

CHREV. 186

## RECENT DEVELOPMENTS IN ION CHROMATOGRAPHY

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### 1. INTRODUCTION

We are approaching the tenth anniversary of one of the youngest chromatographic methods, ion chromatography (IC), which was devised by Small *et al.*<sup>1</sup> in 1975. Since then the method has become a widely used technique for the simultaneous analysis of organic and inorganic ions. It is essentially a high-performance liquid chromatographic (HPLC) method using specific stationary and mobile phases that are suitable for the rapid separation of various ions.

This paper reviews a number of significant innovations:

(a) the introduction of detectors other than conductivity detectors, *e.g.*, spectrophotometric detectors in the UV region<sup>2</sup>, electrochemical detectors using a silver or coated silver electrode<sup>3</sup> and coulometric detectors<sup>4</sup>;

(b) the greater variety of stationary phases used in IC in addition to low-capacity ion exchangers, such as reversed-phase materials<sup>5</sup>, polystyrene-divinylbenzene adsorbents and bonded phases;

(c) investigations of the relative efficiencies of various aromatic acids and their salts as eluents in the chromatographic separation of ions, and the attainment of a better understanding of the specific interactions of these eluents with the stationary phases;

(d) a quantitative interpretation of the injection peak in IC; and

(e) the chromatography of metal cations and complex ions.

All these innovations have advanced IC as a useful tool for solving analytical problems in such fields as agrochemistry, environmental chemistry, geochemistry, plating solutions, analysis of water samples from different sources and food product testing.

## 2 UV AND ELECTROMETRIC DETECTORS

The most commonly used detector in IC is the conductivity detector, which measures the difference in the conductivities of the eluting sample ions and the prevailing eluent ions. If, however, the difference between the equivalent conductance of the sample and that of the eluent ions is small, other detectors should be used. UV detectors have already proved to be suitable in a number of such instances.

There are two ways in which a UV spectrophotometric detector can aid in the detection of ions by IC.

(i) By a direct absorbance measurement of anions in the wavelength range 190–210 nm, when eluents transparent to UV are used. An example of a comparison between conductivity and UV detection is shown in Fig 1. Williams<sup>2</sup> showed that the detection of ions such as nitrite, bromide and nitrate, is more sensitive to UV than to conductivity detection.

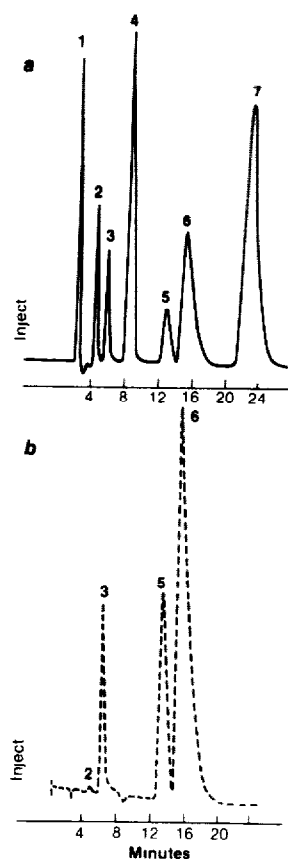


Fig 1 Ion chromatogram of seven common anions (a) Conductivity detector peaks 1, 3 ppm  $F^-$ , 2, 4 ppm  $Cl^-$ , 3, 10 ppm  $NO_2^-$ , 4, 50 ppm  $PO_4^{3-}$ , 5, 10 ppm  $Br^-$ , 6, 30 ppm  $NO_3^-$ , 7, 50 ppm  $SO_4^{2-}$  (b) UV detector at 192 nm, position 2, peaks 2, 4 ppm  $Cl^-$ , 3, 10 ppm  $NO_2^-$ , 5, 10 ppm  $Br^-$ , 6, 30 ppm  $NO_3^-$  (Reproduced with permission from ref 2, copyright 1983 American Chemical Society)

(ii) By indirect spectrophotometric detection, first developed by Small and Miller<sup>6</sup> They showed that anions that do not absorb UV radiation can be chromatographed by introducing UV-absorbing eluents, such as dilute solutions of aromatic acids and their salts Fig 2 shows a chromatogram of a mixture of five ions, which were eluted from a low-capacity ion exchanger by means of a mixture of  $1 \times 10^{-3} M$  sodium phthalate and  $1 \times 10^{-3} M$  boric acid at pH 10

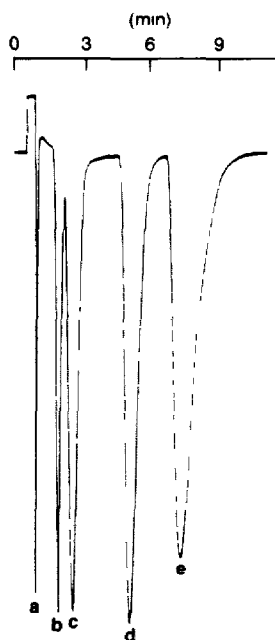


Fig 2 Indirect photometric detection of several "transparent" ions in a chromatogram Peaks (a) carbonate, (b) chloride, (c) phosphate, (d) azide, and (e) nitrate (Reproduced with permission from ref 6, copyright 1982 American Chemical Society)

The peaks recorded on this chromatogram are negative, indicating that the absorbance of the eluent decreases in the presence of a non-absorbing anion in the eluate This idea was applied by Larson and Pfeiffer<sup>7</sup> to the determination of mixtures of quaternary aliphatic ammonium compounds by elution with aromatic ammonium compounds, which absorb at 254 nm Other recent work of interest in this connection is Barber and Carr's<sup>8</sup> paper on the UV detection of "transparent" ions They separated inorganic anions on a reversed-phase column and eluted them with hydrophobic quaternary ammonium compounds, which absorb in the UV region These eluents are now called "ion-interaction reagents" (IIR)

The electrometric detectors developed so far are mainly based on a silver working electrode, which is useful in detecting halide, thiocyanate, hexacyanoferrate(III) and -(II), thiosulphate and sulphide ions

An indicating silver electrode can perform well in three different modes

(i) Controlled-potential coulometry for the chromatographic separation of anions This was developed by Girard<sup>4</sup>, who used a silver working electrode and a carbon-cloth reference electrode

(ii) Amperometric detection of weak-acid anions, such as cyanide and sulphide, was demonstrated by Rocklin and Johnson<sup>9</sup> When silver reacts with cyanide, a very stable complex anion is formed, whereas with sulphide a precipitate having a very low solubility product results, electrons being released in both reactions



The current generated is directly proportional to the ion concentration Fig 3 is a chromatogram in which an amperometric detector was used in conjunction with a conductometric detector This chromatogram shows how well twelve different ions can be resolved and quantated within 16 min

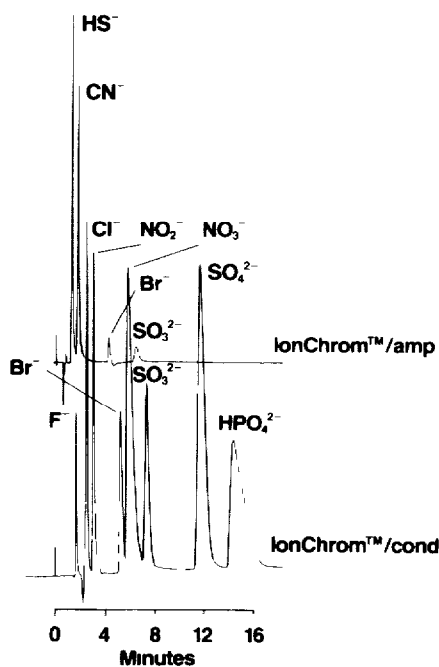


Fig 3 Simultaneous analysis using electrochemical and conductivity detection Concentrations 300 ppb sulphide, 500 ppb cyanide, 1 ppm fluoride, 4 ppm chloride, 10 ppm nitrite, 10 ppm bromide, 25 ppm nitrate, 30 ppm sulphite, 25 ppm sulphate and 50 ppm phosphate (Reproduced with permission from ref 9, copyright 1983 American Chemical Society)

(iii) A potentiometric detector with a coated silver wire was developed by Hershcovits *et al*<sup>10</sup> The eluents were selected for their ability to form sparingly soluble salts with silver, which coat the silver wire with a thin layer Eluents of this kind include salicylic, phthalic and benzoic acids

If a silver wire is coated with a silver salt, AgX, reduction will occur



and the potential difference will be

$$E = E_{\text{Ag/Ag}^+}^0 - E_{\text{ref}}^0 + \frac{RT}{F} \ln [\text{Ag}^+] \quad (4)$$

Fig 4 shows a comparison between the conductometric and potentiometric detection of a mixture of four ions, clearly demonstrating the greater sensitivity of the potentiometric detector

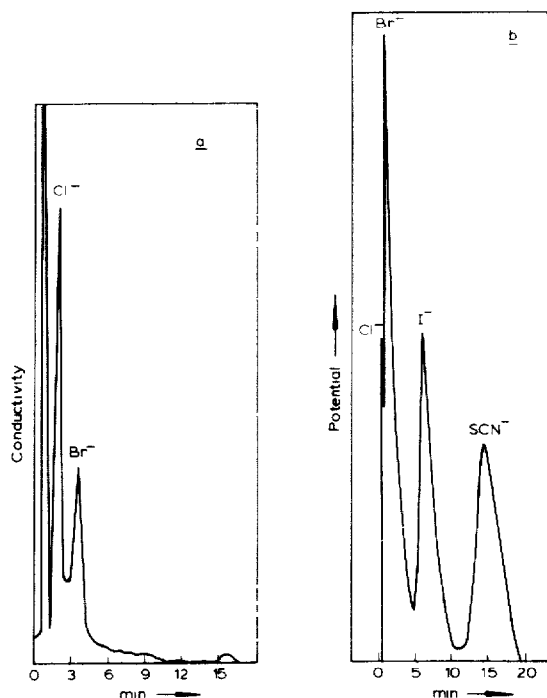


Fig 4 Comparison of chromatograms (a) conductometric detection, (b) potentiometric detection. Eluent,  $1 \times 10^{-3} M$  salicylic acid, pH 4.12, flow-rate, 2.4 ml/min, ion concentrations, 50 ppm each

### 3 SEPARATION OF IONS BY ION-PAIR REVERSED-PHASE CHROMATOGRAPHY

A method for the separation of metal ions and anions that has become very attractive in recent years is the use of non-functionalized stationary phases, such as reversed-phase columns and styrene-divinylbenzene copolymers, with ion-pairing agents as eluents. These stationary phases are readily available and are used by most HPLC practitioners. In these systems a dynamic equilibrium exists between the hydrophilic ion-pairing reagents in the mobile phase and the hydrophobic sites in the stationary phase. This method is therefore often termed "dynamic ion-exchange chro-

matography"<sup>11</sup>, in contrast to "fixed-site ion-exchange chromatography", which utilizes low-capacity ion exchangers in the stationary phase

In 1980 Molnar *et al*<sup>12</sup> separated cations on a LiChrosorb RP-18 column, eluting with an aqueous *n*-heptylsulphonate solution. On the same column they separated anions, using tetrabutylammonium hydroxide and phosphate buffer as the eluent.

Skelly<sup>5</sup> separated anions on an octadecylsilica column, using an eluent containing the octylamine salt of a mineral acid (Fig. 5). Another important application of this concept was shown by Iskandarani and Pietrzyk<sup>13</sup>, who separated  $\text{NO}_3^-$  from  $\text{NO}_2^-$  with good resolution on a polystyrene-divinylbenzene column, using an alkylammonium salt dissolved in acetonitrile-water (1:3) as the eluent. They also applied the method to the analysis of real samples.

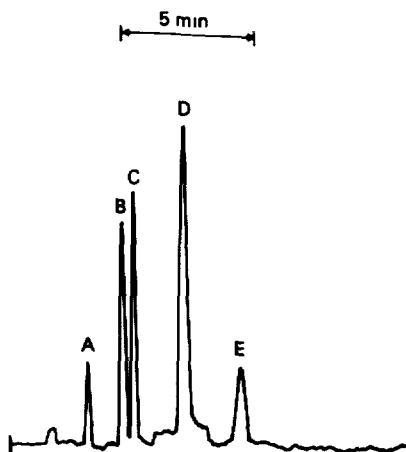


Fig. 5. Determination of trace levels of inorganic anions in water (200  $\mu\text{l}$ ) on a Partisil-10 ODS-3 column. The mobile phase was 0.01 *M* octylamine (aq.) adjusted to pH 6.2 with  $\text{H}_3\text{PO}_4$  and pumped at 2 ml/min. UV detection at 205 nm. A, 240 ppb  $\text{IO}_3^-$ ; B, 200 ppb  $\text{Br}^-$ ; C, 200 ppb  $\text{NO}_2^-$ ; D, 180 ppb  $\text{NO}_3^-$ ; and E, 230 ppb  $\text{I}^-$ . (Reproduced with permission from ref. 5, copyright 1982 American Chemical Society.)

Cassidy and Elchuk<sup>11</sup> used the same columns but coated with large hydrophobic modifiers, and chromatographed inorganic anions successfully and with high sensitivity. More recently, Schwedt's group<sup>14</sup> demonstrated the feasibility of analysing anion mixtures with the aid of a reversed-phase column pre-coated with methyl green dye. The eluent was tetrabutylammonium salicylate.

A careful investigation into the various factors affecting the separation, such as the type of organic modifier, type of apolar stationary phase and concentration of eluents, was carried out by Dreux *et al*<sup>15</sup>.

The mechanism of separation has been the subject of some controversy<sup>16</sup>. It is now believed that the ion interaction model proposed by Iskandarani and Pietrzyk<sup>17</sup>, based on double-layer formation on the stationary phase, best fits the available experimental data.

## 4 ELUTION BEHAVIOUR OF AROMATIC ACIDS AND THEIR SALTS

Aromatic acids and their salts in aqueous solution efficiently elute ions from low-capacity ion exchangers and are therefore useful eluents in non-suppressed ion chromatography<sup>18</sup>. Advantages of these compounds are their relatively low conductivity, which permits sensitive conductometric detection, and their comparatively high molar absorbance in the UV region, which makes them suitable for the indirect UV detection of non-absorbing inorganic ions<sup>8</sup>.

A number of aromatic compounds have been examined as eluents for ions, an indication of their relative efficiencies being obtained by comparing their retention times on the same stationary phase. Fig. 6 shows such a comparison, made with three eluents (salicylate, *p*-hydroxybenzoate and benzoate), each eluting the same four ions, namely chloride, nitrite, bromide and nitrate, on a low-capacity anion exchanger. It can be seen that salicylate is the most efficient eluent for these four monovalent anions and that the efficiency gradually decreases in the order salicylate > *p*-hydroxybenzoate > benzoate. Similar orders of efficiency have been established for many other substituted aromatic acids<sup>19</sup>.

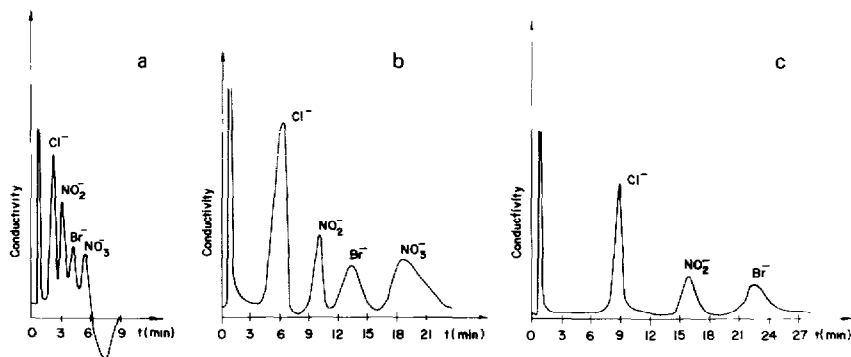


Fig. 6 Comparison of the elution efficiencies of (a)  $1 \cdot 10^{-3} M$  potassium salicylate, (b)  $1 \cdot 10^{-3} M$  potassium *p*-hydroxybenzoate and (c)  $1 \cdot 10^{-3} M$  potassium benzoate

An efficient eluent is one in which there is a large overlap between the aromatic rings in the aqueous solution of the mobile phase and those of the stationary phase. A major factor influencing the extent of this overlap is the stability of the aromatic ring. A hydroxy substituent on the aromatic ring has a ring-stabilizing effect, and therefore *p*-hydroxybenzoic acid is a better eluent than benzoic acid (Fig. 6). Salicylic acid is an even better eluent, because the hydroxy substituent is in the *ortho*-position, causing extra stabilization by hydrogen bonding.

A quantitative correlation of elution efficiencies is given by Strelow and Van der Walt's equation<sup>6</sup>

$$\log (V_e - V_v) = \text{constant} - \frac{1}{x} \log [E^{x-}] \quad (5)$$

where  $V_e$  = elution volume of the injected ion,  $V_v$  = void volume of the ion-exchange column,  $[E^{x-}]$  = concentration of the anionic aromatic molecules in the aqueous

eluent,  $y$  = charge of the injected ions and  $x$  = charge of the aromatic anion in the eluent. Fig 7 shows the straight lines obtained for five eluents when eqn 5 is applied. From eqn 5, it would be expected that all these straight lines would have a slope of unity ( $y/x = 1$ , as only monovalent ions are interacting). This is not so, however, because the charge effect is not the only contributing factor. Other factors, such as aromatic ring stability, acidic strength and steric effects, contribute to the deviation from a slope of unity.

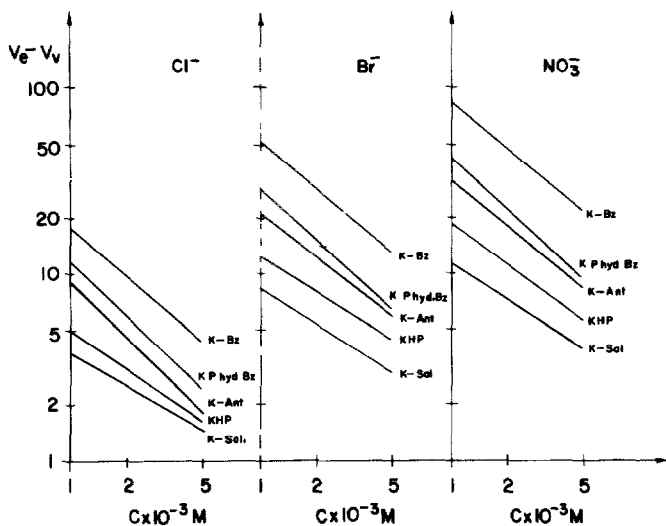


Fig 7 Plots of eqn 5 for five eluents K-Bz = potassium benzoate, K P hyd Bz = potassium *p*-hydroxybenzoate, K-Ant = potassium anthranilate, KHP = potassium biphtalate, K-Sal = potassium salicylate

## 5 THE INJECTION PEAK IN ION CHROMATOGRAPHY

When a mixture of ions is injected into a chromatographic ion-exchange column, the eluent ions are displaced and are the first to emerge from the column. The difference between that peak and the so-called "void volume ( $V_0$ )" peak in liquid chromatography (LC) is that in LC,  $V_0$  is determined by injecting a solute that is not retained on the column, whereas in IC,  $V_0$  is indicated by the first peak, formed as a result of injecting the ionic sample mixture. A knowledge of the exact value of  $V_0$  is important for the determination of the capacity factors. The magnitude of  $V_0$  in LC reflects the porosity of the stationary phase or, in other words, the maximum volume within a column<sup>20</sup> accessible to organic molecules according to their size. In IC on the other hand, at least when conductivity detection is used, the magnitude of the injection peak provides a different kind of quantitative information: it measures the conductivity of eluent ions displaced by the injected ions, and it thereby represents the total of injected ions.

It has been shown that in non-suppressed IC<sup>21</sup> the magnitude of the injection peak can be calculated for a given concentration of injected ions. The known data are eluent concentration, pH and the dissociation constant of the weak acid or base



used as the eluent. From these data the background conductivity is first calculated, and then the change in conductivity as a result of the displacement of eluent ions by the injected ions is determined.

Fig. 8 shows the calculated conductivities when different concentrations of chloride ions are injected. The experimentally found injection peaks are also shown. Very good agreement between the experimental and the calculated data was achieved.

As stated earlier, reversed-phase IC is rapidly developing, and the physical meaning of the injection peak in such systems, where a double layer is formed, is currently being investigated.

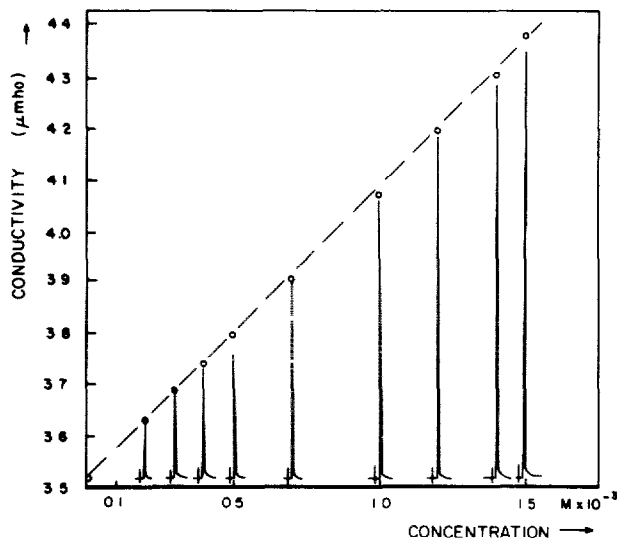


Fig. 8 Dependence of injection peak conductivity on the concentration of an injected monovalent anion. Calculated (○) and experimental values are compared. Eluent:  $2 \cdot 10^{-3} M$  benzoic acid at pH 4.37.

## 6 CHROMATOGRAPHIC DETERMINATION OF METAL IONS

A considerable number of metal cations and complex ions can be determined by IC. Alkali metal and ammonium ions were first determined by Small *et al.*<sup>1</sup>, the separation being effected on a low-capacity ion exchanger with hydrochloric acid as the eluent and the introduction of a suppressor column. Later, Fritz *et al.*<sup>22</sup> determined the same ions but without the need for a suppressor column, using dilute ( $10^{-3} M$ ) nitric acid as the eluent. The resulting peaks are negative because of the high background conductivity of the acid. They also showed that chromatograms of alkaline earth metals are obtainable but a complexant, such as ethylenediammonium nitrate, must be used in order to render the elution of these metals more efficient.

Transition metals were separated by Cassidy and Elchuk<sup>23</sup> with the aid of reversed-phase ion-pair LC (see Fig. 9). The organic modifier was an alkylsulphonate and elution was accomplished with a mixture of a tartrate salt and an alkylsulphonate.

One of the most elegant separations is that of the lanthanides, also carried out

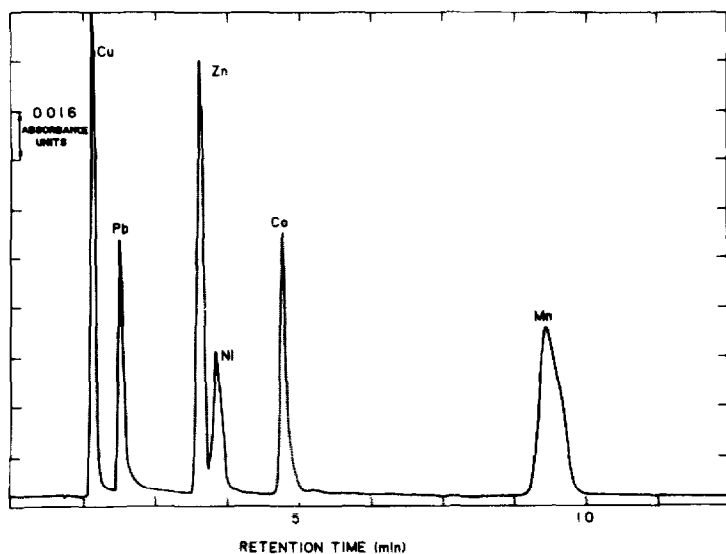


Fig 9 Separation of six metal ions on a 5- $\mu\text{m}$   $\text{C}_{18}$  column in equilibrium with  $\text{C}_8\text{H}_{13}\text{SO}_3\text{Na}$ . Experimental conditions: Supelcosil column, 15 cm, eluent, 0.045 M tartrate (pH 3.4) and 0.01 M  $\text{C}_8\text{H}_{13}\text{SO}_3\text{Na}$  at 1.5 ml/min, sample, 20  $\mu\text{l}$  of a solution containing 2.5–50  $\mu\text{g}/\text{ml}$  of each metal ion, detection, absorption at 530 nm after post-column reaction (Reproduced with permission from ref. 23, copyright 1982 American Chemical Society)

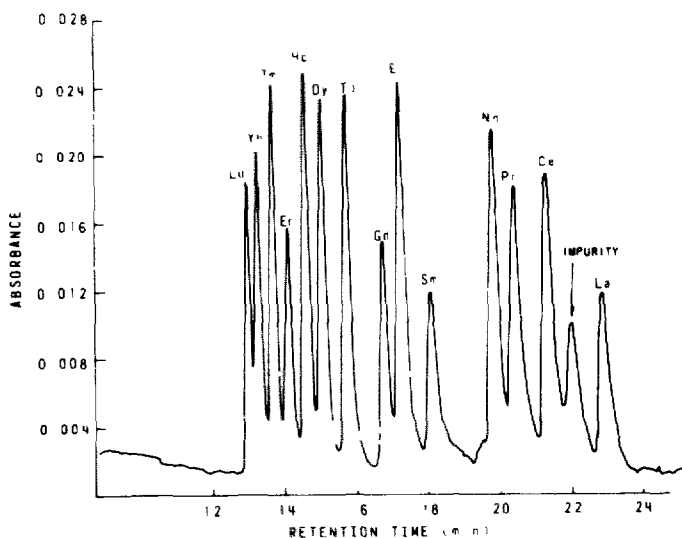


Fig 10 Separation of the lanthanides on Partisil-10 SCX. Experimental conditions: 25 cm  $\times$  4 mm I.D. column, sample 10  $\mu\text{l}$  of a solution containing 10 mg/ml of each lanthanide, linear programme from 0.005 mol/l HIBA over a 30-min period at 1.3 ml/min and pH 4.6, detection at 600 nm after post-column reaction with Arsenazo I (Reproduced with permission from ref. 24, copyright 1979 American Chemical Society)

by Elchuk and Cassidy<sup>24</sup> They separated the fourteen lanthanides in order of their atomic weights, from Lu to Ln, on a bonded-phase cation exchanger, and eluted the trivalent ions by gradient elution with hydroxyisobutyric acid Fig 10 shows the sharp separations achieved The same group<sup>25</sup> also applied this method to the examination of lanthanides in thorium-uranium fuels

Most recently experiments were carried out to separate metal chelates Among these mention should be made of the separation of bipyridyl complexes of nickel and iron<sup>26</sup> and the separation of calcium- and magnesium-EDTA complexes<sup>27</sup>

## 7 CONCLUSION

From many of the methods described here, the conclusion can be drawn that most elements in the Periodic Table are amenable to quantitative determination by IC However, whereas there are many analytical procedures for metal ions, IC has proved especially suitable for the simultaneous determination of mixtures of anions It is therefore only natural that a major effort has been devoted by a number of research groups to the elaboration of the pertinent techniques

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