Journal of Chromatography, 366 (1986) 13–26
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 789

CONDUCTIVITY AND INDIRECT UV ABSORPTION DETECTION OF INORGANIC CATIONS IN NON-SUPPRESSED ION CHROMATOGRAPHY USING AROMATIC BASES AS ELUENTS

I. PRINCIPLES OF OPERATION

R. C. L. FOLEY and P. R. HADDAD*

Department of Analytical Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)

(First received April 21st, 1986; revised manuscript received May 15th, 1986)

SUMMARY

An equation is developed to describe the retention behaviour of inorganic cations in non-suppressed ion chromatography and it is shown that a linear relationship exists between the logarithm of the concentration of the eluting species in the eluent and the logarithm of the solute capacity factor. Moreover, the negative slope of this relationship is equal to the ratio of the charges on the solute and eluent ions, provided only one eluent species is responsible for elution.

The conductivity change accompanying elution of a solute cation can be positive or negative, depending on whether the eluent cation has a high or low limiting equivalent ionic conductance. When an aqueous solution of an aromatic base is used as eluent, the direction of the conductivity signal when a solute cation elutes is dependent on the relative eluting roles of hydrogen ion and the protonated base cation. When both of these species contribute to the elution of a solute, detection sensitivity is decreased in comparison to the situation where only one species is responsible for elution. An equation for the conductivity change occurring on elution of a solute cation is presented.

Indirect UV absorption detection is also possible when aromatic bases are used as eluents, provided the role of hydrogen ion as an eluting species is minimised. This can be achieved using an eluent comprising an aqueous solution of an aromatic base with pK_a value in excess of 7.5, and by maintaining the eluent pH in the neutral to alkaline region. Benzylamine at pH 7.15 is shown to be a suitable eluent for indirect UV absorption and conductivity detection and using this eluent, detection limits in the low parts per billion range (for an injection volume of 10 μl) were obtained for lithium, sodium, ammonium and potassium, with both detection methods.

INTRODUCTION

A typical cation-exchange equilibrium can be represented by the equation:

$$\text{Resin-SO}_3^- \ \text{E}^+ + \text{A}^+ \rightleftharpoons \text{Resin-SO}_3^- \ \text{A}^+ + \text{E}^+ \quad (1)$$

0021-9673/86/$03.50

where E^+ and A^+ are the eluent and solute cations, respectively, and the sulphonated ion-exchange resin is represented as resin-SO_3^-. Implicit in eqn. 1 is the fact that when a solute cation elutes from the ion-exchange column it displaces an equivalent number of eluent cations from the mobile phase in order to preserve electroneutrality.

This situation has great importance in the detection of the eluted solute cations, since it indicates that detection must be based on the difference in a measured property between the solute and eluent cations. Methods where the eluent cation has a lower value of the measured property than the solute cation can be described as direct detection methods, whereas methods in which the eluent cation has a higher value of the measured property than the solute cation can be described as indirect methods. These approaches have been well developed for the detection of anions in non-suppressed ion chromatography where conductivity[1-3] and UV absorbance[4] measurements have been used in the direct detection mode and conductivity[5], UV absorbance[6-8], refractive index[9] and fluorescence[10] measurements have been employed in the indirect detection mode.

In contrast, detection of cations in non-suppressed ion chromatography is much less varied, with indirect conductivity detection being the most widely applied method[11,12]. Indirect UV absorption detection using cupric ions as eluent has been briefly reported[6], however no systematic study of the principles and operational parameters of this approach has been made. In this paper we describe the results of such a study which show that some aromatic bases are suitable eluents for sensitive detection of inorganic cations using the indirect UV absorption method. Quantitative retention data are provided to explain the retention processes occurring, and the origins of the responses of the conductivity and UV absorption detectors are also discussed. The theory of these aspects is treated below.

THEORY

Retention of cations on low-capacity ion-exchange resins

For a solute cation A^{y+} and an eluent cation E^{x+}, the following ion-exchange equilibrium applies:

$$xA_m^{y+} + yE_s^{x+} \rightleftharpoons xA_s^{y+} + yE_m^{x+} \tag{2}$$

where the subscripts m and s refer to mobile and stationary phases, respectively. In ion chromatography, consideration of the low ion-exchange capacity of the columns and the resultant low ionic strength of the eluents used leads to derivation of the following relationship describing retention behaviour of solutes[13,14]:

$$\log k' = \text{constant} - \frac{y}{x} \log\,[E^{x+}]_m \tag{3}$$

Here k' is the solute capacity factor, $[E^{x+}]_m$ is the concentration of eluent ions in the mobile phase and the constant term incorporates the selectivity coefficient, the volumes of the stationary and mobile phases and the concentration of the eluent ion in the stationary phase. This equation predicts that a linear relationship should exist between $\log k'$ and $\log\,[E^{x+}]_m$, with a negative slope equal to the ratio of the charges on the solute and eluent cations.

Principles of conductivity detection

Fritz *et al.*[15] have developed equations for the conductivity change accompanying elution of an anion in ion-exchange chromatography and these equations can be applied to the cation case in the manner shown below.

The conductance, G, of a solution (expressed in microsiemens, μS) is given by the equation

$$G = \frac{(\lambda_{+} + \lambda_{-})CI}{10^{-3}\,K} \tag{4}$$

where λ is the limiting equivalent ionic conductance of the cation or anion, C is the normality, I is the fraction of the eluent which is ionised and K is a constant (called the cell constant) with units cm^{-1} which takes into account the physical dimensions of the cell.

If it is assumed that the eluent has a total concentration of C_{E} and contains the cation E^{+} and the anion E^{-}, then the background conductance (G_{B}) calculated from eqn. 4 is

$$G_{\mathrm{B}} = \frac{(\lambda_{\mathrm{E}^{+}} + \lambda_{\mathrm{E}^{-}})C_{\mathrm{E}}I_{\mathrm{E}}}{10^{-3}\,K} \tag{5}$$

where I_{E} is the degree of ionisation of the eluent.

Remembering that eluted sample cations displace an equivalent number of eluent cations from the mobile phase, it can be seen that when a solute (S^{+}) of concentration $C_{\mathrm{S}^{+}}$ and degree of ionisation $I_{\mathrm{S}^{+}}$ is eluted, the eluent concentration during sample elution is $C_{\mathrm{E}} - C_{\mathrm{S}^{+}}I_{\mathrm{S}^{+}}$. The conductance of the detector cell at this time originates from the eluent and solute cations, together with the eluent anions which are required to maintain electroneutrality. Solute anions need not be considered since these are not retained on the cation-exchange column and elute at a different time (namely, the void volume). The conductance during solute elution (G_{S}) is therefore given by

$$G_{\mathrm{S}} = \frac{(\lambda_{\mathrm{E}^{+}} + \lambda_{\mathrm{E}^{-}})\,(C_{\mathrm{E}} - C_{\mathrm{S}^{+}}I_{\mathrm{S}^{+}})I_{\mathrm{E}}}{10^{-3}\,K} + \frac{(\lambda_{\mathrm{E}^{-}} + \lambda_{\mathrm{S}^{+}})C_{\mathrm{S}^{+}}I_{\mathrm{S}^{+}}}{10^{-3}\,K} \tag{6}$$

The change in conductance (ΔG) which accompanies elution of the solute can be obtained by subtracting G_{B} from G_{S} to give

$$\Delta G = G_{\mathrm{S}} - G_{\mathrm{B}} = \frac{[(\lambda_{\mathrm{E}^{-}} + \lambda_{\mathrm{S}^{+}})I_{\mathrm{S}^{+}} - (\lambda_{\mathrm{E}^{+}} + \lambda_{\mathrm{E}^{-}})I_{\mathrm{E}}I_{\mathrm{S}^{+}}]C_{\mathrm{S}^{+}}}{10^{-3}\,K} \tag{7}$$

The solute concentration (C_{S}) during elution will follow an approximately Gaussian profile and the detector response will therefore change in a similar manner.

Eqn. 7 can be simplified when only fully ionised solutes are considered, so that I_{S} is unity. In such cases,

$$\Delta G = \frac{[\lambda_{\mathrm{E}^{-}}(1 - I_{\mathrm{E}}) + \lambda_{\mathrm{S}^{+}} - \lambda_{\mathrm{E}^{+}}I_{\mathrm{E}}]C_{\mathrm{S}^{+}}}{10^{-3}\,K} \tag{8}$$

Further simplification is possible if the eluent also is fully ionised (*i.e.* I_E is unity) and eqn. 8 now reduces to

$$\Delta G = \frac{(\lambda_{S^+} - \lambda_{E^+})C_{S^-}}{10^{-3}\,K} \tag{9}$$

Eqn. 9 shows that the conductivity signal observed during sample elution is proportional to the solute concentration and to the difference in limiting equivalent ionic conductances between the eluent and solute cations. Thus the detector signal can be positive or negative, depending whether a weakly conducting (low λ_{E^+}) or strongly conducting (high λ_{E^+}) eluent is used. These alternatives correspond to the direct and indirect modes of conductivity detection, respectively, and are schematically illustrated in Fig. 1.

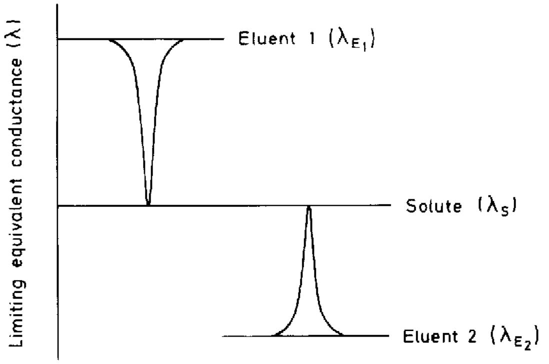


Fig. 1. Schematic representation of indirect (negative peak) and direct (positive peak) conductivity detection using an eluent cation with high (eluent 1) or low (eluent 2) limiting equivalent ionic conductance.

Principles of UV absorption detection

If a cation-exchange system is considered and the same terminology as used above is applied, the background absorbance of the eluent (A_B) is given by

$$A_B = [\varepsilon_{E^+} C_E I_E + \varepsilon_E C_E (1 - I_E)] \cdot l \tag{10}$$

where the eluent E is assumed to exist as the neutral form E and the protonated form E^+, with molar absorptivities ε_E and ε_{E^+}, respectively. As before, the total eluent concentration is given by C_E, I_E is the degree of ionisation of the eluent and l is the path length of the detector cell. It is assumed here that the eluent anion does not absorb radiation at the detection wavelength used.

When a fully ionised solute S^+ is eluted at a concentration C_{S^+}, the concentration of the eluent cation in the detector cell is given by $C_E I_E - C_{S^+}$ and the absorbance signal measured by the detector during sample elution (A_S) is given by

$$A_S = [\varepsilon_{E^+}(C_E I_E - C_{S^+} + \varepsilon_E C_E (1 - I_E) + \varepsilon_{S^+} C_{S^+}] \cdot l \tag{11}$$

where ε_{S^+} is the molar absorptivity of the solute.

The change in absorbance resulting from elution of the sample is obtained by subtracting A_B from A_S to give

$$\Delta A = A_S - A_B = [(\varepsilon_{S^+} - \varepsilon_{E^+})C_{S^+}] \cdot l \quad (12)$$

It is assumed here that the eluent is well buffered and I_E therefore remains constant. Eqn. 12 shows that the detector absorbance signal depends on the solute concentration, the detector cell path length and the difference in molar absorptivities between the solute and eluent cations. As with conductivity detection, the absorbance signal can be positive or negative, depending on whether the eluent is weakly absorbing (low ε_{E^+}) or strongly absorbing (high ε_{E^+}), corresponding to the direct and indirect detection modes, respectively. The indirect detection mode is of most relevance to the detection of alkali metal ions and this mode is illustrated schematically in Fig. 2.

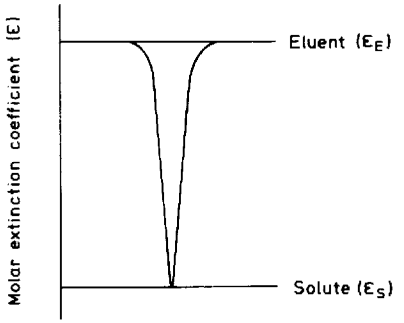


Fig. 2. Schematic representation of indirect UV absorption detection using an eluent cation having a higher molar absorptivity at the detection wavelength than the solute cation.

EXPERIMENTAL

Instrumentation

The liquid chromatograph consisted of a Waters Assoc. (Milford, MA, U.S.A.) Model M6000A pump, Model U6K injector, Model 430 conductivity detector and Model M450 variable-wavelength detector, interfaced to a Houston Instruments (Austin, TX, U.S.A.). Omniscribe Model B5217-1 dual-pen chart recorder. The UV detector preceded the conductivity detector in the flow-stream.

A Waters Assoc. IC-Pak C (50 × 4.6 mm I.D.) low capacity polystyrenedivinylbenzene-based cation-exchange column was used and the column was housed in a Bioanalytical Systems (Lafayette, IN, U.S.A.) Model LC-23A column heater, operated at a temperature of 35°C. The flow-rate used was 1.0 ml/min.

Reagents and procedures

Eluents were prepared from picolinic acid (2-pyridinecarboxylic acid; Sigma, St. Louis, MO, U.S.A.), nitric acid (Ajax, Sydney, Australia), benzylamine (BDH, Poole, U.K.) and aniline (Ajax). These materials were obtained as analytical grade reagents and were used without further purification except for nitric acid, which was distilled in a PTFE still, and aniline which was doubly distilled. Water treated with a Millipore (Bedford, MA, U.S.A.) Milli Q water purification system was used to prepare eluents, with the eluent pH being adjusted as required with dilute nitric acid. Eluents were filtered through a 0.45-μm membrane filter and degassed in an ultrasonic bath prior to use.

Stock solutions (1000 ppm) of individual alkali metal ions and ammonium were prepared from analytical grade chlorides, with the exceptions of lithium and rubidium which were prepared from the sulphate and carbonate salts, respectively. Test solutions and mixtures of these solute ions were prepared from the stock solutions using polypropylene volumetric apparatus and these were injected onto the chromatograph using a 25-μl microsyringe.

Further relevant experimental conditions are provided in the figure captions.

RESULTS AND DISCUSSION

Conductivity detection with nitric acid eluents

The most commonly used eluents for the separation of monovalent cations consist of dilute solutions of nitric acid. Table I lists the limiting equivalent ionic conductances for cations of importance to this study, together with those for some of the eluents to be discussed at a later stage. It is evident from Table I that for nitric acid eluents, the eluent cation (hydrogen ion) has a higher limiting equivalent ionic conductance than any of the solute cations: under these conditions, indirect conductivity detection can be expected to occur and eluted peaks will be detected by a decrease in conductance in comparison to the background conductance. This behav-

TABLE I

LIMITING EQUIVALENT IONIC CONDUCTANCES OF SOLUTE AND ELUENT CATIONS USED IN THIS STUDY

Data for the solute cations were obtained from ref. 19 and the values for the eluent cations were measured using a calibrated conductance meter.

Cation	*Limiting equivalent ionic conductance, λ_+ ($S\ cm^2/equiv.$)*
H^+	349.8
Li^+	38.7
Na^+	50.1
K^+	73.5
NH_4^+	73.5
Cs^+	77.3
Rb^+	77.8
Picolinic acid	30.2
Anilinium ion	5.1
Benzylammonium ion	31.6

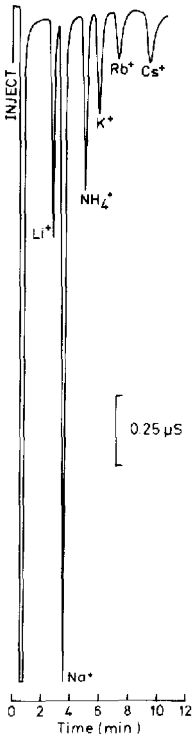


Fig. 3. Typical indirect conductivity detection of inorganic cations using nitric acid as eluent. Column: Waters Assoc. IC-Pak C, 50 × 4.6 mm I.D., low capacity polystyrene–divinylbenzene-based cation-exchanger. Eluent: 2.0 m*M* nitric acid (pH 2.70). Flow-rate: 1.0 ml/min. Injected amounts: 8 µl of a solution containing 0.1 ppm lithium, 0.3 ppm sodium, 0.2 ppm ammonium, 0.4 ppm potassium, 1.7 ppm rubidium and 1.8 ppm cesium.

iour was observed in practice and Fig. 3 shows a typical chromatogram obtained using 2.0 m*M* nitric acid as eluent.

Eqn. 9 predicts that the peak areas obtained for eluted solute cations should be in proportion to the limiting equivalent ionic conductances for these cations. To verify this, eluent conditions were successively varied so that each cation eluted at approximately the same retention time and peak areas were measured. The results are shown in Table II, which lists eluent composition, retention time and peak areas for each solute cation. It can be seen from Table II that the peak areas followed the sequence of limiting equivalent conductances, in accordance with eqn. 9.

The validity of eqn. 3 for the retention behaviour of cations was examined using nitric acid eluents of differing strengths. The results are shown in Fig. 4, from which it can be seen that the predicted linear relationship between log [eluent] (in this case, log $[H^+]$) and log k' was observed in practice. Moreover, the slopes of these plots were measured to be -1.13, -1.07, -1.06 and -1.07 for lithium, sodium, ammonium and potassium, respectively, and these values were in excellent agreement with the theoretical slope of -1.00 predicted from eqn. 3 when both eluent and solute were singly charged.

TABLE II

PEAK AREAS OBTAINED FOR INORGANIC CATIONS ELUTED AT THE SAME RETENTION TIME WITH NITRIC ACID ELUENTS

10 μl of a $1 \cdot 10^{-4}$ M solution of the cation was injected in each case.

Cation	*[nitric acid] in eluent (mM)*	*Retention time (min)*	*Peak area*
Li^+	0.32	1.80	418
Na^+	0.43	1.60	368
NH_4^+	1.02	1.65	319
K^+	1.02	1.80	312
Rb^+	1.55	1.75	267
Cs^+	1.90	1.75	277

Picolinic acid and aniline as eluents

Before commencing the discussion on the use of aromatic bases as eluents for indirect UV absorption and conductivity detection in ion chromatography of inorganic cations, it is instructive to review the extensive application of these detection techniques to inorganic anions. In the ion chromatographic separation of inorganic anions, use has been made of eluents comprising aqueous solutions of aromatic acids or their salts. Examples include benzoate[1,2], phthalate[6–9], sulphobenzoate[16] and benzenetricarboxylate[6]. The pH of these eluents is generally maintained in the vicinity of the pK_a of the eluent acid, so that the eluents are well buffered and the percentage of the eluent existing in the anionic form can be varied by pH adjustment as a means of manipulating retention of solute anions. The acid dissociation constants for the abovementioned weak acids are such that the working pH range for eluents is in the

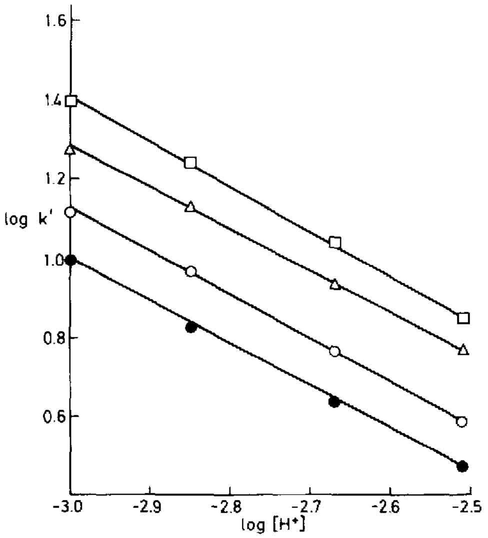


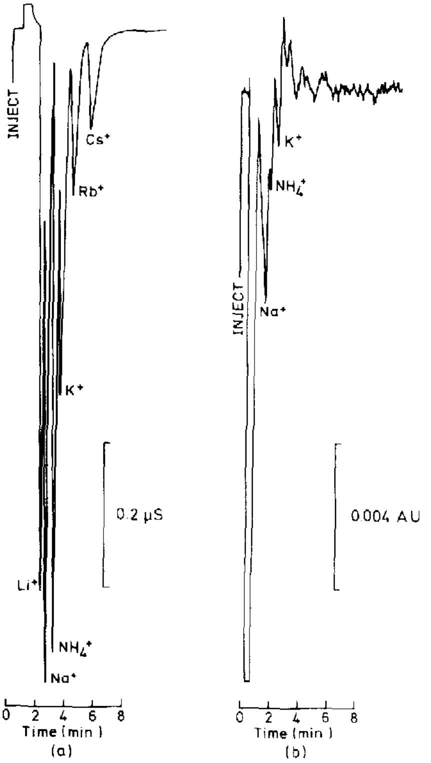
Fig. 4. Plot of log [H⁺] *versus* the logarithm of the solute capacity factor for various inorganic cations using nitric acid eluents. Key to symbols: ●, Li^+; ○, Na^+; △, NH_4^+; □, K^+.

acidic region. Aromatic acid salts have low limiting equivalent ionic conductances (for example, 32 and 38 S cm^2/equiv. for benzoate and fully ionised phthalate, respectively[17]) and also have high molar absorptivities in the UV region, due to the aromatic moiety. Accordingly, these eluents are suitable for direct conductivity detection as well as indirect UV absorption detection.

Extension of the above approach to the cation case suggests that aqueous solutions of aromatic bases should be appropriate eluents for direct conductivity detection of cations, since Table I shows that these species typically have low limiting equivalent ionic conductances, and the same eluents should be suitable for indirect UV detection of cations because they also show strong UV absorption. Picolinic acid (2-pyridinecarboxylic acid, with pK_a for the protonated pyridine nitrogen atom equal to 5.39) has been reported as an eluent for the ion chromatography of monovalent inorganic cations[18], and at first sight, this eluent appears to be an ideal candidate for use with indirect UV absorbance and conductivity detection. Chromatograms were obtained using 0.5 m*M* picolinic acid at pH 3.22 as eluent, with both UV and conductivity detectors being used to monitor the eluted cations. The results are shown in Fig. 5 from which it can be seen that the conductivity signal was indirect and a weak indirect UV absorption response was also observed.

The fact that the conductivity signal was indirect showed that hydrogen ion was exerting a contribution as the displacing cation in the ion-exchange process, since the measured limiting equivalent ionic conductance of protonated picolinic acid (30.2 S cm^2/equiv., see Table I) was sufficiently low that a direct conductivity signal would have resulted if this was the eluting cation. On the other hand, the UV absorbance detector also gave an indirect signal, showing that some protonated picolinic acid cations in the eluent were also participating in the elution process. Clearly, both hydrogen ions and protonated picolinic acid acted simultaneously as eluting cations, with hydrogen ions playing the dominant role in the particular case considered. Further evidence for this proposal arises from a comparison of Figs. 3 and 5 from which it can be seen that the conductivity detection sensitivity observed for picolinic acid (Fig. 5) was greatly reduced in comparison to that obtained with the nitric acid eluent (Fig. 3), evident from the disparity in the injected amounts of solutes in the two figures. This reduced sensitivity arises from the fact that the detection signal resulting when hydrogen ions act as the eluting species is in the opposite direction to that when protonated picolinic acid ions are responsible for the elution of solute cations (see Fig. 1). It follows that when both of these ions act simultaneously as eluting species, the conductivity signal is smaller than when elution is caused by one ion only. Furthermore, retention times for solutes in Fig. 5 were considerably shorter than those in Fig. 3 even though the hydrogen ion concentration in the eluent was lower in Fig. 5. This was indicative of the participation of protonated picolinic acid in the elution process.

The indirect UV absorption detection achieved in Fig. 5 is clearly of limited value. The excessive baseline noise resulted from the high background absorbance and the necessity for operation of the detector on a sensitive range in order to detect the small changes in absorbance which occurred. One obvious approach to improvement of the UV detector signal was to raise the eluent pH in an effort to decrease elution by hydrogen ions. For picolinic acid, the maximum pH commensurate with retaining a sufficient percentage of the eluent in the protonated form is 5.4: when an



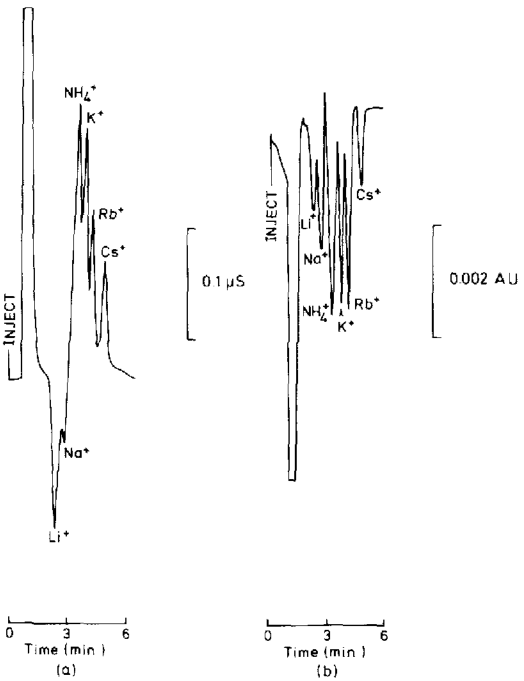


Fig. 5. Chromatograms obtained with conductivity (a) and UV absorption (b) detectors when an aqueous solution of picolinic acid was used as eluent. Eluent: 0.5 m*M* picolinic acid at pH 3.22. Injected amounts: 25 µl of a solution containing 5 ppm lithium, 10 ppm sodium, 10 ppm ammonium, 15 ppm potassium, 20 ppm rubidium and 25 ppm cesium. Other conditions as for Fig. 3.

Fig. 6. Chromatograms obtained with conductivity (a) and UV absorption (b) detectors when an aqueous solution of aniline was used as eluent. Eluent: 1.0 m*M* aniline at pH 4.43. Other conditions as for Fig. 5.

eluent of this pH was employed, the conductivity signal was direct, however no indirect UV absorption signal was observed since the eluent concentration required to elute solute cations was so high that the background absorbance of the eluent could not be offset with the zero control of the detector.

The considerations discussed above can be further illustrated when aqueous solutions of anilinium ion are used as eluent. Aniline has a pK_a of 4.63, and when a 1.0 m*M* aqueous solution of aniline was adjusted to pH 4.43 and employed as eluent, the chromatogram shown in Fig. 6 resulted. At this pH, aniline was 61.2% protonated and the pH was sufficiently high that the hydrogen ion was expected to play only a minor role in elution of the solute cations. The chromatogram recorded with the conductivity detector (Fig. 6a) showed indirect detection of lithium and sodium, but direct detection of the remainder of the solutes. This trend was in accordance with the fact that lithium and sodium have lower limiting equivalent ionic conductances (and hence gave larger indirect conductivity signals) than the other ions. Clearly, the relative concentrations of hydrogen and anilinium ions in the eluent were such

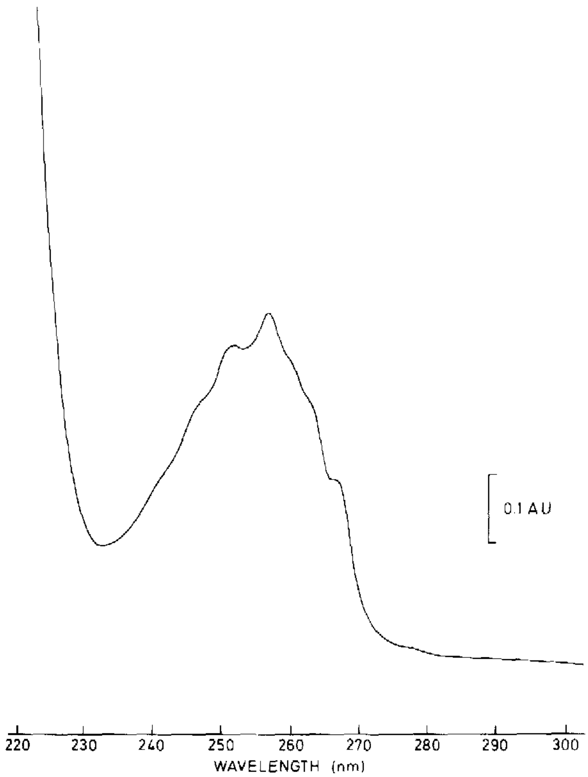


Fig. 7. UV absorption spectrum of benzylamine at pH 7.0.

that the transition from indirect conductivity detection (due to hydrogen ion) to the direct mode (due to anilinium ion, which has a low limiting equivalent ionic conductance, see Table I) was in process. Nevertheless, the UV absorbance detector provided a chromatogram showing indirect detection (Fig. 6b), which further confirmed the eluting role of anilinium ions. However, the detection sensitivity obtained in this case was poor.

Use of benzylamine eluents

The results presented thus far have indicated that the ideal eluent for indirect UV absorption detection of cations was an aqueous solution of an aromatic base with a pK_a value of 7.5 or greater, since this would enable the eluent cation to be formed at neutral to alkaline pH values and so eliminate the deleterious effect on detection caused by hydrogen ion. Using these criteria, benzylamine (pK_a 9.39) was selected as a suitable eluent and Fig. 7 shows the UV absorption spectrum for this species. The molar absorptivity at the wavelength of maximum absorption (257 nm) was calculated to be 232 l/mol/cm. Chromatograms obtained using an aqueous 0.5 m*M* solution of benzylamine at pH 7.15 as the eluent with detection by both conductivity and UV absorption at 257 nm are shown in Fig. 8. This particular eluent did not provide good resolution between some of the alkali metal ions, so Fig. 8 only

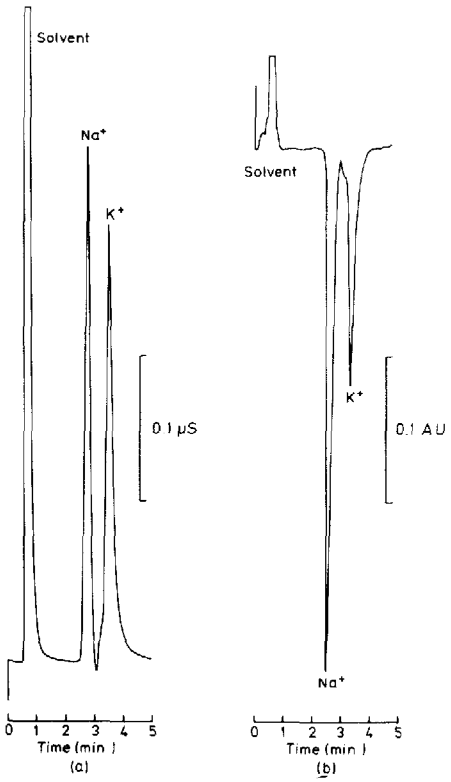


Fig. 8. Chromatograms obtained with conductivity (a) and UV absorption (b) detectors using an aqueous solution of benzylamine as eluent. Eluent: 0.5 m*M* benzylamine at pH 7.15. Injected amounts: 10 µl of a solution containing 2 ppm of sodium and potassium. The UV detector was operated at 257 nm.

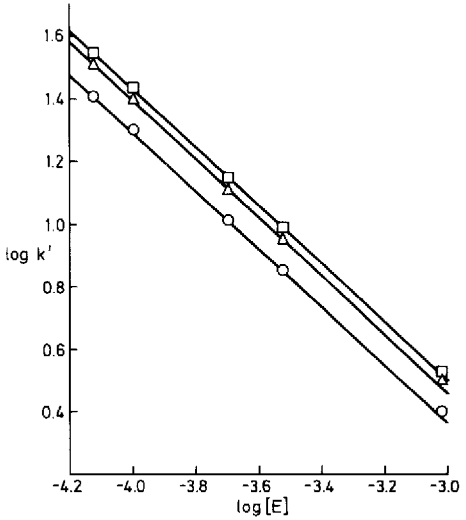
shows the separation of sodium and potassium ions. The conductivity signal was direct (Fig. 8a) since the benzylammonium ion has a low limiting equivalent ionic conductance (31.6 S cm^2/equiv) and the UV absorbance signal was indirect (Fig. 8b), with the detection sensitivity being excellent for both detection modes. Limits of

TABLE III

DETECTION LIMITS OBTAINED USING BENZYLAMINE ELUENTS FOR CONDUCTIVITY AND INDIRECT UV ABSORPTION DETECTION METHODS

An injection volume of 10 µl was used.

Cation	*Detection limit (ppb)*	
	Conductivity	*Indirect UV absorption*
Li^+	1.2	1.1
Na^+	4.2	9.0
NH_4^+	5.0	19.5
K^+	4.1	16.0



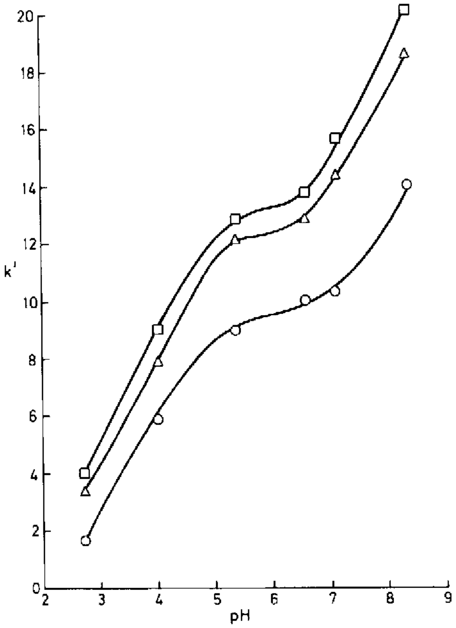


Fig. 9. Plot of log [eluent] *versus* the logarithm of solute capacity factor for benzylamine eluents at pH 7.15. Key to symbols: ○, Na$^+$; △, NH$_4^+$; □, K$^+$.

Fig. 10. Variation of solute capacity factor with eluent pH for benzylamine eluents. The benzylamine concentration was 0.2 m*M*. Key to symbols as for Fig. 9.

detection for conductivity and UV absorption detection, calculated for lithium, sodium, ammonium and potassium are given in Table III.

Confirmation that the protonated benzylamine species was responsible for the elution of the injected solute cations was obtained by observing the changes in retention times resulting from variations in the concentration of benzylamine in the eluent, at constant pH. Fig. 9 shows a plot of log [benzylamine] *versus* log k' for sodium, ammonium and potassium, and the linear relationship predicted by eqn. 3 was observed. The measured slopes were -0.94, -0.93 and -0.93 for sodium, ammonium and potassium, respectively, and these values were close to the theoretical slope of -1.0.

The effect of variation of the pH of benzylamine eluents was also studied and the results are given in Fig. 10, which shows the capacity factors measured for sodium, ammonium and potassium with 0.2 m*M* benzylamine eluents at various pH values. As the eluent pH fell below the pK_a of benzylamine, increasing amounts of the eluent became protonated and retention times decreased due to the greater concentration of eluting ions in the eluent. This trend continued until the eluent was fully protonated, after which further decreases in eluent pH had only a minimal effect on retention: from Fig. 10, it can be seen that this plateau region extended from pH 5.2 to 6.5. Still further decreases in eluent pH produced lower solute capacity factors due to the concommitant increased concentration of hydrogen ion which then assumed the elution role. The optimal pH for benzylamine eluents was therefore 5.2–6.5 since within this range retention was not strongly dependent on eluent pH and the fully protonated benzylamine acted as the eluting ion, leading to maximum sensitivity for the indirect UV absorption detection mode.

CONCLUSIONS

This study has shown that the retention behaviour of inorganic cations in non-suppressed ion chromatography followed a linear relationship between log [eluent] and log k' and provided only one eluent species was responsible for elution of solute ions, the negative slope of this relationship was given by the ratio of the charges on the eluent and solute cations.

When aqueous solutions of aromatic bases were used as eluents the conductivity change accompanying the elution of a solute cation was positive or negative, depending on the relative participations of hydrogen ions and protonated base ions in the elution process. Maximum sensitivity for conductivity detection occurred when only one of these species was responsible for the elution of solute cations: when both species participated in elution, the detection sensitivity decreased because each of the eluting species exerted an opposite effect on the measured conductivity signal.

Indirect UV absorption detection was possible with these same eluents, provided appropriate consideration was given to the choice of the aromatic base and to the pH at which it was used. For maximum sensitivity, the influence of hydrogen ion as an eluting species must be minimised and for this reason, aromatic bases with pK_a values in excess of 7.5 were preferred, and the eluent pH was maintained in the neutral to alkaline region. Benzylamine has been shown to be a suitable eluent species for this application and we are presently examining a wide range of other aromatic bases as potential eluents for indirect UV absorption detection in non-suppressed ion chromatography of inorganic cations.

ACKNOWLEDGEMENT

We thank Waters Associates for technical advice.

REFERENCES

1 D. T. Gjerde, J. S. Fritz and G. Schmuckler, *J. Chromatogr.*, 186 (1979) 509.
2 D. T. Gjerde, G. Schmuckler and J. S. Fritz, *J. Chromatogr.*, 187 (1980) 35.
3 P. R. Haddad and A. L. Heckenberg, *J. Chromatogr.*, 300 (1984) 357.
4 P. E. Jackson, P. R. Haddad and S. Dilli, *J. Chromatogr.*, 295 (1984) 471.
5 T. Okada and T. Kuwamoto, *Anal. Chem.*, 55 (1983) 1001.
6 H. Small and T. E. Miller, Jr., *Anal. Chem.*, 54 (1982) 462.
7 R. A. Cochrane and D. E. Hillman, *J. Chromatogr.*, 241 (1982) 392.
8 P. R. Haddad and A. L. Heckenberg, *Chem. Aust.*, 50 (1983) 275.
9 P. R. Haddad and A. L. Heckenberg, *J. Chromatogr.*, 252 (1982) 177.
10 S.-I. Mho and E. S. Yeung, *Anal. Chem.*, 57 (1985) 2253.
11 J. S. Fritz, D. T. Gjerde and R. M. Becker, *Anal. Chem.*, 52 (1980) 1519.
12 M. Ahmad and A. Khan, *Nucleus (Karachi)*, 18 (1981) 29.
13 M. Lederer and S. Kertes, *Anal. Chim. Acta*, 15 (1956) 226.
14 P. R. Haddad and C. E. Cowie, *J. Chromatogr.*, 303 (1984) 321.
15 J. S. Fritz, D. T. Gjerde and C. Pohlandt, *Ion Chromatography*, Huthig, Heidelberg, 1982, p. 119.
16 C. A. Hordijk, C. P. C. M. Hagenaars and Th. E. Cappenberg, *J. Microbiol. Methods*, 2 (1984) 49.
17 D. T. Gjerde and J. S. Fritz, *Anal. Chem.*, 53 (1981) 2324.
18 J. R. Benson and D. J. Woo, *J. Chromatogr. Sci.*, 22 (1984) 386.
19 R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Academic Press, New York, 1959.