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ISOCRATIC ELUTION OF SODIUM, AMMONIUM, POTASSIUM, MAGNESIUM AND CALCIUM IONS BY ION-EXCHANGE CHROMATOGRAPHY

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SUMMARY

Isocratic elution conditions for five cationic species were investigated using conductivity and UV absorption detectors. Using several kinds of eluents and silica and styrene–divinylbenzene separating columns, the detection sensitivity, separation efficiency, separation time, system peak interference, etc., were examined. As a result, two types of eluents were concluded to be useful: a solution of benzylamine, citric acid and N-hydroxyethylenediamine-N,N′,N′-triacetic acid (EDTA · OH) and a solution of 1,1′-di-*n*-heptyl-4,5′-bipyridinium (DHBP) ion and citric acid. When the former eluent is used, monovalent cations are separated clearly and divalent cations can be eluted without being captured in the column. With a slightly lower precision, divalent cations at the parts per million level can also be determined. The latter eluent is suitable mainly for determining Mg^{2+} and Ca^{2+} ions with no interference from heavy metal ions. The separation of monovalent ions was poor with a commercially available separation column, but the detection sensitivity with a UV absorption detector was higher than that with the benzylamine eluent. Several examples of application are shown.

INTRODUCTION

Monovalent sodium, ammonium and potassium ions and divalent magnesium and calcium ions are found together in various aqueous samples such as environmental waters and biological fluids, and often all these species need to be determined. Although ion-exchange chromatography is usually suitable for multi-component analysis, the simultaneous determination of these monovalent and divalent cations by isocratic elution is not easy because of their very different properties. Therefore, since the development of ion chromatography[1] many studies[2–6] have concerned monovalent and divalent species under separate elution conditions. However, when monovalent cations are eluted with dilute nitric acid or hydrochloric acid, any divalent cations, when present, are captured in the column and as a result the effective ion-exchange capacity of the column is reduced. To eliminate this drawback, it is necessary to use a precolumn to prevent divalent sample cations from entering to the separation column or to clean up the column frequently. Even when only monovalent

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cations are to be determined, elution conditions that prevent divalent cations from being in the column are desirable. Small and Miller[3] proposed a column switching method by using two separating columns and switching them to change the flow path during the elution. However, this method is generally not easy to use. If a gradient elution method is used, it will be easy to elute monovalent and divalent species successively. However, suitable detection methods are difficult to establish.

A few methods have been reported for handling monovalent and divalent species simultaneously by isocratic elution with the use of a universal UV spectrophotometric (hereinafter referred to as a UV) detector. Miyazaki *et al.*[7] reported a simultaneous determination method for alkali metal, ammonium, magnesium and calcium ions by combining a silica gel-based cation-exchange column with a copper sulphate eluent. In this method, however, a column having a high theoretical plate number (more than about 5000) is needed to separate monovalent cations if calcium ions are to be eluted within a reasonable time (*e.g.*, 20 min). Sherman and Danielson[8] reported that the simultaneous determination of monovalent and divalent species could be effected by using a styrene–divinylbenzene (St–DVB)-based cation exchanger (500 μequiv./g, 5 μm), a cerium(III) eluent and indirect absorption detection. In our experiments with this method with a column packed with an ordinary sulphonated St–DVB resin, it was found to be effective for separating Na^+, K^+, Mg^{2+}, and Ca^{2+}, but NH_4^+ and K^+ overlapped and could not be separated, and a system peak appeared between the peaks of Mg^{2+} and Ca^{2+} at some sample pH values and interfered with their determination. Further, in the method using these metal ion solutions as eluent, various divalent metal ions appear in the vicinity of the peak of Mg^{2+}, and no effective method for masking them could be found.

In order to find novel approaches that permit the isocratic elution of sample species from Na^+ to Ca^{2+} and their determination with a conductivity or UV absorption detector, we have studied extensively various eluents and combinations of separation columns. As the elution system for eluting monovalent and divalent cations isocratically, combinations of a monovalent ion and a strong complex-forming agent, or of a divalent cation and a comparatively weak complex-forming agent, were chosen. Complex-forming agents are necessary for accelerating the elution of the divalent cations.

Eluting ions are required to effect good separations and to have a low equivalent conductivity or large UV absorption. In addition, the exchange capacity and the base material of the ion exchanger are important factors. From such viewpoints, a Li^+, tetrabutylammonium, anilinium, benzylammonium and trimethylbenzylammonium ions were selected as the monovalent eluting ions and EDTA or analogous compounds were used as the complex-forming agents. Hexamethylenediammonium, cyclohexanediammonium, hexamethonium, *m*-phenylenediammonium and diheptylbipylidinium ions were used as divalent eluting ions combined with citric acid.

Using these diverse eluents and silica and St–DVB separating columns, we examined the detection sensitivity, separation efficiency, separation time, system peak interference, etc. As a result, two elution types have been concluded to be useful: a combination of benzylamine with citric acid and N-hydroxyethylenediamine-N,N′-triacetic acid (EDTA · OH), and a combination of 1,1′-di-*n*-heptyl-4,5′-bipyridinium (DHBP) ion and citric acid. This paper describes these methods and gives examples of applications to some common samples.

EXPERIMENTAL

Equipment

The liquid chromatograph consisted of a pump system (Tosoh, CCPM, metal-free model), a conductivity detector (Tosoh, CM-8000) and a UV–visible detector (Tosoh, UV-8000). To inject the sample, a Rheodyne loop injector (100-μl loop) was used. The separation columns were a Tosoh IC cation (St–DVB, low exchange capacity, 50 × 4.6 mm I.D.), a Tosoh IC cation SW (silica gel, medium exchange capacity, 50 × 4.6 mm I.D.), a Tosoh SCX (St–DVB, ordinary exchange capacity, 50 × 4.6 mm I.D.) and stainless-steel columns packed with cation exchangers manufactured by Tosoh (sulphonated St–DVB, 4% DVB, average diameter 11 μm, exchange capacity 24, 50 and 85 μequiv./ml).

Reagents

Various amines, DHBP bromide and EDTA · OH were obtained from Tokyo Kasei Kogyo. All other reagents were of guaranteed grade and used without further processing. Distilled, deionized water was used. Benzylamine-type eluents were prepared from solutions 100 m*M* of benzylamine, EDTA · OH and citric acid by mixing them in various proportions by volume. To prepare DHBP-type eluents, 2.572 g ($5 \cdot 10^{-4}$ mol) of DHBP-bromide were dissolved in 80 ml of water, the solution was allowed to flow through an anion-exchange column (20 × 100 mm bed) which had been converted to the citrate ion form by running 200 ml of 1 *M* sodium citrate solution beforehand, and the column was eluted with water to give 500 ml of solution (DHBP 10 m*M*, pH 8.0). To use this solution as an eluent, it was diluted with an appropriate amount of citric acid.

The sample ion solutions used were aqueous solutions of NaCl, KCl and NH_4Cl and dilute HCl solutions of MgO and $CaCO_3$.

Chromatographic operation

The eluent flow-rate was 1.0 ml/min. Elution was performed mostly at room temperature (15–25°C). The cell of the conductivity detector was maintained at 35°C.

RESULTS AND DISCUSSION

Benzylamine–EDTA · OH–citric acid type eluents

Benzylammonium ion allows monovalent cations to be separated at weakly acidic or neutral pH[9]. If this species is combined with EDTA and used with a sulphonated St–DVB column for separation, Ca^{2+} ions are eluted first, followed by monovalent cations and then Mg^{2+} ions. In this instance, even if the benzylamine to EDTA ratio, pH, etc., are varied, the peak of Ca^{2+} appears too fast, and is deformed by the overlapping system peak, so the determination of Ca^{2+} is difficult because the complex formation constant of EDTA with Ca^{2+} ions[10] is too large. If the determination of Ca^{2+} is not necessary, this method may be useful for the determination of monovalent cations and Mg^{2+} ion.

EDTA · OH[10] was selected as a complex-forming agent as it does not have such a large difference as EDTA in the complex formation constants between Ca^{2+} and Mg^{2+} ions. It was found that Ca^{2+} ions are eluted early and overlap with K^+ with the

use of a combination of benzylamine and EDTA · OH alone when the pH is adjusted to nearly 6.5 so as to allow Mg^{2+} ions to be eluted within a moderate time. On the other hand, with a combination of benzylamine and citric acid alone, Ca^{2+} ions are eluted following Mg^{2+} at pH 6–7, so the overall elution time becomes long. Ca^{2+} can be eluted rapidly by using a relatively concentrated eluent, but the separations of monovalent ions are unsatisfactory. Hence, a long time is required between the elution of the monovalent group and the divalent group. Addition of EDTA · OH makes it possible for Ca^{2+} to be eluted before Mg^{2+}. Based on this finding, the eluent system benzylamine–EDTA · OH–citric acid was examined. Separations of Na^+, NH_4^+,K^+, Ca^{2+} and Mg^{2+} are good, and high sensitive detection by either UV absorption or conductivity is possible.

Ion retention time vs. eluent composition. When a 15-cm separation column packed with 50 μequiv./ml of sulphonated St–DVB is used, monovalent cations can be separated with a 5 m*M* or lower concentration of benzylammonium ions. The elution time for each ion depends on the ratios of the three components, benzylamine, EDTA · OH and citric acid, the total concentration and the ion-exchange capacity of the column. Further, with UV detection, it is not preferable to raise the benzylamine concentration too high so as not to reduce the detection sensitivity. The background absorbance of 5 m*M* benzylammonium is about 1.2 at the peak wavelength in the vicinity of 257 nm, just falling within the limits of the linear response of the detector used. Fig. 1 shows the retention time of each ion when the ratio of EDTA · OH to citric acid is varied with the benzylammonium ion concentration fixed at 5 m*M*.

The retention times of the monovalent ion vary very little. When the total concentration of citric acid and EDTA · OH is fixed at 2 mM and their ratio is varied from 2:0 to 1:1, the eluent pH varies from 6.12 to 7.32. In this instance, the retention time of Mg^{2+} ions varies slightly. When the citric acid to EDTA · OH ratio is fixed at

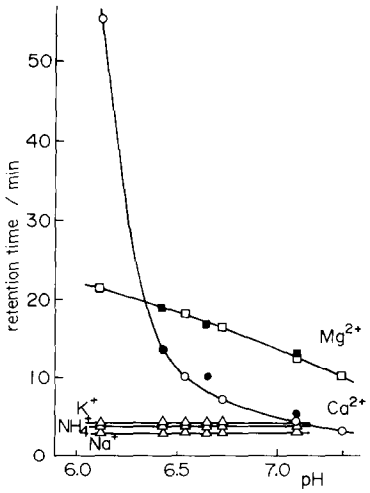

Fig. 1. Relationship between the retention time of cations and the pH of the benzylamine–EDTA · OH–citric acid eluent. △, monovalent cations; □, ■, Mg^{2+}; ○, ●, Ca^{2+}; concentration of benzylamine, 5.0 m*M* (constant). □, ○, Total concentration of EDTA · OH and citric acid 2.0 m*M*; ■, ●, citric acid to EDTA · OH ratio = 3:1.

3:1 and the total concentration is changed, the retention behaviour of Mg^{2+} is similar, and so can be regarded as almost determined by the pH. On the other hand, the retention time of Ca^{2+} varies significantly with increasing pH. When the citric acid to EDTA · OH ratio is 3:1–2.5:1 and the pH is 6.5–6.7, five ion species are separated and eluted within 20 min. Fig. 2 shows a typical chromatogram for alkali metal ions, including Rb^+ and Cs^+ ions, Ca^{2+} and Mg^{2+} ions. As Rb^+ and Cs^+ are not present in ordinary samples, they can be utilized as internal standards. Ca^{2+} is eluted earlier than Mg^{2+} owing to the complex-forming effect of EDTA · OH. In spite of the later elution of Mg^{2+} than Ca^{2+}, the peak of Mg^{2+} is sharper than that of Ca^{2+}, reflecting a smaller interaction between Mg^{2+} and EDTA · OH.

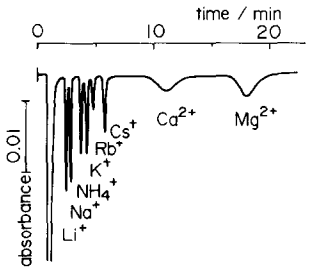

Fig. 2. Typical chromatogram of alkali metal, ammonium, magnesium and calcium ions using benzylamine–EDTA · OH–citric acid eluent and UV detection. Eluent, benzylamine (5.0 m*M*)–EDTA · OH (0.475 m*M*)–citric acid (1.425 m*M*) (pH 6.6); flow-rate, 1.0 ml/min. Column, 150 × 4.6 mm I.D., sulphonated St–DVB, 50 μequiv./ml. Sample, each ion $1 \cdot 10^{-4}$ *M* except for Rb^+ ($5 \cdot 10^{-5}$ *M*); 100 μl. Detection: UV absorption at 257 nm.

Conductivity detection and UV detection. The equivalent conductivity of benzylammonium ions (*ca.* 30 μS/cm) is lower than that of Li^+ and peaks of Na^+, NH_4^+ and K^+ appear in the direction of increasing conductivity. With equal molar concentrations, the peak height of Na^+ is as small as about half of that of NH_4^+. Mg^{2+} and Ca^{2+} partially form complexes and their apparent equivalent conductivities are very small, so their peaks appear in the direction of decreasing conductivity. Fig. 3 shows an example of such behaviour. Benzylammonium ion has a local absorption maximum in the vicinity of 257 nm. At a concentration of 5 m*M*, the background absorption at this wavelength falls within the limit of the linear response of detectors in common use. The larger the molar absorption coefficient, the greater is the detection sensitivity of the detector. However, with too large a background absorption, the apparent sensitivity may become low[11]. Moreover, at shorter wavelengths, citric acid and EDTA · OH show large absorption. Therefore, it was concluded that the local maximum in the vicinity of 257 nm was a suitable detection wavelength. In this instance, absorption detection and conductivity detection methods show approximately similar sensitivity responses when recorded at the same attenuation of the integrator. With respect to the relatively large peak intensity of divalent species, conductivity detection is superior to indirect UV detection. However, the indirect UV method has the advantage that all peaks appear in one direction and the tailing of the first dip peak originated by the sample injection is smaller than that with conductivity detection.

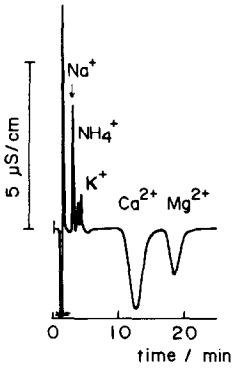

Fig. 3. Chromatogram of a river water sample. Eluent as in Fig. 2. Sample, Tama river water, 100 µl. Result: Na^+ 20.3, NH_4^+ 2.1, K^+ 5.9, Ca^{2+} 19.2 and Mg^{2+} 4.6 mg/l.

Influence of temperature, hydrogen ion concentration, heavy metal ions, etc. As can be seen from Figs. 2 and 3, the peaks of divalent ions are wider than those of monovalent ions. This seems to show an influence of complex formation reactions which are fairly slow. The column temperature was changed from room temperature (20°C) to 40°C; the peak widths of Ca^{2+} and Mg^{2+} were unchanged, but elution of Mg^{2+} was slightly faster. In addition, the peaks of NH_4^+ and K^+ began to approach each other at *ca.* 35°C and the detection sensitivity for NH_4^+ became low. Hence a temperature of 20–30°C is the most suitable for both separation and detection. With increase in temperature, the NH_4^+ detection sensitivity is reduced probably because the dissociation constant of NH_4^+ increases with increasing temperature. However, this assumption is uncertain as the retention time does not change with temperature. The presence of hydrogen ions in the sample has no effect when the pH is above 2. Heavy metal ions (Ni, Co, Zn, Cd, Pb, etc.) are eluted faster than the Na^+ ion, and have no influence except at very high concentrations. The presence of EDTA below 10^{-3} *M* does not affect the elution of Mg^{2+} and Ca^{2+}.

A problem is that once the eluent has stopped flowing and is then switched on after a lapse of time, it takes a long time for the baseline to stabilize. If a solution of double the concentration is allowed to flow for a short period, the baseline stabilization is faster.

Quantification. Table I summarizes the results for four repetitive analyses of a 100-µl sample solution containing $2 \cdot 10^{-4}$ M Na^+, K^+, Ca^{2+} and Mg^{2+} using UV detection. The reproducibility of the peak heights is fairly good for each ion.

The peak area is good for Na^+ and K^+ but poor for Ca^{2+} and Mg^{2+}, possibly owing to the larger peak widths. In the range $0–2 \cdot 10^{-4}$ *M* concentration of each ion, the peak areas show good linearity. The peak height of Na^+ is not proportional to the concentration at concentrations above $1 \cdot 10^{-4}$ *M*.

Applications. Fig. 3 shows a chromatogram for a river water sample obtained with conductivity detection. All ions from Na^+ to Mg^{2+} are present at a level suitable for the present method. The sample water was only filtered with a 0.1-µm membrane filter and then injected. In this example, the content of NH_4^+ is high. Fig. 4 shows a chromatogram of milk obtained with indirect UV detection. The sample was first

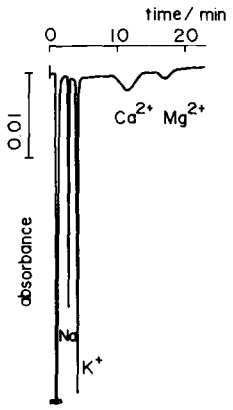

Fig. 4. Chromatogram of milk. Eluent as in Fig. 2. Sample, cow milk filtered with an ultrafiltration membrane, diluted 100-fold with water, 100 μl. Result: Na^+ 0.43, K^+ 1.57, Ca^{2+} 0.34 and Mg^{2+} 0.057 g/l.

filtered through an ultrafiltration membrane (Tosoh, UNISEP) and diluted 100-fold with water. "Non-bound" calcium and magnesium were separated.

Diheptylbipyridinium–citric acid type eluents

To determine divalent cations by ion-exchange chromatography, the conductivity detection method using the ethylenediammonium ion as eluent is well known. If ions from Na^+ to Ca^{2+} are to be handled simultaneously, ethylenediammonium, hexamethylenediammonium, etc., cannot be used because a system peak appears in the vicinity of the peaks of monovalent sample ions.

As a divalent eluting ion showing UV absorption, *m*-phenylenediamine has been used, but because it is easily oxidized and unstable in air, its application is difficult. For this reason, we searched extensively for stable divalent ions other than metal ions, and found that the DHBP ion is effective when a silica-based separation column is used. This eluting ion cannot be used with St–DVB-based cation exchangers because of the strong absorption behaviour.

DHBP is a quaternary ammonium ion, available commercially as the bromide, and is in the form of a divalent ion over a wide pH range. In this work, to separate Ca^{2+} and Mg^{2+} ions from other divalent metal ions, it was converted to the citrate, to which a further excess of citric acid was added to give an eluent of suitable pH. With water alone as the solvent, the separations of Na^+ and K^+ were poorer. When 10% (v/v) of acetonitrile was added, clear separations were obtained. The addition of acetonitrile hardly affected the separation of divalent ions.

Ion retention time vs. eluent composition. The characteristics of DHBP–citric acid eluents vary with the concentration of DHBP, the total concentration of citric acid and the pH. If no electrolyte is added other than DHBP and citric acid, the pH is determined approximately by the mixing ratio of DHBP and citric acid. Fig. 5 shows the retention time of monovalent and divalent cations *versus* the pH of the DHBP–citric acid eluent prepared by varying the citric acid concentration with a constant DHBP concentration of 1 m*M*. A pH of 5.6 was obtained with an aqueous solution of DHBP bromide containing no citric acid. It is considered that the acidic pH

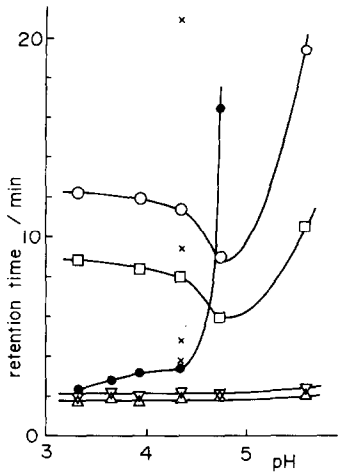

Fig. 5. Relationship between the retention time of cations and the pH of the DHBP–citric acid eluent. Eluent, DHBP (1.0 m*M*)–citric acid (variable) + 10% (v/v) acetonitrile. △, Na^+; ▽, K^+; □, Mg^{2+}; ○, Ca^{2+}; ●, ghost peak; ×, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} (from bottom to top).

is due to dissolved carbon dioxide. In this experiment, all eluents contained 10% (v/v) of acetonitrile. For reference, the retention times of some divalent heavy metal ions are also shown in Fig. 5.

Fig. 5 shows that the retention time of monovalent ions hardly depends on pH, indicating that the complex formation with citrate ions can be ignored. NH_4^+ has been omitted from Fig. 5 because of its significant overlap with Na^+. The slope of the log k' *vs.* log C plots for Na^+ and K^+ at pH 4.6 is about -0.53, indicating that ion exchange of monovalent ions with divalent ions has occurred.

As the pH decreases, Mg^{2+} and Ca^{2+} first elute faster, but then more slowly again. The probable reason is that the accelerating effect of the complex formation with increasing citrate ion concentration and the retarding effect of the complex dissociation with decreasing pH are in competition.

With the aqueous DHBP bromide solution, the elution of Ca^{2+} is slow and hardly practical. On addition of citric acid to reduce the pH from 5 to 3, elution of Ca^{2+} becomes faster and more practically useful. However, this addition of citric acid causes a system peak to appear and its retention time decreases with decreasing pH. The slope of the log k' *vs.* log C plots is -0.82, corresponding to the dissociation state of citrate ions between monovalent and divalent species. At pH 4–4.5, the system peak appears between K^+ and Mg^{2+} and does not affect their determination. The reason for the appearance of the system peak will be described elsewhere. An eluent pH of 4–4.5 (1 m*M* DHBP citrate + 1 m*M* citric acid) is suitable. The lower the DHBP concentration, the smaller the background absorption becomes, and hence higher sensitivities can be achieved by changing the detection wavelength toward higher absorption. However, with 0.5 m*M* DHBP, it takes about 23 min for Ca^{2+} to elute, and in this respect it can be concluded that a DHBP concentration of about 1 m*M* is suitable for the faster elution of Ca^{2+}.

Fig. 6 shows a typical chromatogram for Na^+, K^+, Mg^{2+} and Ca^{2+} obtained

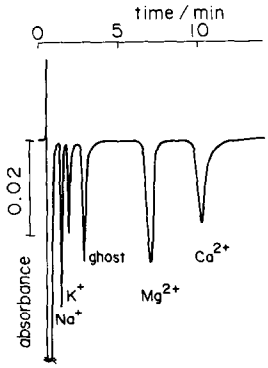

Fig. 6. Typical chromatogram of sodium, potassium, magnesium and calcium ions using DHBP–citric acid eluent and UV detection. Eluent, DHBP citrate (1.0 m*M*)–citric acid (1.0 m*M*) (pH 4.3); flow-rate, 1.0 ml/min. Column, IC cation SW. Sample, each ion $0.8 \cdot 10^{-4}$ *M*, 100 µl. Detection, UV absorption at 300 nm.

with the elution conditions determined as described above. The presence of NH_4^+ ion can be ascertained as the peaks of Na^+ and NH_4^+ are separated from each other by using two SW columns in series. If it becomes possible to use a column with a higher theoretical plate number, it will be possible to separate Na^+, NH_4^+ and K^+.

UV detection and conductivity detection. The solution of DHBP shows a UV absorption peak in the vicinity of 262 nm and the molar absorption coefficient is about $2.4 \cdot 10^4$. When a 1 m*M* solution of DHBP is used as the eluent, it is necessary to hold the background absorption at the detection wavelength below about 1, and therefore, a wavelength of about 300 nm is appropriate. If the linear response region of the detector can be widened, it will be possible to achieve higher detection sensitivities at a wavelength below 300 nm. A conductivity detector also can be used. With 1 m*M* DHBP citrate + 1 m*M* citric acid, the background conductivity is as low as 137 µS/cm, so that the equivalent conductivity of $DHBP^{2+}$ ions is very small. For this reason, the detection sensitivity for monovalent ions is high. With divalent ions, peaks appear in the direction toward decreasing conductivity. This effect is the same as with the benzylamine-type eluents mentioned above and the appearance of both positive and negative peaks is inconvenient. Moreover, the detection sensitivity for divalent ions is slightly lower than that with UV detection and therefore, in general, the UV detection method is more advantageous.

Influence of temperature and heavy metal ions. With increasing temperature, separations of monovalent ions become poor, as with benzylamine-type eluents. At 27°C, Na^+ and K^+ are separated from each other, but at 45°C they overlap. A suitable temperature is 20–30°C. The peaks of Mg^{2+} and Ca^{2+} are sufficiently sharp at room temperature. Heavy metal ions elute at positions that vary with the pH of the eluent. In most instances, specific heavy metal ions can be eluted so that they do not overlap with the peaks of Mg^{2+} and Ca^{2+}. If they coexist in large amounts, EDTA may be added so that they can be eluted faster. With tap water samples, a peak which seems to be Fe^{2+} appears in the vicinity of the peak of Mg^{2+}. If EDTA (acid form) is added to the sample water in a small amount as a solid, and the solution is mixed well, filtered and then injected, the interfering peak disappears.

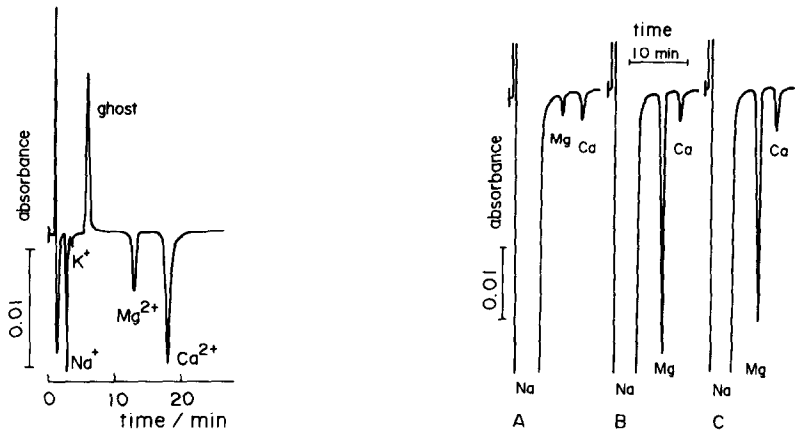

Fig. 7. Chromatogram of a mineral water. Elution conditions as in Fig. 6. Sample, commercial mineral water, 100 μl. Result: Na^+ 12.7, K^+ 2.4, Mg^{2+} 6.8 and Ca^{2+} 39.1 mg/l.

Fig. 8. Chromatograms of raw salt samples. Elution conditions as in Fig. 6. Samples, raw salt for industrial use from Mexico, Australia and China, aqueous solutions filtered with a 0.1-μm membrane filter, 100 μl. Results: (A) Mexico, Mg^{2+} 0.146, Ca^{2+} 0.397 ppt; (B) Australia, Mg^{2+} 2.05, Ca^{2+} 0.470 ppt; and (C) China, Mg^{2+} 2.69, Ca^{2+} 1.008 ppt.

Quantification. Calibration graphs were obtained by using 1 m*M* DHBP citrate + 1 m*M* citric acid-type eluent within the range $0–2 \cdot 10^{-4}$ *M* Na^+, K^+, Mg^{2+} and Ca^{2+}. The peak area for each ion showed good linearity. At concentrations above $1 \cdot 10^{-4}$ *M*, the peak heights of Na^+ and K^+ deviated from a linear relation with concentration.

Applications. Fig. 7 shows a chromatogram of a commercial mineral water, which was injected without any treatment. Fig. 8 shows chromatograms obtained by applying the present method to the determination of Mg^{2+} and Ca^{2+} in raw salt samples, although it is not an example with conditions allowing the determination of both monovalent and divalent species. Suitable amounts of solid samples were dissolved in water and filtered with a 0.1-μm membrane filter. This example makes use of the advantage of indirect UV detection in that the tailing of a large peak due to Na^+

TABLE I

REPRODUCIBILITY OF PEAK HEIGHT AND PEAK AREA WITH BENZYLAMINE ELUENT

Four replicate analyses with $2 \cdot 10^{-4}$ *M* samples and UV detection; all values relative.

Parameter	Na^+	K^+	Ca^{2+}	Mg^{2+}
Peak height				
Average	1.1855	0.9108	0.2105	0.2590
Standard deviation	0.0030	0.0016	0.0024	0.0028
Peak area				
Average	0.2003	0.1919	0.3954	0.4016
Standard deviation	0.0010	0.0017	0.0101	0.0076

is less than that with conductivity detection. This indicates the possibility that Ca^{2+} and Mg^{2+} in raw salts for industrial use can be determined simply and with good precision.

CONCLUSION

It was difficult to find elution conditions that allow Na^+, K^+, NH_4^+, Mg^{2+} and Ca^{2+} to be determined with equal precision. The methods with monovalent eluting ions are mainly suitable for the determination of monovalent sample ions, and the methods with divalent eluting ions are suitable mainly for the determination of divalent sample ions. However, if benzylamine–EDTA · OH–citric acid eluent is used, divalent sample ions can be eluted without being retained in the column. With a slightly lower precision, their determination is also possible.

DHBP–citric acid eluents are disadvantageous in that the separation of monovalent ions is poor and NH_4^+ can hardly be identified. Moreover, polymer-type packing agents cannot be used in the column. These eluents are suitable mainly for determining divalent Mg^{2+} and Ca^{2+} ions while circumventing the interference of heavy metal ions. However, the detection sensitivity is higher than with benzylamine or many other amines.

REFERENCES

1 H. Small, T. S. Stevens and W. C. Bauman, *Anal. Chem.*, 47 (1975) 1801.
2 J. S. Fritz, D. T. Gjerde and R. M. Becker, *Anal. Chem.*, 52 (1980) 1519.
3 H. Small and T. E. Miller, Jr., *Anal. Chem.*, 54 (1982) 462.
4 H. Shintani, *J. Chromatogr.*, 341 (1985) 53.
5 M. Ishikawa, M. Yamamoto, Y. Masui, K. Hayakawa, M. Miyazaki, H. Nakazawa and M. Fujita, *Bunseki Kagaku*, 35 (1986) 309.
6 N. T. Basta and M. A. Tabatabai, *J. Environ. Qual.*, 14 (1985) 450.
7 M. Miyazaki, K. Hayakawa and S.-G. Choi, *J. Chromatogr.*, 323 (1985) 443.
8 J. H. Sherman and N. D. Danielson, *Anal. Chem.*, 59 (1987) 490.
9 R. C. L. Foley and P. R. Haddad, *J. Chromatogr.*, 366 (1986) 13.
10 L. G. Sillèn and A. E. Martell, *Stability Constants of Metal-Ion Complexes*, Chemical Society, London, 1964.
11 Y. Yokoyama and H. Sato, *J. Chromatogr. Sci.*, 26 (1988) 11.