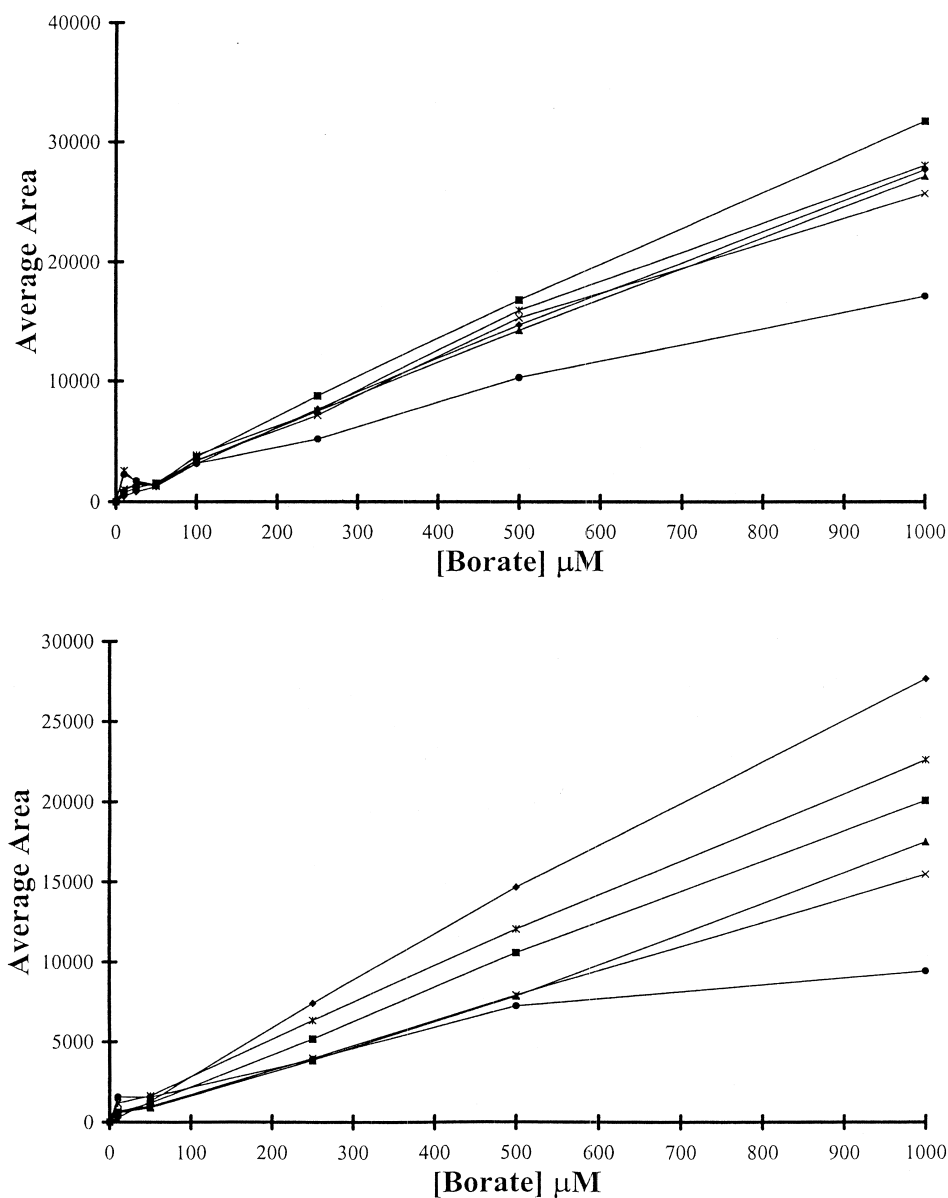


Fig. 2. Average peak area for various borate concentrations, with EDTA at: \blacklozenge 10 mM, \blacksquare 20 mM, \blacktriangle 40 mM, \times 60 mM, \blackstar 80 mM and \bullet 100 mM EDTA. (a) Old and (b) new set of micromembrane suppressors, respectively (see Table 1).

In order to explain the dip, we need to consider the reactions that are occurring in the membrane suppressor. The eluent stream from the first suppressor should contain some sulfuric acid leakage (estimated at 4 μM from conductivity measurements) from the regenerant (50 mM). The second suppressor (the IER) provides a higher amount of NaOH

leakage (about 65 μM) into the eluent stream from the IER reagent (100 mM EDTA at pH 11), neutralising the sulfuric acid and hence providing the background conductivity, comprising a mixture of NaOH and Na_2SO_4 . When a weak acid HA enters the IER there are two possible mechanisms by which it can be converted to the conjugate salt: (i) ioniza-

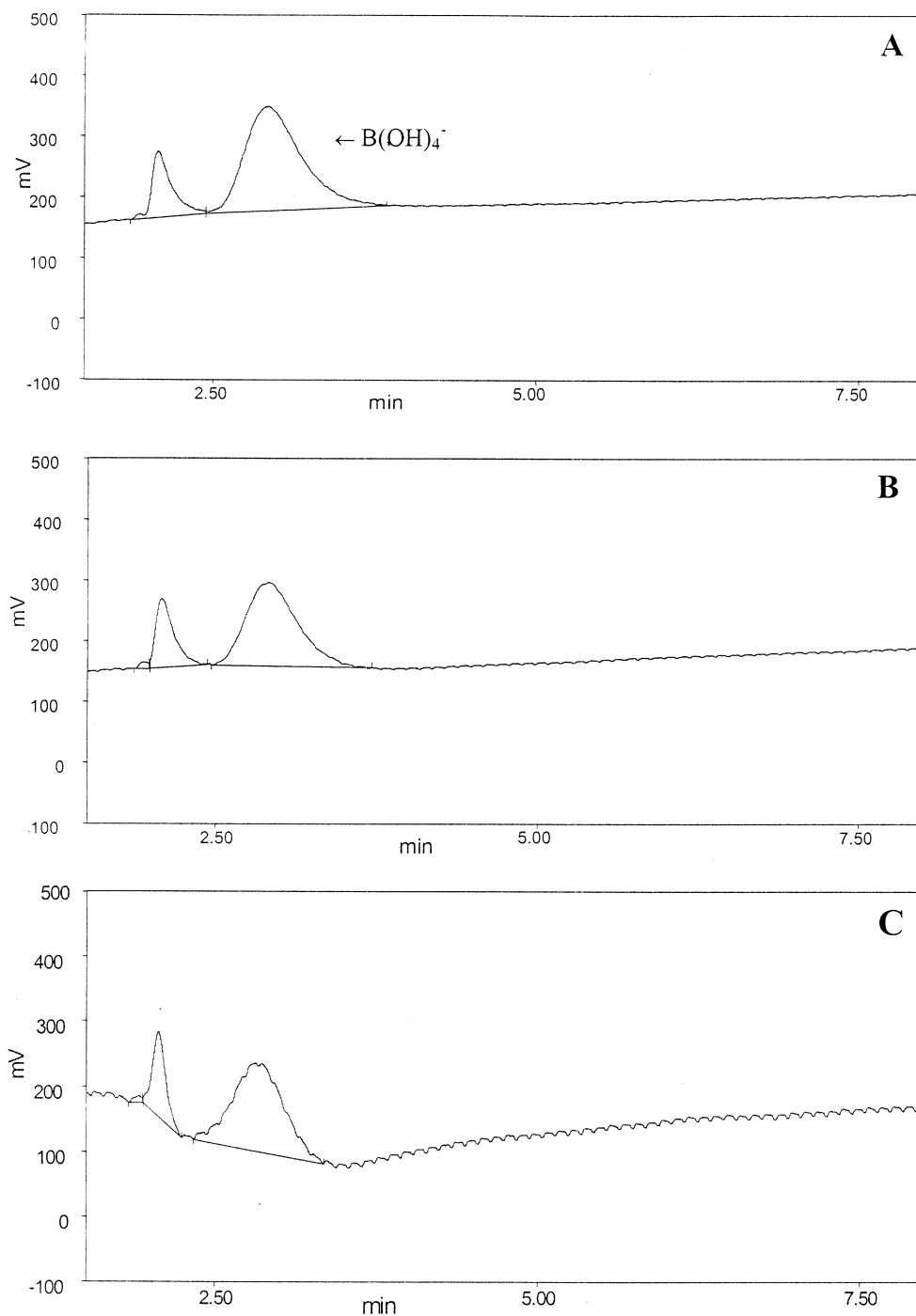


Fig. 3. Chromatograms of borate solutions with EDTA at pH 11 acting as IER reagent. Borate solutions $250 \mu\text{M}$ with EDTA concentrations of: (A) 20 mM , (B) 60 mM and (C) 100 mM EDTA. Borate concentrations of: (D) $10 \mu\text{M}$, (E) $500 \mu\text{M}$ and (F) $1000 \mu\text{M}$ run using 100 mM EDTA. (Continued on next page)

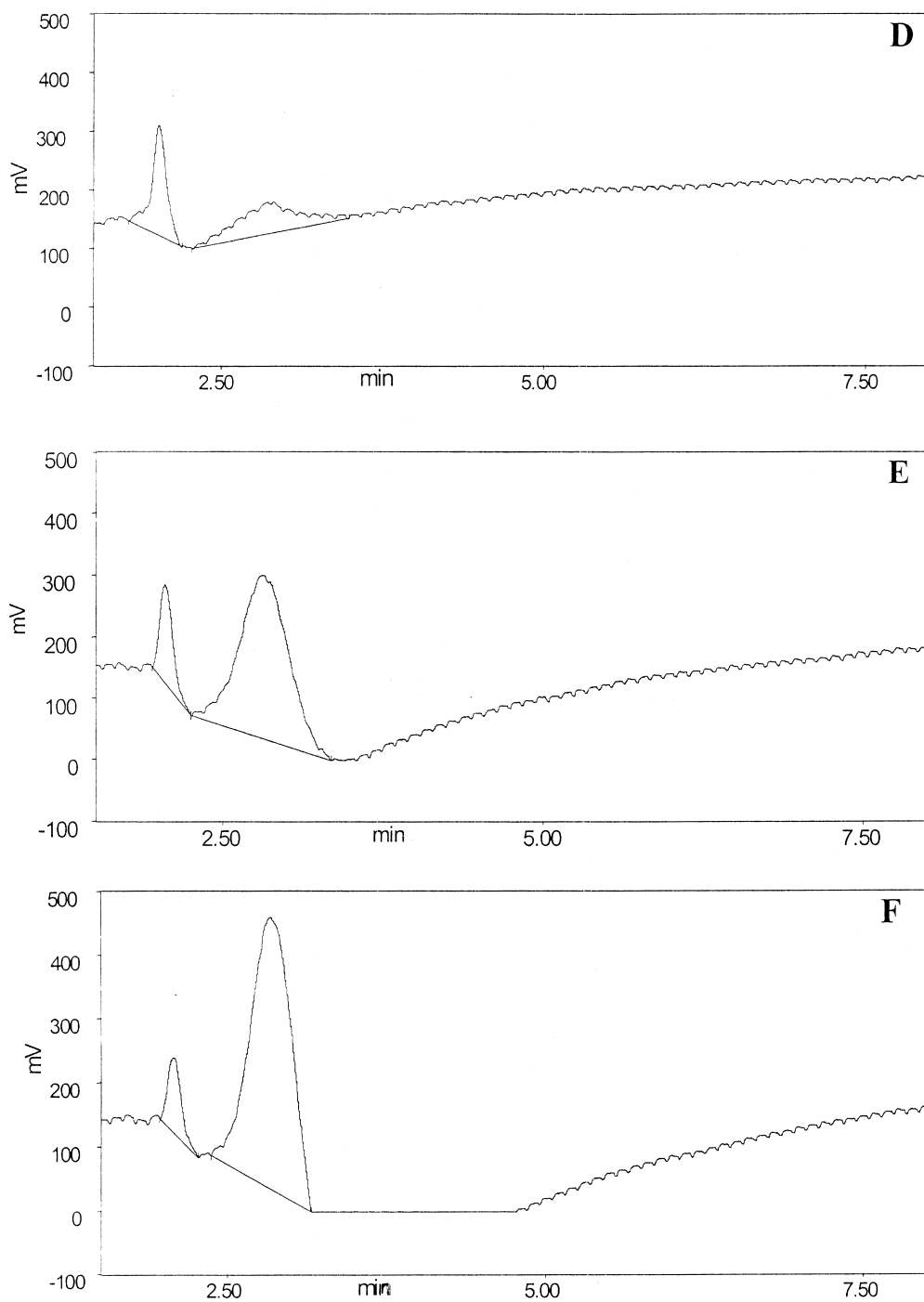


Fig. 3. (continued)

Table 1

Background conductivity and estimated NaOH concentration variations with increase in EDTA concentration at pH 11 (data are shown for an old and for new sets of suppressors)

[EDTA] (mM)	Old suppressors		New suppressors	
	Conductivity ($\mu\text{S}/\text{cm}$)	[NaOH] ^a (μM)	Conductivity ($\mu\text{S}/\text{cm}$)	[NaOH] ^a (μM)
10	5.28	20	3.67	15
20	6.29	25	6.20	25
40	9.76	40	7.58	30
60	11.8	47	8.90	36
80	12.8	51	9.56	38
100	19.1	77	15.8	63

^a Estimated from the background conductivity measurements, corrected for the contribution from sodium sulfate.

tion followed by ion-exchange of the hydrogen ions for sodium ions, or (ii) direct neutralization of the weak acid (with or without prior ionization) by NaOH which has leaked across the membrane. The former mechanism (hereafter Mechanism 1) should not affect the diffusion of NaOH across the membrane and hence would result in a positive peak on a constant background. However, the latter mechanism (Mechanism 2) would result in consumption of some or all of the NaOH, which has leaked across the membrane. As the leading edge of an analyte concentration peak starts passing through the IER suppressor, the initial extremely low HA concentrations would enhance ionization [14] and Mechanism 1 could dominate, resulting in a small increase in conductivity. However, as HA concentrations rise, ionization would decrease, and Mechanism 2 could dominate, resulting initially in replacement of background hydroxide ions with A^- ions having lower molar ionic conductivity and hence giving a drop in the conductivity. The maximum magnitude of the drop will depend on the usual background concentration of hydroxide, and explains why the observed dips were greatest with 100 mM EDTA (Fig. 3C–F) where hydroxide leakage was highest (Table 1). Indeed, this mechanism is used by Berglund and co-workers [9–11], to detect weak acids as negative peaks in a high NaOH background. In our work, however, the consumption of some NaOH would lead to increased diffusion of NaOH across the membrane and hence the relationship between negative peak response and HA concentration would not

be linear. As the analyte peak progresses through the IER suppressor, the HA concentration will rise to the point where all of the usual background NaOH and some of the additional NaOH (through increased diffusion) has been consumed by the HA. This will result in a conductivity peak of NaA on a background of Na_2SO_4 . We estimate from Fick's first law of diffusion [16] that 10 mM EDTA at pH 11 should be able to supply sufficient NaOH by leakage to neutralise around 7 mM of boric acid. Mechanism 2 should thus result in a dip on the leading and trailing edges of the borate peaks, as observed for the higher EDTA concentrations (Fig. 3). The same pattern was observed for 10 mM EDTA at pH 5 (Fig. 1). At this pH, 92% of the EDTA is calculated to be present as the disodium salt and the remainder as the trisodium salt [15]. This results in about 21 mM sodium ions and only 1 nM hydroxide. Despite the low hydroxide concentration, the results suggest that Mechanism 2 (requiring leakage of sodium hydroxide) is still important in the conversion of boric acid to borate at pH 5. The results for pH 7, 9 and 11 however, do not show any sign of dips (Fig. 1). Given the increased concentrations of sodium and hydroxide ions able to leak across the membrane at these higher pH, it seems unlikely that the lack of dips would be due to Mechanism 1 dominating the conversion of boric acid to sodium borate. Rather, the increased response of borate at the higher pH (more than 20-fold), the change in output range from 3 to 30 $\mu\text{S}/\text{cm}$ and the relatively low background observed for 10 mM EDTA, even at pH 11 (Table 1) have combined to

conceal the dips. As discussed earlier, the results obtained for lower borate concentrations and higher EDTA concentrations at pH 11 do show dips (Fig. 3).

The earlier discussion also suggested that there could be a small peak preceding the leading edge dip (and following the trailing edge dip). No such peaks were observed for borate. The small peak at 2.1 min, just before borate peak at 2.9 min (Fig. 3) was tentatively identified from retention time as *o*-phthalate impurity. The phthalate, and also carbonate, from absorption of carbon dioxide from the air into the 5 mM NaOH, could have contributed to the magnitude of the dips either side of the borate peaks. Further work in this area is continuing.

We can now propose a mechanism for the increase in baseline ripple with EDTA concentration observed in the chromatograms (Fig. 3). A fluctuation in NaOH concentration caused by the pump proportioning system would not explain the observation. It could conceivably lead to a fluctuation in the amount of sulfuric acid in the eluent from the first suppressor and hence in sodium sulfate in the eluent from the second suppressor. This would lead to a constant ripple in the background conductivity, not the observed dependence on EDTA concentration. However, the presence of a weak-acid-anion impurity in the 100 mM NaOH solution would explain the observations. This impurity would be converted to an acid in the first suppressor and progressively more would then be reconverted to the salt by the hydroxide from the second suppressor (most probably by Mechanism 1) as EDTA concentration increased. This would result in a conductivity ripple that was dependent on EDTA concentration, as was observed.

From an analytical point of view, the results show that at pH 11, 10 to 20 mM EDTA gave the highest responses (Fig. 2). Higher concentrations of EDTA did not in fact increase sensitivity due to the presence of the dips and the associated difficulties in quantification. Hence it was decided to investigate 1 to 20 mM EDTA solutions at pH 9 and 11 as IER reagent. Once again 10 to 1000 μ M borate solutions were used for the analysis.

For EDTA solutions at pH 9, there was a small increase in sensitivity when EDTA concentration was increased from 1 to 5 mM, but there was no further significant improvement up to 20 mM (Fig. 4,

top). However, the 20 mM EDTA responses were marginally the most linear. In contrast, at pH 11, there was no significant increase in sensitivity when EDTA concentration was increased from 1 to 10 mM (where it peaked) and then decreased significantly at 15 mM and 20 mM (Fig. 4, bottom). The responses at pH 11 showed a significant jump from 0 to 1 mM EDTA (Fig. 4, bottom), suggestive of a blank problem, and were then reasonably linear. It should be noted at this point that the conditions used were such that there were no dips evident and hence there were no quantification problems. The 10 mM EDTA responses were marginally the most linear. The maximum responses at both pH values were not significantly different. Overall, the optimum reagent for the IER was 20 mM EDTA at pH 9, as it gave (equal) highest and most linear responses for both height (not shown) and area data.

In order to determine the efficiency of the 20 mM EDTA at pH 9 as IER reagent for converting boric acid to sodium borate, a series of borate standards were run under the conditions outlined in Table 2. Comparison of Sets 1 and 2 should give an indication of the conversion being achieved in the IER, while a comparison of Sets 2 and 3 should show the effect of the column in the analysis. The results are shown in Fig. 5. The maximum height response was obtained by Set 1, followed by Sets 2 and 3 (Fig. 5, top). If the reduction in response for Set 2 were attributed to incomplete conversion of boric acid to sodium borate in the IER, it would suggest that the efficiency of the IER was about 80%. The further reduction in height data that was observed with the introduction of the column (Set 3 in Fig. 5, top) would then be attributable to the usual dispersion that occurs in the column. However, the area data do not seem consistent with these interpretations. First, there is negligible difference between the area responses for Sets 1 and 2 (Fig. 5, bottom) suggesting there is around 100% conversion efficiency in the IER. Second, the area responses obtained in the presence of the column (Set 3) were around twice as large as for Set 2 (Fig. 5, bottom). One possible explanation is that the greater dispersion of the analyte plugs in Set 3 results in more analyte contact with the IER suppressor (i.e., the analyte has a higher residence time in the suppressor), thus increasing the conversion of the acid to its sodium salt

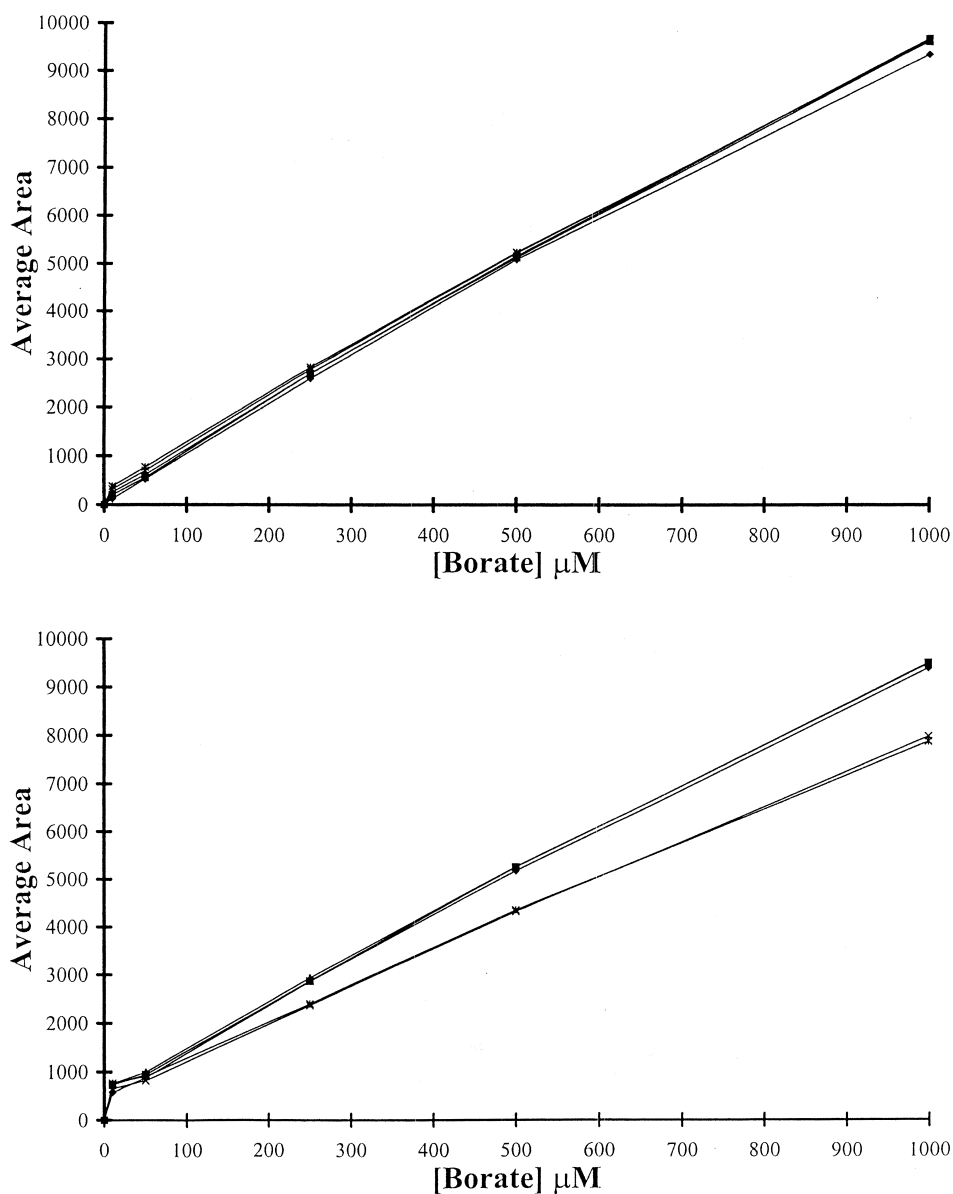


Fig. 4. Average peak area for various borate concentrations, with EDTA at (top) pH 9 and (bottom) pH 11 acting as IER reagent. EDTA concentrations in both cases were: \blacklozenge 1 mM, \blacksquare 5 mM, \blacktriangle 10 mM, \times 15 mM and \blackstar 20 mM.

and hence its response is increased. This explanation requires that conversion efficiency in the IER for Sets 1 and 2 is less than 100%.

3.2. Flow-rate variation

It is clear from the above observations that the

residence time of the analyte plug in the IER suppressor plays a major role in the conversion of the acids to salts and thus should be further investigated. To do this, Sets 1 and 2 were repeated with the Milli-Q flow-rate reduced to 0.2 ml/min. The results (Fig. 6) show an area increase of seven-fold for Set 1 and 14-fold increase for Set 2 at 0.2

Table 2

Experimental conditions used to investigate the efficiency of using 20 mM EDTA at pH 9 as IER reagent with a second micromembrane suppressor for the conversion of 10 to 1000 μM borate solutions to sodium borate

Set	Column	Eluent	Suppressor 1	Suppressor 2
1	No	Milli-Q	EDTA	EDTA
2	No	Milli-Q	H ₂ SO ₄	EDTA
3	Yes	5 mM NaOH	H ₂ SO ₄	EDTA

ml/min when compared to the results obtained at 1.0 ml/min. Interestingly, at 0.2 ml/min higher area responses were obtained using Set 2 than with Set 1 (Fig. 6). Hence, converting the sodium borate solutions to boric acid in the first suppressor and then converting them back to the salt in the IER suppressor resulted in a much higher area response than obtained with injected sodium borate solutions. This contrasts with the similar area responses obtained at 1.0 ml/min.

These observations can be explained by considering that in aqueous solutions boron can exist not only as boric acid and borate, but as a range of polynuclear species formed by condensation, with the loss of water [17]. As these species form, we expect the net conductivity of the solution to drop, thus decreasing the conductivity observed for Set 1 solutions. When sulfuric acid is used in the first suppressor, some (at 1.0 ml/min) or perhaps all (at 0.2 ml/min) of these polynuclear anions are converted to B(OH)₃ that is then, at least partially, reconverted to sodium borate in the second suppressor. At 0.2 ml/min the extent of the conversion(s) in the suppressor(s) must be higher than at 1.0 ml/min, giving higher area responses. Even at 0.2 ml/min, the solution that enters the conductivity cell could still contain a combination of sodium borate and polynuclear anions, making the IER system particularly difficult to optimise for borate.

The effect of flow-rate in the range 0.2 to 1.0 ml/min on height and area data for a 500 μM borate solution was investigated further using Sets 2 and 3 (i.e., without and with a column present, respectively). The results (Fig. 7) again demonstrate the response advantages of decreasing flow-rate from 1.0 to 0.2 ml/min. Over this flow-rate range, area data for Set 2 (no column) increased 12-fold, while for Set 3 (column) the increase was six-fold (Fig. 7,

top). The peak areas at 0.2 ml/min were not significantly different, suggesting that conversion was complete at this flow-rate regardless of whether the column was present or not. Peak heights decreased in the presence of the column, as expected from normal chromatographic broadening processes. However, peak heights still increased as flow-rate decreased (Fig. 7, bottom), again highlighting the sensitivity advantages obtained at the lower flow-rates. Over the same flow-rate range, the background conductivity increased three-fold for both sets. Some of this increase would be due to changes in detector sensitivity with flow-rate, but increased diffusional leakage of sulfuric acid and NaOH across their respective suppressor membranes would also be a contributing factor.

Hence for borate, flow-rates down to 0.2 ml/min produced increases in both peak height and peak area through higher conversion of the boric acid to sodium borate in the second suppressor (Figs. 6 and 7), which could well be advantageous to an analyst, especially when coupled with improved chromatographic efficiency expected at lower flow-rates ([18], see also Ref. [19]). These advantages need to be weighed by the analyst against possible peak broadening, tailing and longer retention times expected at lower flow-rates.

4. Conclusions

The optimal conditions for the conversion of boric acid to sodium borate by use of a micromembrane suppressor and sodium salt solutions of EDTA at various pH and concentrations has been investigated. The optimum conditions found were 20 mM EDTA at pH 9, although excellent response was still obtained with concentrations down to 5 mM. Higher pH and higher EDTA concentrations led to increased leakage of NaOH across the suppressor membrane, a corresponding increase in the background conductivity and the formation of dips in the leading and trailing edges of the borate analyte peak.

Two mechanisms were proposed for the conversion of boric acid to sodium borate in the suppressor – ionization followed by ion-exchange of hydrogen ions for sodium ions across the membrane and; direct reaction of the leakage NaOH with the weak acid

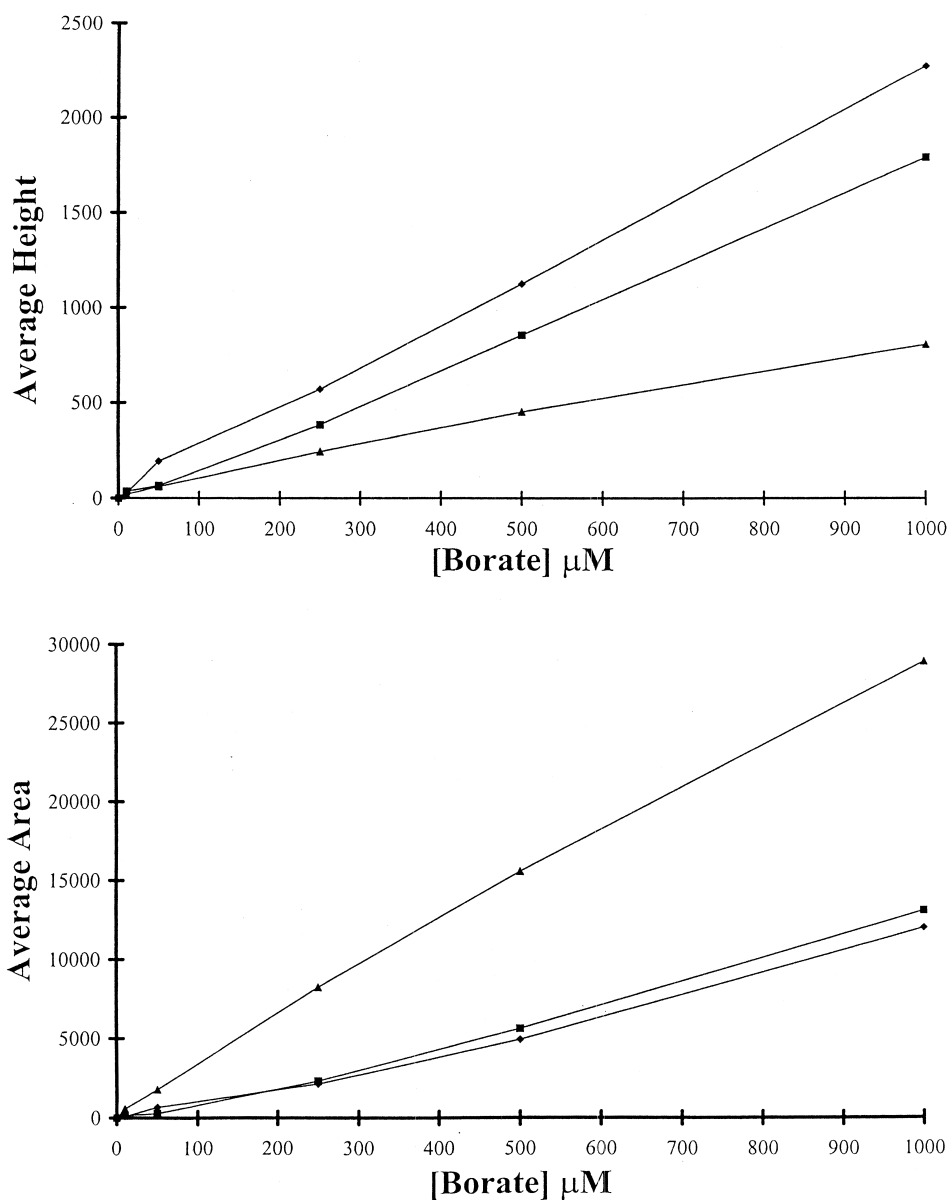


Fig. 5. Average peak (top) height and (bottom) area responses for various borate concentrations obtained with: \blacklozenge Set 1, \blacksquare Set 2 and \blacktriangle Set 3 experimental conditions, as described in Table 2. Flow-rate was 1.0 ml/min.

(with or without prior ionization). The dips provided evidence that direct reaction was more important than ion-exchange for boric acid and the same is probably true of other weak acids.

The aqueous chemistry of boron has made it difficult to determine the absolute efficiency of the membrane suppressor for the conversion of boric

acid to sodium borate. In particular, the presence of polynuclear borates in the injected solutions resulted in lower responses compared with those obtained by converting the polynuclear species to boric acid in the first suppressor and then converting back to sodium borate in the IER suppressor just prior to detection. The area response obtained without a

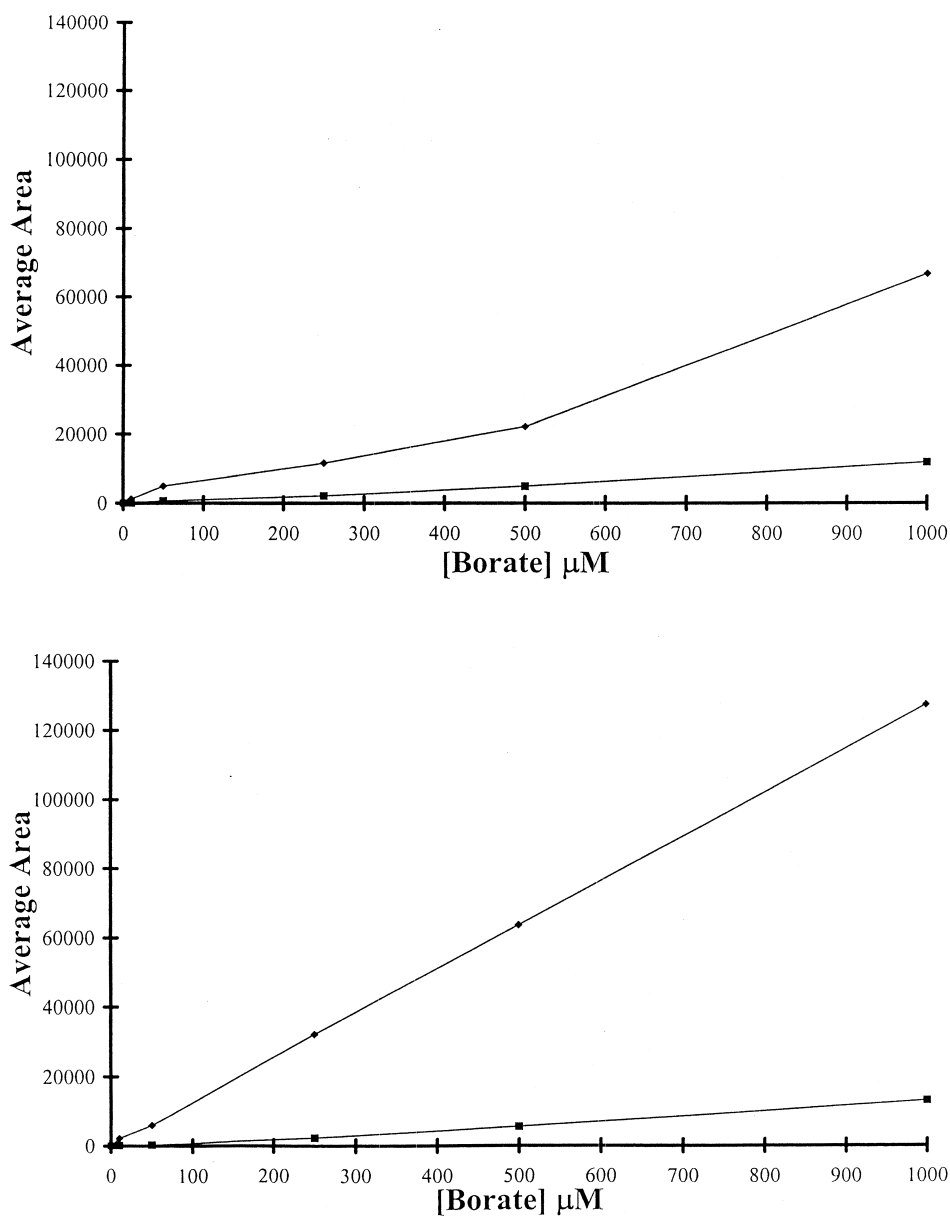


Fig. 6. Average peak area for various borate concentrations, with (top) Set 1 and (bottom) Set 2 experimental conditions (as described in Table 2) at flow-rates of: \blacklozenge 0.2 ml/min and \blacksquare 1.0 ml/min.

column in the system was doubled by using a column, which increased dispersion of the borate peak and hence allowed greater total residence time of the analyte in the IER suppressor.

Decreases in flow-rate from 1.0 to 0.2 ml/min had dramatic impact, increasing borate areas six-fold and

background conductivity three-fold. In a real analysis, other factors such as peak broadening and run time must also be considered when carrying out an analysis. A retention time of 14 min at 0.2 ml/min is not very time efficient, especially when compounds may take several hours to elute. Thus a compromise

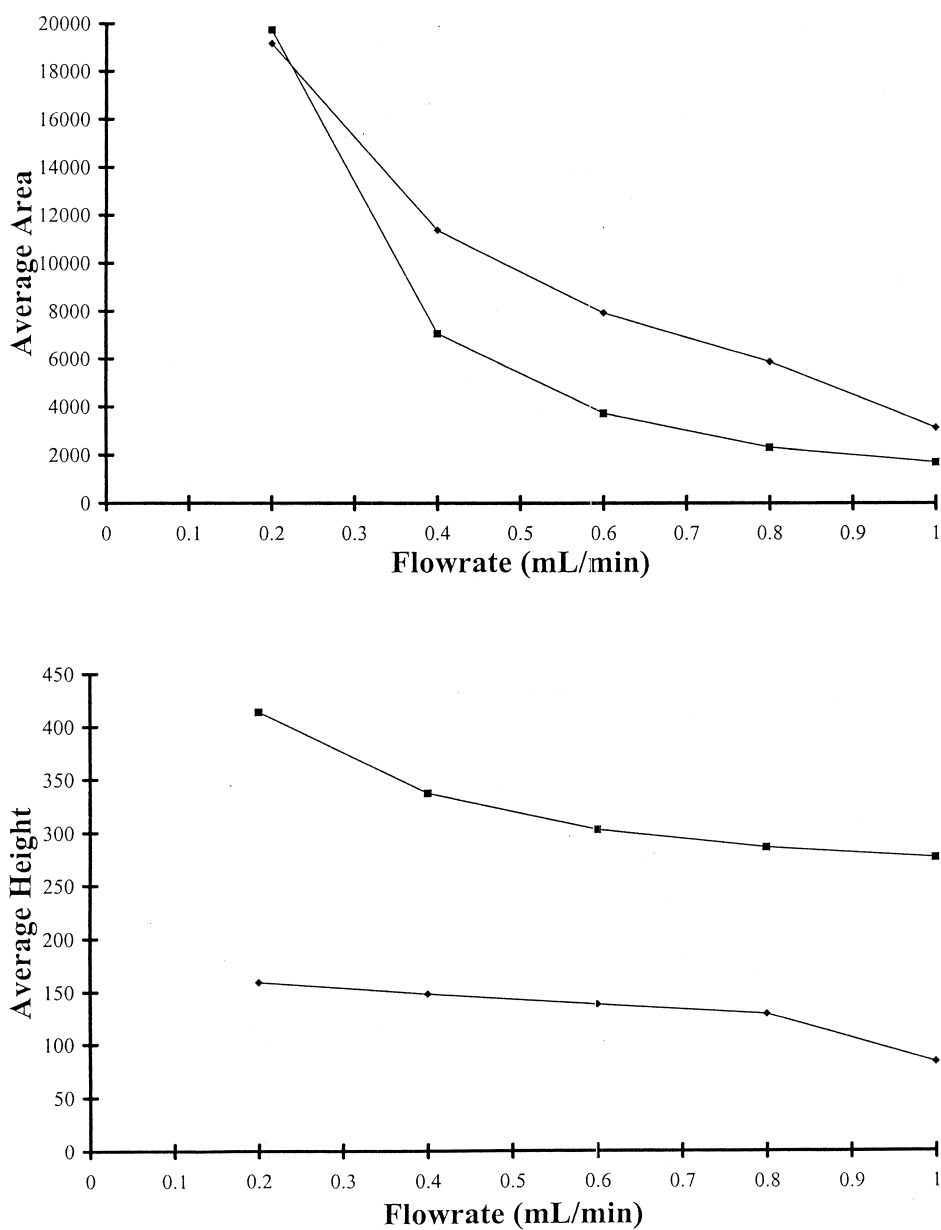


Fig. 7. Average peak (top) area and (bottom) height responses for 500 μM borate solution at various flow-rates obtained with: ■ Set 2 and ♦ Set 3 experimental conditions, as described in Table 2.

between borate response and time efficiency must be determined, depending on the type of analysis to be done and the time frame required.

Future work will be focused on investigating the conversion of another weak acid to the sodium salt,

probably cyanide, as it has a simpler aquatic chemistry and then applying the optimum conditions found to a range of weak acids. It is hoped that this process will also provide further insights into the mechanisms involved in the conversion process.

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