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STUDIES ON SAMPLE PRECONCENTRATION IN ION CHROMATOGRAPHY

III*. FACTORS INFLUENCING ELUENT SELECTION IN PRECONCENTRATION METHODS

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SUMMARY

The desirable properties of eluents for preconcentration methods in non-suppressed ion chromatography are discussed and it is shown that the eluent should be univalent, have low equivalent conductance, and when employed at pH < 6, should elute all solute ions within the range $4 < k' < 30$. In addition, the eluent should permit quantitative binding of sample ions onto the concentrator column to ensure that the preconcentration process is quantitative. A wide range of aromatic carboxylic and sulphonic acids are evaluated for their suitability to preconcentration methods. The most suitable eluents tested are *p*-toluenesulphonic acid and 2-naphthylamine-1-sulphonic acid, with the latter being especially applicable to the analysis of univalent solute ions using either conductivity or indirect UV absorption as the detection mode. Detection limits attainable for a 10-ml sample volume are 0.07, 0.03, 0.05, 0.07 and 0.1 ppb for fluoride, chloride, nitrite, nitrate and sulphate, respectively.

INTRODUCTION

As the technique of ion chromatography has developed, increasing numbers of new separation and detection methods have been introduced[1], leading to the necessity for a wide range of different eluents. Eluents employed for ion chromatography of anions have included carbonate–bicarbonate buffer for use with the suppressed approach[2], and aromatic carboxylic acids[3,4], aliphatic sulphonic acids[5] and hydroxide[6] for the non-suppressed approach. These eluents permit detection of eluted anions to be accomplished (either directly or indirectly) using measurements of conductivity, UV absorbance or refractive index.

Whilst a number of studies have been directed towards the evaluation of eluents suitable for non-suppressed ion chromatography[7,8], there has been no sys-

* For Part II, see ref. 12.

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tematic study of the requirements for an eluent to be suitable for sample preconcentration. In most reported preconcentration studies, the eluents used have been restricted to those most commonly employed for manual injection techniques; these have included carbonate–bicarbonate buffer[9] and benzoate, phthalate or citrate[10]. Since the type of eluent used governs the success of the sample preconcentration process by controlling whether the binding of sample ions onto the concentrator column is quantitative and reproducible, it is surprising that so few eluents have been employed.

In previous papers[11,12], we have described the design and operation of an automated, single pump preconcentration system for use with conductivity and direct UV absorption detection. We now report an investigation of the factors which influence eluent selection in sample preconcentration methods, together with an evaluation of the suitability of a range of eluents for preconcentration with conductivity detection.

EXPERIMENTAL

Instrumentation

The liquid chromatograph used consisted of a Waters Assoc. (Milford, MA, U.S.A.) Model M590 programmable pump and events unit, Model M430 conductivity detector, together with a solvent select valve, two pneumatically controlled switching valves and a Model M730 data module. For manual injection methods, a

TABLE I

SPECIES EVALUATED AS ELUENTS FOR NON-SUPPRESSED ION CHROMATOGRAPHY

Acid	*Manufacturer*	pK_a
Benzoic acid	BDH, U.K.	4.20
o-Nitrobenzoic acid	Fluka, Switzerland	2.21
m-Nitrobenzoic acid**	BDH, U.K.	3.45
Phthalic acid (potassium hydrogen salt)**	Ajax, Australia	2.95, 5.41
Methanesulphonic acid	Tokyo Kasei, Japan	<1
Gluconic acid (sodium salt)	Fluka, Switzerland	3.76
Boric acid	May & Baker, U.K.	9.24
Gluconate–borate buffer**	–	–
Salicylic acid	BDH, U.K.	2.97, 13.40
Sulphosalicylic acid	Townson & Mercer, Australia	<1, 2.67, 11.67
p-Hydroxybenzoic acid**	BDH, U.K.	4.61, 9.32
Benzenesulphonic acid	Merck, F.R.G.	2.55
p-Toluenesulphonic acid**	Aldrich, U.K.	<1
Naphthalenesulphonic acid	BDH, U.K.	<1
2-Naphthylamine-1-sulphonic acid**	Judex, U.K.	<1, 3.5
2-Naphthol-6-sulphonic acid (sodium salt)	BDH, U.K.	<1, 8.9

* The cell constant was measured to be 11.8 cm^{-1}.

** Eluent selected for use with the preconcentration method.

Waters Assoc. Model U6K injector and M450 variable-wavelength UV detector were added.

A Waters Assoc. IC Pak A (50 × 4.6 mm I.D.) methacrylate-based anion-exchange column was used as the separator column and the concentrator column was a Waters Assoc. IC concentrator (5.0 × 6.0 mm I.D.), packed with methacrylate-based anion-exchange material. The concentrator column was housed in a Waters Assoc. Guard Pak precolumn module.

Reagents

All water was doubly distilled and passed through a Millipore (Bedford, MA, U.S.A.) Milli Q water purification system. Standard solutions and mixtures (1000 ppm) of fluoride, chloride, nitrite, bromide, nitrate and sulphate were prepared by dissolving appropriate amounts of analytical grade sodium salts in pure water. These solutions were diluted daily to give trace solutions which were made up in polypropylene volumetric flasks which had been previously rinsed with water.

Table I lists the reagents which were studied as eluents, together with the supplier from which they were obtained and their pK_a values[13,14]. Where necessary, these reagents were recrystallised before use. Eluents were prepared by dissolving a weighed amount of the reagent in approximately 800 ml of water, after which the pH was adjusted by dropwise addition of 0.1 *M* sodium hydroxide and the solution diluted to 1 l with water. Each eluent was prepared daily and was filtered through a 0.45-μm filter and degassed in an ultrasonic bath prior to use.

Eluent conditions	*Background conductivity** ($\mu S\ cm^{-1}$)	*Retention time (min)*			
		Cl^-	NO_2^-	NO_3^-	SO_4^{2-}
10 m*M*, pH = 6.0	920	–	–	–	13.2
10 m*M*, pH = 6.0	901	–	–	–	12.0
3 m*M*, pH = 6.0	282	3.15	3.74	5.05	20.46
0.6 m*M*, pH = 6.0	138	4.04	5.70	9.37	18.39
10 m*M*, pH = 6.0	850	8.31	–	–	–
2.0 m*M*, pH = 6.0	197	12.43	–	–	–
8.0 m*M*, pH = 9.5	482	2.81	3.58	5.30	15.26
1.0 m*M* tetraborate, 1.0 m*M* gluconate, 4.4 m*M* boric acid, pH = 8.5	249	3.96	5.44	8.69	20.21
2 m*M*, pH = 6.0	190	3.24	3.74	4.90	21.24
0.2 m*M*, pH = 5.3	48	3.79	4.40	6.40	13.92
1.75 m*M*, pH = 8.7	211	2.76	3.43	4.79	12.03
5.0 m*M*, pH = 6.0	470	3.31	4.22	6.12	18.40
3.5 m*M*, pH = 6.0	299	3.31	4.19	5.97	16.03
1.0 m*M*, pH = 6.0	109	2.35	2.87	3.65	11.62
0.8 m*M*, pH = 6.0	78	2.80	3.28	4.19	16.82
0.75 m*M*, pH = 6.0	54	3.51	4.22	5.49	23.80

Procedure

The pump microprocessor was programmed to actuate the valves in a timed sequence, the details of which are given in our previous paper[12]. When sample preconcentration was employed, a wash volume of 200 μl and a sample strip volume of 500 μl were used (see ref. 12 for definitions of these terms). Details of mobile phases and experimental conditions are provided in Table I and the figure captions.

RESULTS AND DISCUSSION

Eluent requirements in sample preconcentration methods

In considering the requirements of an eluent to be used for a sample preconcentration method with non-suppressed conductivity detection, a number of important features emerge.

Selectivity. The eluent should provide suitable separation of typical solutes such as chloride, nitrite, nitrate and sulphate. Moreover, it is essential that the earliest eluting peak has $k' > 4$ to avoid interference from the large solvent peak normally associated with preconcentration methods. This necessarily results in divalent anions such as sulphate having long retention times and in order to ensure that the peak shapes for such species are acceptable, the eluent should give $k' < 30$ for sulphate.

Sensitivity. A paramount requirement is that solute ions are sensitively detected, since the primary purpose of sample preconcentration is the determination of ions at ultra-trace levels. In the non-suppressed mode of ion chromatography, the signal (ΔG) produced by a conductivity detector when a solute ion S^- elutes in an eluent containing E^- is given by[15]

$$\Delta G = \frac{(\lambda_{E^-} - \lambda_{S^-})}{10^{-3} K} C_S \qquad (1)$$

where λ_{E^-} and λ_{S^-} are the equivalent conductances of the solute and eluent ions, respectively, K is the cell constant and C_S is the concentration of the solute ion. This equation assumes that the sample and eluent are fully ionised at the eluent pH value used.

Eqn. 1 shows that the conductivity signal is dependent on the difference between the equivalent conductances of the solute and eluent anions. The solute anions generally have relatively high equivalent conductances, so in order to maximise the conductivity signal, an eluent of low equivalent conductance should be used. This produces the further advantage that the total background conductivity of the eluent will then be low, which minimises baseline noise and permits the conductivity detector to be operated on a sensitive range. The working range of most conductivity detectors is governed by the amount of offset required to electronically suppress the background conductivity of the eluent.

A further factor to be considered in maximising the detection sensitivity attainable with an eluent is the charge on the eluent anion. Since detection is based on changes in conductivity resulting from replacement of eluent ions by solute ions on the basis of charge equivalence, it follows that an eluent containing divalent ions will generally give less sensitive detection than a univalent eluent. This statement assumes that both types of eluent have similar values of equivalent conductance. For this reason, univalent eluents are preferable.

Eluent pH. Two types of interference are ubiquitous in preconcentration techniques and both can be overcome by judicious selection of eluent pH. The first interference arises from bicarbonate ion which is present in most samples at levels far exceeding those of the solute anions to be determined. During the concentration process, these bicarbonate ions accumulate on the concentrator column and often produce a very large peak in the final chromatogram. If the determination of bicarbonate in the sample is unimportant, the most simple way to eliminate the bicarbonate peak is to use an eluent with pH < 6, under which conditions the bicarbonate becomes protonated and elutes with the solvent front. In most cases, it is therefore desirable that the eluent pH be maintained at pH < 6.

The second type of interference is that resulting from system peaks which can arise from elution of the neutral, fully protonated form of the eluent under a reversed-phase mechanism[16]. Characteristically, system peaks are large when large sample volumes are used. Such system peaks may be avoided by choosing an eluent pH at which the eluent components are fully ionised, or alternatively selecting an eluent which is a strong enough acid to be ionised over a wide pH range.

Fritz and co-workers[7,17] have shown that weak acid eluents in non-suppressed ion chromatography are more sensitive than eluents containing acid salts. Moreover, they have suggested that sensitivity of detection improves as the degree of dissociation of the eluent acid decreases because the undissociated eluent acid can displace solute ions bound to the ion-exchange resin. When this displacement occurs, a neutral eluent molecule is replaced in the mobile phase by a solute ion and a highly conducting hydrogen ion, leading to a large change in the measured conductivity and hence to sensitive detection. In our studies on sample preconcentration methods, we have chosen to use fully ionised eluents in order to minimise eluent adsorption on the column and so avoid system peaks and also to provide suitable retention characteristics, as discussed above. However, this would undoubtedly lead to some loss of sensitivity in comparison to that attainable with partly dissociated weak acid eluents.

Nature of the eluent. Implicit in the successful operation of sample preconcentration is the quantitative binding of sample ions to the concentrator column during sample loading. Previous studies[12] have shown that sample binding is very dependent on the type of eluent used to condition the precolumn prior to sample loading. In most cases, this eluent is the same as that used for elution of sample ions onto the separator column and their resultant separation on that column. The eluent must therefore serve three functions; it must be sufficiently weak to permit quantitative sample binding on the concentrator column, it should be sufficiently strong to elute sample ions from the concentrator column as a compact band (which is essential to the operation of the sample stripping technique previously reported[12]) and the eluent must also provide acceptable resolution of sample ions on the separator column. When it is recognised that the ion-exchange capacities of the concentrator and separator columns are often dissimilar, it can be seen that it may never be possible for a single eluent to successfully serve all of the above functions. In such cases, it may be necessary to use different eluents for each function and the automated preconcentration system previously reported[12] was designed to permit the use of three different eluents. However, in the present paper, the eluents examined were evaluated for their overall performance in all three stages of the sample preconcentration method.

Preliminary assessment of eluents using manual injection

In order to determine whether the eluent species listed in Table I would provide the selectivity required for sample preconcentration, they were first examined as eluents for manual injection methods. Eluent conditions were based on the pK_a value of the eluent acid, with consideration to the eluent pH requirements discussed earlier and the eluent strength required to achieve the desired retention behaviour for sulphate. Table I shows these conditions, together with the background conductivity of each eluent and the retention data obtained for the ions injected.

From Table I, it can be seen that a number of eluents were clearly unsuitable. Benzoic acid and *o*-nitrobenzoic acid were too weak to achieve suitable elution of sulphate without giving an unacceptably high background conductivity; salicylic acid and sulphosalicylic acid proved to have unsuitable selectivity in that they gave poor resolution of early eluting species; methanesulphonic acid and benzenesulphonic acid gave adequate resolution but high background conductivities; naphthol-5-sulphonic acid gave very poor peak shape, and both naphthalene sulphonic acid and sulphosalicylic acid gave interfering system peaks under all conditions.

Eluents selected for further study with preconcentration methods included *m*-nitrobenzoic acid, *p*-hydroxybenzoic acid, potassium hydrogen phthalate, gluconate–borate buffer, *p*-toluenesulphonic acid and 2-naphthylamine-1-sulphonic acid. It was noteworthy that gluconic and boric acids when used separately were both very weak eluents, but when combined proved to be an effective eluent. This can be attributed to formation of an anionic complex between the two species, which then acts as the major eluent anion. A system peak was observed with *p*-hydroxybenzoic acid unless the eluent pH was raised to 11; however, a lower eluent pH value was employed because the system peak eluted late in the chromatogram and was well resolved from sulphate.

Two of the above eluent species, *p*-toluenesulphonic acid and 2-naphthylamine-1-sulphonic acid, appeared particularly promising. *p*-Toluenesulphonic acid gave a relatively low background conductivity and good separation of anions (Fig. 1). The 2-naphthylamine-1-sulphonic acid eluent did not give good resolution of early eluting ions under conditions where sulphate showed the desired degree of retention (Table I), but its background conductivity was very low (78 μS). This eluent was therefore used for monovalent anions and the separation of these ions is shown in Fig. 2, which illustrates the high sensitivity attainable. Under the conditions shown in Fig. 2, it would be possible to detect low ppb* levels of monovalent anions by direct injection. In addition, the high UV molar absorptivity of 2-naphthylamine-1-sulphonic acid (3490 l mol^{-1} cm^{-1} at 300 nm) suggested that this eluent would be ideal for use with indirect UV absorption detection[18]. This suggestion is realised in Fig. 3, which shows a 500 μl injection of a 20 ppb mixture of chloride, nitrite, bromide and nitrate with indirect UV absorption detection at 300 nm.

Preconcentration studies

The eluents selected for evaluation with the sample preconcentration method are indicated in Table I. With each eluent, sulphate eluted with a retention time of approximately 20 min, with the exception of *p*-hydroxybenzoic acid which was slight-

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

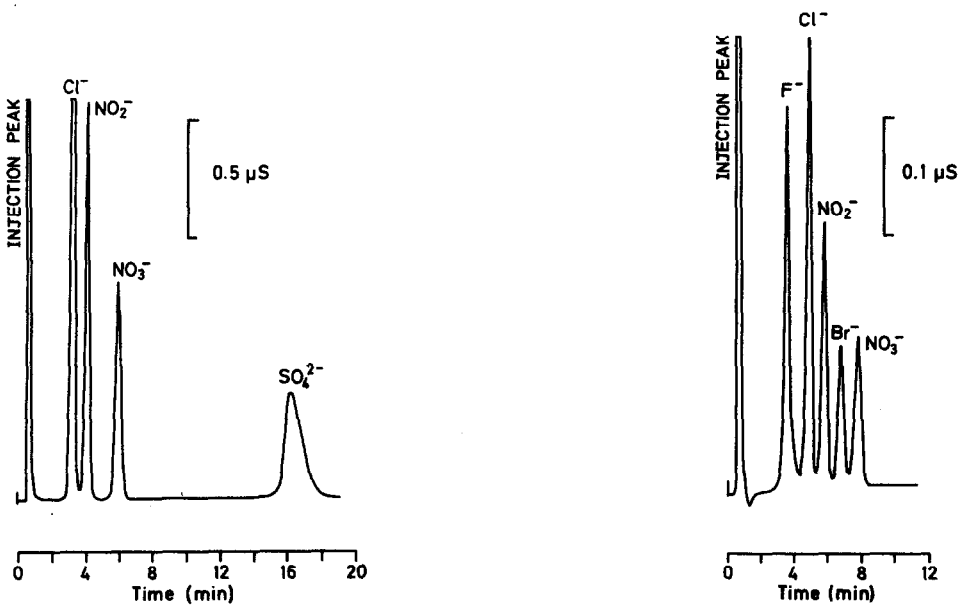


Fig. 1. Manual injection of a standard mixture with *p*-toluenesulphonic acid as eluent. Conditions: column, Waters IC Pak A; eluent, 3.5 m*M* *p*-toluenesulphonic acid (pH 6.0); flow-rate, 1.0 ml/min; sample, 25 μl of a solution containing 100 ppm of each of the indicated ions.

Fig. 2. Manual injection of a standard mixture with 2-naphthylamine-1-sulphonic acid as eluent. Conditions: eluent, 0.4 m*M* 2-naphthylamine-1-sulphonic acid (pH 6.0); sample, 100 μl of a solution containing 1 ppm of each of the indicated ions. Other conditions as for Fig. 1.

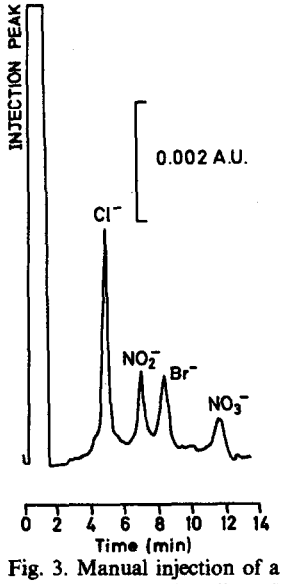


Fig. 3. Manual injection of a standard mixture of univalent anions using 2-naphthylamine-1-sulphonic acid as eluent with indirect UV absorption detection. Conditions: eluent, 0.3 m*M* 2-naphthylamine-1-sulphonic acid (pH 6.0); sample, 500 μl of a solution containing 20 ppb of each of the indicated ions; detector wavelength, 300 nm. Other conditions as for Fig. 1.

ly stronger in order to resolve sulphate from the system peak, and the dilute 2-naphthylamine-1-sulphonic acid eluent which was suitable only for monovalent anions. All eluents were used for the preconcentration of 10 ml of a mixture containing 50 ppb each of chloride, nitrite, nitrate and sulphate.

The chromatograms obtained all showed a large solvent peak and with *m*-nitrobenzoic acid and *p*-hydroxybenzoic acid, the solvent peak showed considerable interference with chloride and nitrite ions. Moreover, the necessity to use a high eluent pH (8.7) with *p*-hydroxybenzoic acid in order to resolve sulphate from the system peak resulted in the appearance of a large bicarbonate peak which co-eluted with chloride in the chromatogram. Similarly, the gluconate–borate eluent gave a bicarbonate peak but in this case, interference with chloride was not as severe. On the other hand, phthalate (Fig. 4) and *p*-toluenesulphonic acid (Fig. 5) gave satisfactory chromatograms for the mixture of ions, and 2-naphthylamine-1-sulphonic acid was suitable for monovalent ions.

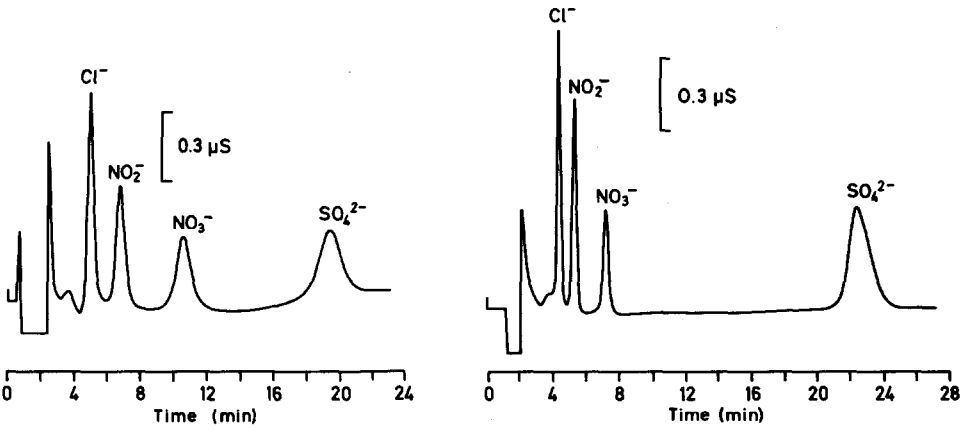


Fig. 4. Preconcentration of a standard mixture with phthalic acid as eluent. Conditions: eluent, 0.6 m*M* phthalic acid (pH 6.0); sample, 10 ml of a solution containing 50 ppb of each of the indicated ions, loaded at 1.0 ml/min. Other conditions as for Fig. 1.

Fig. 5. Preconcentration of a standard mixture with *p*-toluenesulphonic acid as eluent. Conditions: eluent, 3.5 m*M* *p*-toluenesulphonic acid (pH 6.0). Other conditions as for Fig. 1.

A convenient method for assessing the degree of quantitation of the sample loading and stripping steps in the preconcentration method is to calculate the recovery of each solute ion, expressed as the percentage ratio of the peak area obtained by preconcentration to that obtained with a manual injection of the same amount of solute. In this case, a 100-µl manual injection of a 5-ppm solution was compared with a preconcentration run using 10 ml of a 50-ppb solution, using chloride, nitrite, nitrate and sulphate as the solute ions. The results obtained with this method are given in Table II, for which the solute ions were injected separately, and Table III, for which the solute ions were injected as a mixture. In all cases, chloride showed the lowest recoveries and sulphate showed the highest; this trend is consistent with the relative affinities of these two ions for ion-exchange resins. In addition, Tables II and III indicate that the recovery of a particular ion was generally lower when the ion

TABLE II

RECOVERIES OF PRECONCENTRATED SAMPLES OF INDIVIDUAL IONS

A 10-ml sample containing 50 ppb of an individual ion was preconcentrated. Eluent compositions are given in Table I.

Anion	*Recovery (%)*		
	Phthalic acid	*Gluconate–borate*	*p-Toluenesulphonic acid*
Chloride	68.7	78.8	78.4
Nitrite	94.7	96.0	98.1
Nitrate	88.5	97.3	102.2
Sulphate	97.3	100.0	101.2

was concentrated as part of a mixture. This is attributable to the fact that the total amount of ionic species in the sample is greater for the mixture and displacement of weakly bound ions (such as chloride) by strongly bound ions (such as sulphate) can be expected to occur to some extent.

Of particular interest are the comparative recoveries obtained with the three eluents. Phthalate generally gave the lowest recoveries and *p*-toluenesulphonic acid the highest. Calibration plots prepared for each eluent were linear, indicating that the observed recoveries were not dependent on concentration. The total amount of ionic species in the samples used was less than 0.05 μequiv., and this is small in comparison to the total ion-exchange capacity of the concentrator column, which from the manufacturer's data was calculated to be 2.5 μequiv. These results suggest that the most probable source of the observed variation in recovery was that the binding of solute ions onto the concentrator column during sample loading was dependent on the eluent used. The best eluent in this respect was *p*-toluenesulphonic acid.

Applications

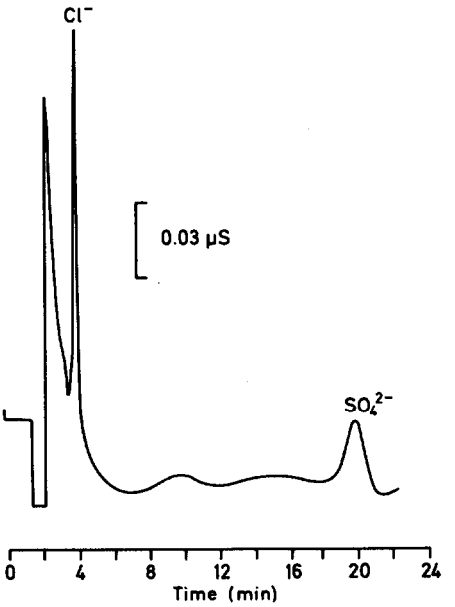
From Fig. 5 it is clear that *p*-toluenesulphonic acid would be a suitable eluent for the determination of ions in the 1–5 ppb range, if the sample volume was increased appropriately. In some applications, such as high purity water for fuel cells or for

TABLE III

RECOVERIES OF PRECONCENTRATED SAMPLE MIXTURES

A 10-ml sample containing 50 ppb of each ion was preconcentrated. Eluent compositions are given in Table I.

Anion	*Recovery (%)*		
	Phthalic acid	*Gluconate–borate*	*p-Toluenesulphonic acid*
Chloride	60.7	79.0	76.4
Nitrite	75.0	82.2	90.1
Nitrate	78.5	97.8	96.3
Sulphate	100.1	100.5	102.3



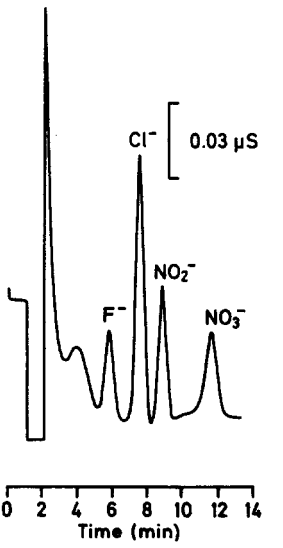


Fig. 6. Preconcentration of chloride and sulphate with 2-naphthylamine-1-sulphonic acid as eluent. Conditions: eluent, 0.8 m*M* 2-naphthylamine-1-sulphonic acid (pH 6.0); sample, 10 ml of a solution containing 1.0 ppb chloride and 0.5 ppb sulphate, loaded at 1.0 ml/min. Other conditions as for Fig. 1.

Fig. 7. Preconcentration of a standard mixture of univalent anions using 2-naphthylamine-1-sulphonic acid as eluent. Conditions: eluent, 0.3 m*M* 2-naphthylamine-1-sulphonic acid (pH 6.0); sample, 10 ml of a solution containing 1.0 ppb of each of the indicated ions, loaded at 1.0 ml/min. Other conditions as for Fig. 1.

use in turbines in power generating stations[19], lower detection limits are required, particularly for chloride and sulphate. Further increases in the volume of sample concentrated could lead to improved detection limits, but would inevitably lead to diminished recoveries and lengthy analysis times. For such cases, use of a high sensitivity eluent such as 2-naphthylamine-1-sulphonic acid would be preferable.

Fig. 6 shows a chromatogram obtained with this eluent for a 10-ml preconcentrated sample containing 1 ppb chloride and 0.5 ppb sulphate. A sample of monovalent anions at the 1-ppb level can be analysed with a more dilute eluent, as shown in Fig. 7. The detection limits attainable for a 10-ml sample are 0.07, 0.03, 0.05, 0.07 and 0.1 ppb for fluoride, chloride, nitrite, nitrate and sulphate, respectively.

CONCLUSIONS

The choice of eluent for sample preconcentration in non-suppressed ion chromatography has a marked effect on the success of the method. Many eluents which are quite suitable for manual injection techniques can be inappropriate for use with preconcentration due to the occurrence of unstable baselines, poor sensitivities, interference from bicarbonate, or inadequate binding of sample ions onto the concentrator column during sample loading.

Of the eluents examined in this study, *p*-toluenesulphonic acid proved to be ideal for the separation and detection of a mixture of mono- and divalent anions at levels as low as 1 ppb. At lower levels, 2-naphthylamine-1-sulphonic acid can be used, provided that monovalent and divalent ions are determined in separate chromatograms. The UV absorption characteristics of this eluent also enable it to be used as a sensitive eluent for direct sample injection, using the indirect UV absorption detection mode.

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