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STUDIES ON SAMPLE PRECONCENTRATION IN ION CHROMATOGRAPHY

II. AN AUTOMATED, SINGLE PUMP PRECONCENTRATION SYSTEM FOR NON-SUPPRESSED ION CHROMATOGRAPHY WITH CONDUCTIVITY DETECTION

A. L. HECKENBERG and P. R. HADDAD*
Department of Analytical Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)
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SUMMARY

A modified automated preconcentration system for non-suppressed ion chromatography is described which uses a microprocessor-controlled pump coupled to a low-pressure switching valve and two high-pressure switching valves. This system is applicable to conductivity detection because it permits the concentrator pre-column to be removed from the flow path after elution of adsorbed ions onto the analytical column, and also allows the concentrator column to be washed with a small volume of eluent prior to elution. Both of these steps serve to minimise baseline perturbations in the final chromatogram resulting from disequilibration of the concentrator column due to the loss of bound eluent ions during the sample loading process. It is shown that both steps are necessary for quantitative removal of adsorbed sample from the concentrator column and that the efficiency of sample loading is strongly dependent on the type of eluent used to equilibrate the concentrator column. Under optimal conditions, recoveries of preconcentrated samples varied from 99 to 106% for 50 ppb of chloride, nitrate and sulphate, when compared with manual injection of equivalent amounts of these ions.

INTRODUCTION

Trace analysis of ppb* levels of inorganic anions by ion chromatography has been achieved using very large injection volumes[1,2] or sample preconcentration techniques[3]. The latter method is most generally applicable and involves the use of a small ion-exchange pre-column mounted before the analytical column. A measured volume of sample is passed through the pre-column using a syringe or pump, and the solute ions become trapped on the pre-column. These ions are then eluted onto

* Throughout this article, the American billion (10^9) is meant.

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the analytical column and are separated in the usual manner. If the pre-column has sufficient total ion-exchange capacity to retain quantitatively solute ions and its internal volume is small, then very large sample preconcentration factors may be achieved. For this reason, the pre-column is often referred to as a "concentrator" column.

The success of sample preconcentration techniques is dependent on reproducible and quantitative retention of solute ions by the concentrator column, followed by quantitative elution of these ions onto the analytical column. In an effort to study the parameters which influence these factors, we have designed an automated, single-pump system for sample preconcentration which uses a microprocessor controlled pump, a low-pressure valve for solvent selection and two high-pressure column switching valves[4]. This system permitted precise control of flow-rate and volume of sample loaded onto the concentrator column and was applied to the detection of anions by direct UV absorption, using methanesulphonate as eluent.

In this paper, we describe a modified system design for use with conductivity detection. This detection method introduces some problems not encountered when direct UV absorption detection was used and two approaches to the solution of these problems are evaluated.

EXPERIMENTAL

Instrumentation

The liquid chromatograph consisted of a Waters Assoc. (Milford, MA, U.S.A.) Model M590 pump and events unit, Model M481 variable wavelength UV detector and Model M430 conductivity detector, together with a solvent select valve, two pneumatic column switching valves and a Model M730 data module. The separator columns used were a Waters IC Pak A (50 × 4.6 mm I.D.) methacrylate-based anion exchanger (10 μm, 30 μequiv./ml) and a Hamilton PRP-X100 anion exchanger (150 × 4.6 mm I.D.). The concentrator column was a Waters IC-concentrator column (6.0 × 5.0 mm I.D.) packed with methacrylate anion exchanger. The concentrator column was housed in a Waters Assoc. Guard Pak pre-column module.

Reagents

All water used was doubly distilled and passed through a Millipore (Bedford, MA, U.S.A.) Milli-Q water purification system. Standard solutions (1000 ppm) of fluoride, chloride, nitrite, bromide, nitrate, sulphate and iodide were prepared by dissolving appropriate amounts of analytical grade sodium salts in pure water. These solutions were diluted daily to give the trace solutions required.

The eluents used were 0.8 m*M* potassium hydrogen phthalate at pH 7.0 or 7.15 and 1.0 m*M* potassium hydrogen phthalate at pH 6.1, prepared by adjusting the pH of a solution of a weighed amount of the salt with sodium hydroxide, followed by dilution to volume. The gluconate/borate eluent was 1.1 m*M* gluconate, 5.3 m*M* boric acid and 1.2 m*M* tetraborate at pH 8.0, prepared by adjusting the pH of a solution of weighed amounts of the sodium salts with sodium hydroxide, followed by dilution to volume. A 0.1 *M* methanesulphonate eluent at pH 4.0 was prepared by adjusting the pH of a suitable weight of methanesulphonic acid with sodium hydroxide solution.

Each eluent was freshly prepared daily and was filtered through a 0.45-μm filter and degassed in an ultrasonic bath before use.

Procedure

The pump microprocessor was programmed to actuate the switching valves in a timed sequence, the details of which are discussed under Results and discussion (Table I, Figs. 2, 3).

RESULTS AND DISCUSSION

Preconcentration with conductivity detection

The preconcentration system described previously[4] was applied to conductivity detection, using methanesulphonate as eluent. The chromatograms obtained for a 15-ml sample of 40 ppb chloride, nitrite, nitrate and bromide, with conductivity and

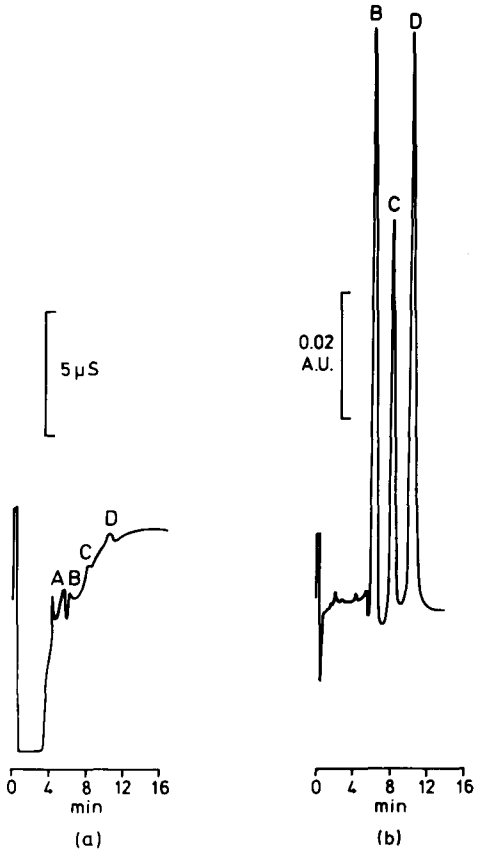


Fig. 1. Chromatograms obtained after preconcentration of a trace mixture of chloride (A), nitrite (B), bromide (C) and nitrate (D), using conductivity detection (a) and direct UV absorption detection (b). Conditions: analytical column, Hamilton PRP-X100 (150 × 4.6 mm I.D.); concentrator column, Waters Assoc. IC-concentrator (6.0 × 5.0 mm I.D.); eluent, 0.1 *M* methanesulphonate at pH 4.0; flow-rate, 2.0 ml/min; detector sensitivity, 25 μS f.s. (a), 0.1 a.u.f.s. (b) at 205 nm; sample, 15 ml of a 40-ppb mixture of the indicated ions.

direct UV absorption detectors connected in tandem are shown in Fig. 1. UV detection gave excellent results for all ions with the exception of chloride, which was not detected at the wavelength used (205 nm). On the other hand, conductivity detection gave very poor results, with barely discernible peaks appearing on a drifting baseline. The reason for the discrepancy between conductivity and direct absorption detection is apparent when the features of both detection methods are examined and related to the preconcentration system used.

In this system, the concentrator and analytical columns were intially equilibrated with eluent, after which the sample was pumped through the concentrator column, with the effluent being directed to waste. Eluent was then used to carry the concentrated sample ions onto the analytical column and the concentrator column remained in the flow path during the entire separation process. It is also noteworthy that a "back flushing" technique was used; that is, the sample ions were eluted from the concentrator column in the opposite flow direction to that in which they were loaded. It is important to consider the effects of these processes on the equilibration of the concentrator column with eluent ions.

Before the sample is introduced to the concentrator column, both concentrator and analytical columns are allowed to equilibrate with eluent ions, *i.e.*, methanesulphonate ions, leading to a constant background conductivity of the eluent reaching the detector. During the sample loading process, some of the adsorbed eluent ions are removed from the concentrator column, due either to adsorption of sample ions or to the washing effect of the large sample volume used (15 ml). Whilst it may be expected that the aqueous sample would cause very slow removal of bound eluent ions (for example, through displacement by hydroxide ions), the volume of sample used represents some 300 concentrator column volumes, which suggests that this effect would occur to a significant extent. Indeed, we have confirmed this using ultrapure water as sample.

When eluent is then passed through the concentrator column in order to remove the trapped solute ions, some of the eluent ions initially reaching the concentrator column will be adsorbed onto the resin surface as equilibrium is re-established. The time taken for restoration of the equilibrium between the concentrator column and eluent ions will be dependent on a variety of factors, including the eluent concentration, the ion-exchange capacity and volume of the concentrator column, the amount and volume of sample loaded and the eluent flow-rate used. It is clear that until equilibrium is attained, the concentration of eluent ions reaching the detector will be less than the baseline level established prior to sample loading. With conductivity detection, severe baseline disturbances can therefore be expected because the detector baseline is governed by the concentration of eluent ions in the detector cell. In contrast, UV absorption detection should give stable baselines because the eluent is essentially UV transparent. These effects are clearly illustrated in Fig. 1 and baseline disturbances similar to those observed for conductivity detection can also be expected to occur with indirect UV absorption (or "vacancy") detection[5,6], in which a significant background UV absorbance is provided by the use of UV absorbing eluents such as phthalate.

Modified system design

In order to permit the use of conductivity detection with automated sample

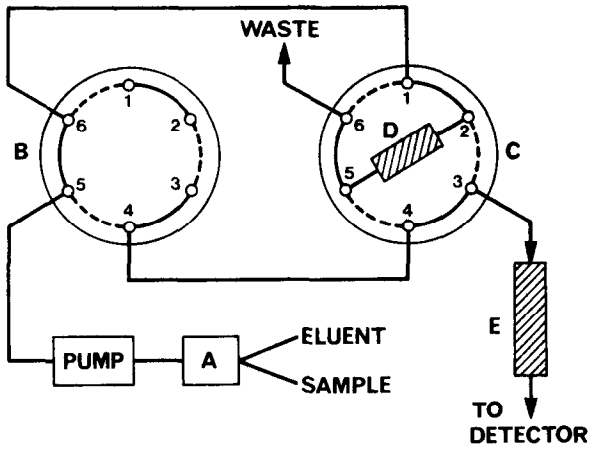


Fig. 2. Details of interconnections used for a preconcentration system applicable to conductivity detection. A = Solvent select valve; B, C = six port high pressure switching valves; D = concentrator column; E = analytical column.

preconcentration, a modified system design was necessary to eliminate or reduce the problem of unstable baselines. After consideration of the origin of this problem as discussed above, two approaches were envisaged as possible solutions.

(a) Sample "stripping". In this approach, the adsorbed sample ions were to be eluted from the concentrator column and then the concentrator column removed from the flow path. This step should be achievable with minimal eluent volumes provided the sample ions were bound as a narrow band close to the input end of the concentrator column, allowing the sample ions to be stripped from the concentrator column in the opposite flow direction to that in which they were loaded.

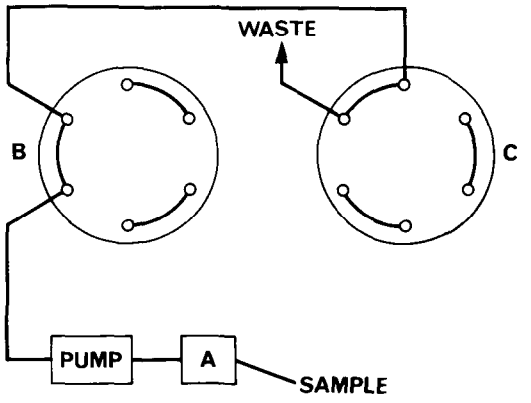
A further variation of sample stripping can be considered in which a small volume of a more concentrated solution of the eluent is used for sample stripping in order to remove adsorbed sample from the concentrator column in the smallest possible volume.

(b) Concentrator column "washing". This approach involves pumping a small volume of eluent through the loaded concentrator column, in the direction of sample loading. The purpose of this step is to assist with re-equilibration of the column with eluent and to remove residual sample from the interstices of the concentrator column and from the connecting tubing.

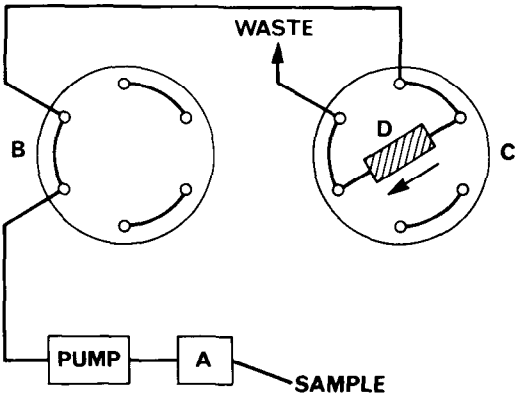
Using the same instrumental components and system configuration described in our previous paper[4], the valve interconnections were redesigned in order to permit the above approaches to be studied. Details of the valve interconnections are given in Fig. 2.

System operation

The basic steps involved in sample preconcentration and analysis incorporating sample stripping and concentrator column washing steps are given in Fig. 3. The pump microprocessor was used to operate the solvent select valve and to determine the flow path using the pneumatically operated column switching valves. All valves were actuated by electronic pulses from the pump microprocessor via the events unit.


WASTE
B
C
PUMP
A
SAMPLE

(a)


WASTE
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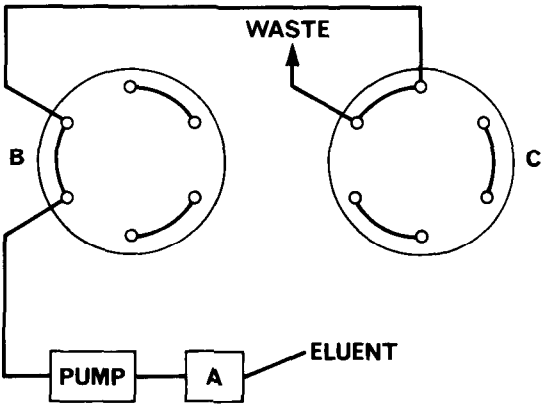
SAMPLE

(b)


WASTE
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C
PUMP
A
ELUENT

(c)

Fig. 3.

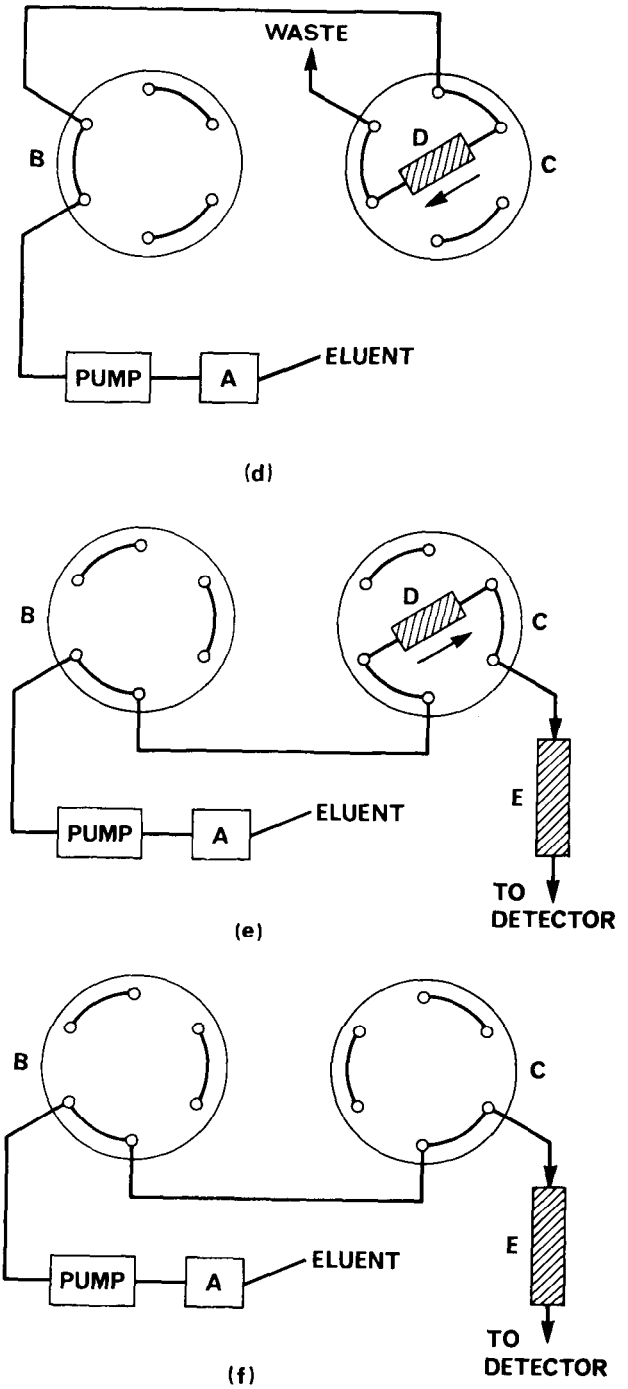

Fig. 3. Flow paths used at various stages of sample preconcentration and elution. See text for discussion. (a) Sample flush mode; (b) sample load mode; (c) eluent flush mode; (d) concentrator wash mode; (e) sample strip mode; (f) analysis mode. A–E as in Fig. 2.

TABLE I

BASIC PROGRAM FOR THE PRECONCENTRATION AND ANALYSIS OF A SAMPLE, INCORPORATING SAMPLE STRIPPING AND CONCENTRATOR COLUMN WASHING

The flow-rates, etc., shown are representative of those used in routine analysis. The flow paths in the table refer to those given in Fig. 3.

Step	*Mode*	*Duration (min)*	*Solvent*	*Flow path (see Fig. 3)*	*Flow-rate (ml/min)*	*Volume delivered (ml)*
1	Sample flush	2.0	Sample	a	20.0	40.0
2	Sample load	5.0	Sample	b	1.0	5.0
3	Eluent flush	2.0	Eluent	c	20.0	40.0
4	Concentrator wash	0.75	Eluent	d	0.2	0.15
5	Sample strip	0.5	Eluent	e	1.0	0.5
6	Analysis	10.0	Eluent	f	1.2	12.0
7	Re-equilibrate	5.0	Eluent	e	1.2	6.0

In Fig. 3a, the two column switching valves (labelled B and C) have determined the flow path indicated, and the solvent select valve was set to draw sample. This configuration is the "sample flush mode" and permits sample to be drawn through the pump inlet line and pumped at high flow-rate through all interconnecting tubing prior to the concentrator column.

Loading of a sample onto the concentrator column was achieved when the valves were switched to the positions shown in Fig. 3b, termed the "sample load mode". Here a known volume of sample was delivered at a precise flow-rate to the concentrator column, with the effluent directed to waste.

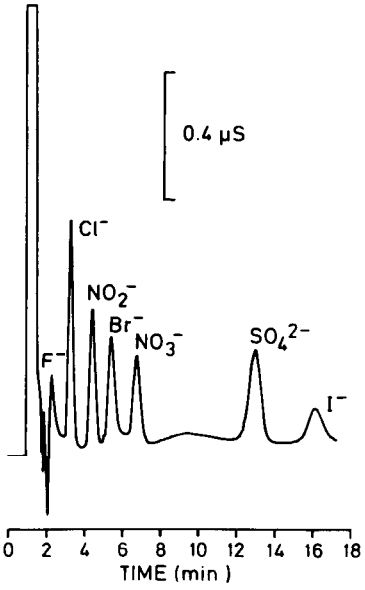

Fig. 4. Chromatogram obtained for a preconcentrated sample using sample stripping. Conditions: analytical column, Waters Assoc. IC Pak A (50 × 4.6 mm I.D.); concentrator column, Waters Assoc. IC-concentrator (6.0 × 5.0 mm I.D.); eluent, 0.8 m*M* phthalate at pH 7.2; flow-rate, 1 ml/ min; sample, 5 ml of a 100-ppb mixture of the indicated ions; sample strip volume, 500 µl.

The next stage was the "eluent flush mode" (Fig. 3c), in which the pump inlet line and all tubing prior to the concentrator column were flushed with eluent, using a high flow-rate. After all sample had been purged from the interconnecting tubing, the system entered the "concentrator wash mode", which is depicted in Fig. 3d. In this step, a known small quantity of eluent was pumped through the concentrator column, in the direction of sample loading, in order to re-equilibrate partially the concentrator column.

Sample ions were then removed from the concentrator column using the "sample strip mode" (Fig. 3e). Here, an accurate volume of eluent was pumped through the concentrator column in the flow direction opposite to that used for sample loading. When all sample had been transferred to the analytical column, the valves were switched to the "analysis mode", which is shown in Fig. 3f. In this mode, eluent was pumped directly to the analytical column, with the concentrator column removed from the flow path. At the commencement of this step, an electronic pulse from the pump was used to activate the data module.

Pumping a small volume of concentrated eluent solution through the concentrator column in order to elute more rapidly sample ions from the concentrator column was also possible with the flow paths shown in Fig. 3. This step was achieved using the valve positions shown in Fig. 3c and e, except that the solvent select valve was positioned to draw the concentrated eluent solution. The solvent select valve used in this study could accommodate up to four different solvents without modification.

The relative merits of the two approaches of sample stripping and concentrator column washing are discussed below. In routine operation, a combination of these two approaches yielded optimal results. Table I shows the essential steps of a pump program which incorporates these steps and illustrates the typical duration and flow-rate employed for each step in the program. It is noteworthy that the pump was required to operate at extremes of flow-rate, for example from 200 μl/min up to 20 ml/min. For clarity, the program shown in Table I is greatly simplified in comparison to the program used in practice, which incorporated numerous additional steps to permit gradual changes in flow-rate in order to minimise pressure damage to the resin-based columns used in this study.

Sample stripping

The concept of removal of the concentrator column from the flow path after elution of the sample ions was examined as a method for minimising baseline drift after sample preconcentration. Comparison of retention times obtained using a concentrator column remaining in the flow path during analysis with those obtained using direct manual injection onto the analytical column suggested that when phthalate at pH 7.0 was used as eluent, sulphate ion was eluted from the concentrator column after the passage of approximately five column volumes of eluent. In contrast, the baseline was not re-established until some 70 column volumes (3.5 ml) of eluent had passed through the concentrator column. Clearly, the volume of eluent used for sample stripping must be sufficiently great to ensure that sample ions are quantitatively removed from the concentrator column, yet as small as possible to minimise baseline disturbance resulting from re-equilibration of the concentrator column. In view of these factors, a sample strip volume of 500 μl was applied to a 5-ml concen-

trated sample of 100 ppb of fluoride, chloride, nitrite, bromide, nitrate, sulphate and iodide. The chromatogram obtained is shown in Fig. 4, which reveals that baseline disturbance was minimal and adequate resolution of solute ions was obtained.

At the concentration shown in Fig. 4 (100 ppb), it was possible to quantitate manually peak areas when the analysis was performed without the sample stripping step, *i.e.*, with the concentrator column remaining in the flow path during the analysis, despite the drifting baseline obtained. This permitted a comparison of peak areas obtained with and without sample stripping, thereby enabling the recovery of the sample stripping process to be ascertained. Recovery data obtained with several sample strip volumes are presented in Fig. 5 which shows that sample strip volumes in excess of 500 μl were required for quantitative removal of sample ions from the concentrator column. Moreover, with the phthalate eluent used, sulphate was more readily eluted from the concentrator column than other ions, despite its higher ion-exchange affinity. This behaviour can be explained by recognising that sulphate would be expected to accumulate at the head of the concentrator column during sample loading because of its ability to displace bound eluent and other solute ions. This in turn suggests that sulphate would therefore be likely to elute quite rapidly during the sample stripping step carried out in the opposite flow direction. The presence of strongly bound solute ions (such as sulphate) in a sample poses an obvious limitation to the amount of sample used for preconcentration, in that such ions may displace more weakly bound solute ions, leading to losses.

When larger sample volumes were employed to permit more dilute samples to be analysed, it became evident that whilst the sample stripping step was successful,

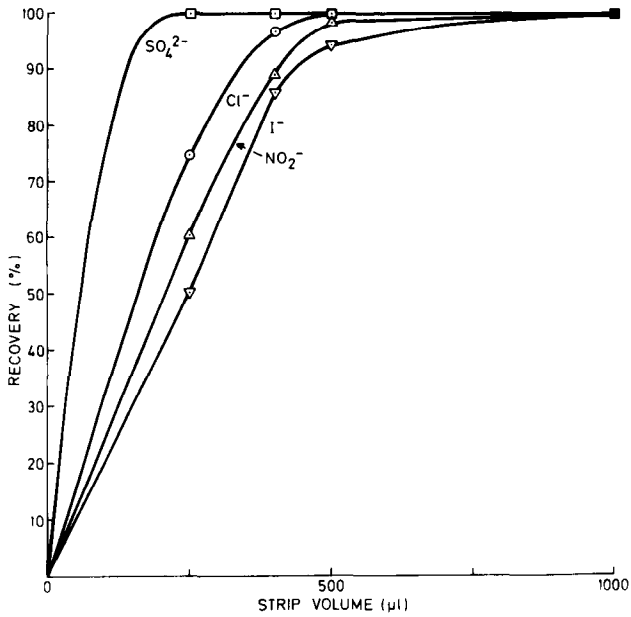

Fig. 5. Percentage recoveries obtained at various sample strip volumes. Recoveries were calculated by expressing the peak areas obtained with the sample stripping method as a percentage of the peak areas obtained when the concentrator column remained in the flow path for the entire analysis. Chromatographic conditions as for Fig. 4.

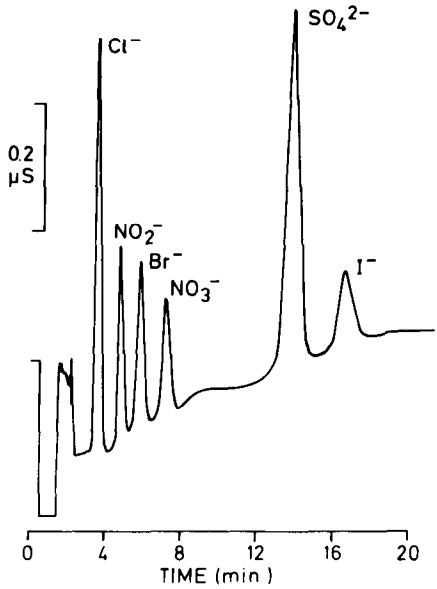

Fig. 6. Typical chromatogram obtained when the sample stripping method was used for a dilute sample requiring a large sample volume. Conditions: sample, 20 ml of a 50-ppb mixture of the indicated ions; eluent 1.0 m*M* phthalate at pH 6.1; other conditions as for Fig. 4.

sample binding was non-quantitative. Fig. 6 shows the results obtained under similar conditions to Fig. 4, using a 20-ml sample of 50 ppb of chloride, nitrite, bromide, nitrate, sulphate and iodide. This figure shows that baseline drift was encountered and peak areas were not in proportion to sample concentration. Moreover, comparison of Figs. 4 and 6 reveals that the peak areas obtained in Fig. 6 were considerably less than expected, taking into account the sample volume, the sample concentration and also the detector sensitivity.

Table II gives a comparison of average peak areas obtained using manual injection and sample preconcentration, both with and without sample stripping. These results show that manual injection gave the greatest peak areas for early eluting ions such as chloride and nitrite, but for later eluting species, the three sample introduction methods were roughly equivalent. The two preconcentration methods gave almost identical results, suggesting that removal of bound sample ions from the concentrator was quantitatively achieved. On the other hand, the disparity between the manual injection and preconcentration methods observed for weakly retained ions indicated that these ions were not quantitatively bound during the concentration step. This could be due either to self elution by the sample or an inability of some solute ions to compete with phthalate ions for ion-exchange sites on the column. It is also noteworthy that a sample volume of 5 ml was used for the preconcentrated samples in Table II, and the problem of non-quantitative binding of sample ions illustrated in this table can be expected to worsen for larger sample volumes.

The baseline drift in Fig. 6 was attributed to greater disequilibration of the concentrator column than that occurring in Fig. 4, due to the much larger sample volume used. This could be caused by loss of bound eluent ions resulting from the

TABLE II

COMPARISON OF PEAK AREAS OBTAINED USING DIRECT INJECTION AND PRECONCENTRATION, BOTH WITH AND WITHOUT SAMPLE STRIPPING

Conditions: manual injection, 100 μl of a 5-ppm mixture of the indicated ions, eluent 1.0 m*M* phthalate at pH 7.2; preconcentration of 5 ml of a 100-ppb mixture of the indicated ions, eluent 1.0 m*M* phthalate at pH 7.2. A sample strip volume of 500 μl was used.

Solute	*Peak area (arbitrary units)*		
	Manual injection	*With sample stripping*	*Without sample stripping*
Chloride	957	619	618
Nitrite	492	475	475
Bromide	432	405	403
Nitrate	336	334	334
Sulphate	658	634	638
Iodide	280	280	272

washing effect of the large volume of dilute sample passed through the concentrator column. In order to correct this disequilibration, an alternative sample stripping method which used a small volume of concentrated eluent to facilitate rapid elution of sample ions from the concentrator column was also examined. An eluent of 0.8

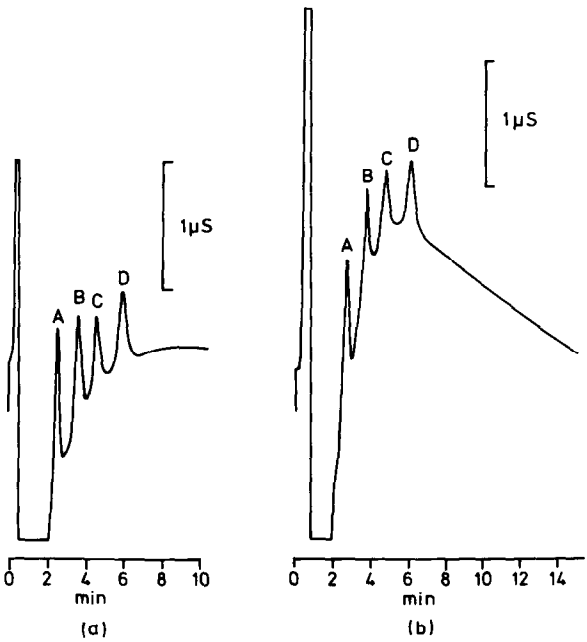

Fig. 7. Chromatogram obtained when sample stripping with a concentrated eluent solution was used. Conditions: sample, 5 ml of a 100-ppb mixture of chloride (A), nitrite (B), bromide (C) and nitrate (D); eluent, 0.8 m*M* phthalate at pH 7.0; flow-rate, 1.2 ml/min; detector sensitivity, 5 μS f.s.; sample stripping with 25 μl of 10 m*M* (a) or 50 m*M* (b) phthalate at pH 7.0, followed by 250 μl of 0.8 m*M* phthalate at pH 7.0; other conditions as for Fig. 4.

m*M* phthalate at pH 7.0 was employed for sample analysis and 25-μl volumes of 10 m*M* or 50 m*M* phthalate at pH 7.0 were pumped through the loaded concentrator column, followed by 250 μl of the 0.8 m*M* phthalate eluent. The resulting chromatograms appear in Fig. 7, from which it is apparent that the baseline has not been effectively restored. Indeed, the results obtained with this approach were inferior to those obtained previously when sample stripping was carried out with the same eluent used for separation of the sample ions on the analytical column.

Under the conditions used throughout this study of sample stripping, the eluent contained doubly ionised phthalate, which shows a strong affinity for anion-exchange resins. It is therefore likely that preconditioning of the concentrator column with this eluent could contribute to incomplete binding of those solute ions which are unable to displace effectively phthalate ions. Our previous study[4] showed that weakly retained solute ions such as nitrite could be quantitatively preconcentrated on a column which had been conditioned with methanesulphonate eluent. Unfortunately, this eluent was unsuitable for use with conductivity detection because of its relatively high background conductivity, so an alternative eluent with a similar ion-exchange affinity was sought. An appropriate eluent was gluconate in borate buffer and this was used for all further studies in an effort to increase the efficiency of the sample loading process.

Concentrator column washing

The rationale of this approach was that pumping a small volume of eluent into the concentrator column, in the flow direction of sample loading, would serve to minimise baseline disturbances by partial re-equilibration of the concentrator column

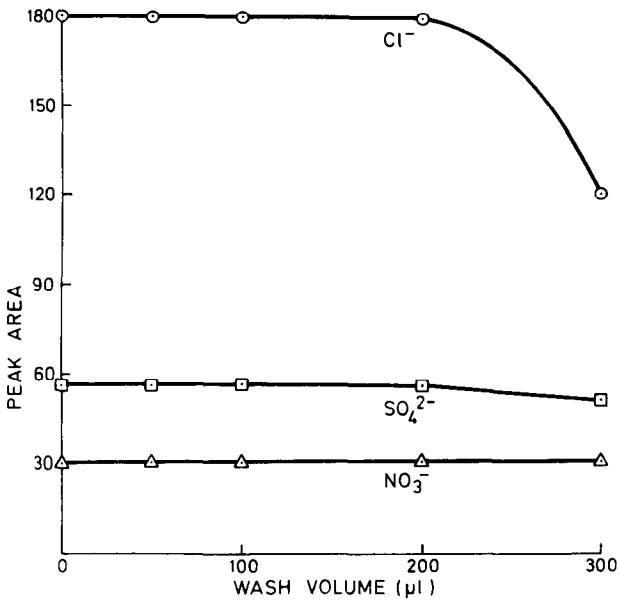

Fig. 8. Peak areas (arbitrary units) obtained using various concentrator column wash volumes. Conditions: sample, 5 ml of a 50-ppb mixture of the indicated ions; detector sensitivity, 1 μS f.s.; sample strip volume, 1000 μl; eluent, 5.3 m*M* boric acid, 1.2 m*M* tetraborate and 1.1 m*M* gluconate at pH 8.0. Other conditions as for Fig. 4.

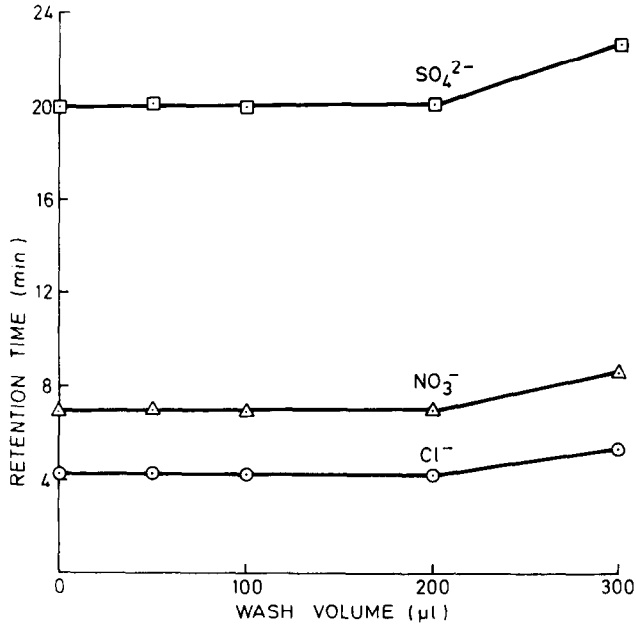

Fig. 9. Retention times obtained using various concentrator column wash volumes. Conditions: as for Fig. 8, except that a sample strip volume of 800 μl was used.

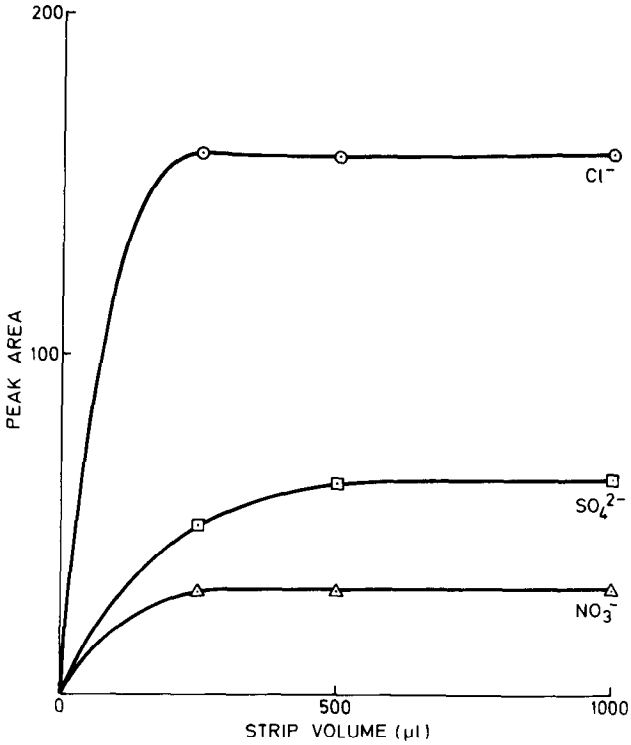

Fig. 10. Peak areas (arbitrary units) obtained using various sample strip volumes. Conditions: as for Fig. 8, except that a constant concentrator column wash volume of 150 μl was used.

with eluent and by removing residual sample from the interstices of the concentrator column. The drawback with this method was the possibility of loss of adsorbed sample during the washing process. To minimise loss, washing was carried out in the direction of sample loading on the basis that adsorbed sample would be located close to the head of the concentrator column. This aspect was verified experimentally.

Retention times of some anions were measured on an equilibrated concentrator column and it was found that several column volumes of eluent could be passed through the concentrator column before elution of any ions. Various wash volumes within this range were studied and Fig. 8 shows the relationship between wash volume and peak area for 5-ml sample volumes of a 50-ppb mixture of chloride, nitrate and sulphate, using a gluconate/borate eluent. It can be seen from Fig. 8 that wash volumes of up to 200 μl could be employed without loss of adsorbed sample, suggesting that a large proportion of the eluent ions contained in this volume were consumed in the re-equilibration of the concentrator column. The relationship between wash volume and solute retention times is given in Fig. 9, which indicates that when wash volumes in excess of 200 μl were used, appreciable elution of adsorbed ions along the concentrator column occurred, leading to increased retention times during the analysis step.

Optimised procedure

All of the above studies strongly suggested that a combination of sample stripping and concentrator column washing would yield optimum results, provided that a weak eluent such as gluconate/borate was employed. The best sample strip volume for use with this eluent was determined by plotting peak area against sample strip volume, using a constant concentrator column wash volume of 150 μl. The results are given in Fig. 10 which shows that a sample strip volume of 500 μl was necessary to maximise the peak area of eluted ions.

Comparison of Figs. 5 and 10 highlights the effect of the type of eluent used for the sample stripping step. In Fig. 5, sulphate was easily stripped from the concentrator column by the phthalate eluent. In contrast, Fig. 10 shows that sulphate was the most difficult ion to strip when an eluent of lower ion-exchange affinity was employed.

TABLE III

COMPARISON OF PEAK AREAS OBTAINED USING MANUAL INJECTION AND PRECONCENTRATION WITH SAMPLE STRIPPING AND CONCENTRATION COLUMN WASHING

Conditions as for Fig. 11.

Solute	*Peak area (arbitrary units)*		*Recovery (%)***
	Manual injection	*Preconcentration**	
Chloride	152	154	101
Nitrate	49	52	106
Sulphate	86	85	99

* The peak areas for the blank preconcentration run (Fig. 11c) have been subtracted.

** Calculated by expressing the preconcentration value as a percentage of the manual injection value.

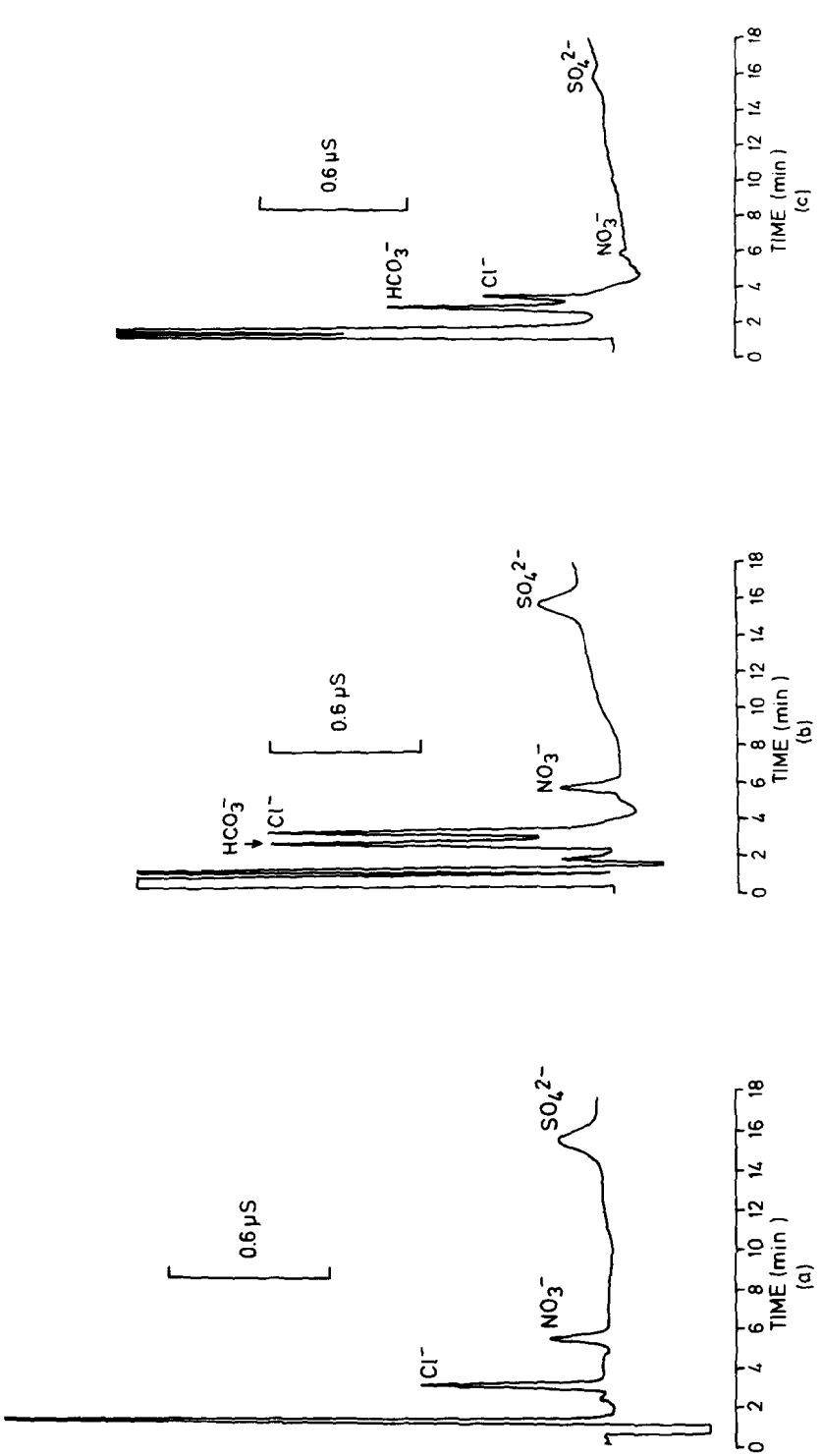

Fig. 11. Chromatograms obtained using manual injection (a) and sample preconcentration incorporating sample stripping and concentrator column washing (b). A blank preconcentration run (c) is also shown. Conditions: sample, (a) 100 µl of a 2.5-ppm mixture of the indicated ions, (b) 5 ml of a 50-ppb mixture of the indicated ions, (c) 5 ml of water; sample strip volume, 500 µl; concentrator column wash volume, 150 µl; detector sensitivity, 2.5 µS f.s.; eluent and other conditions as for Fig. 8.

Using a 500-μl sample strip volume and 150-μl concentrator column wash volume, a 5-ml sample of 50 ppb chloride, nitrate and sulphate was analysed and compared with a manual injection of equivalent amounts of the same ions. The results appear in Fig. 11, which shows the chromatograms obtained for manual injection and preconcentrated sample, together with a preconcentrated blank. The water used for sample preparation contained dissolved carbon dioxide, leading to a significant interfering peak in the chromatogram. Table III lists average peak areas for solute ions obtained from triplicate measurements of the chromatograms shown in Fig. 11. Excellent agreement between manual injection and preconcentration was obtained, indicating that both the sample loading and sample stripping steps were quantitative.

CONCLUSIONS

Sample preconcentration is a complex process, the success of which depends on numerous factors such as the efficiency of sample loading and sample stripping and the stability of the baseline in the final chromatogram. No single set of conditions is applicable to all analyses and it is clear that the parameters used for each determination must be carefully optimised. The type of sample analysed and the anions of interest must be considered when selecting the eluent and column to be used.

Further work is required to ascertain the role of such parameters as the volume and flow-rate used for all steps in the concentration and stripping process, inerference effects between ions, the optimal relationship between the ion-exchange capacities of the concentrator and analytical columns and the ideal dimensions of the concentrator column.

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