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Note

Ion chromatography of Mg, Ca, Sr and Ba ions using a metallic copper electrode as a potentiometric detector

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The determination of inorganic cations by high-performance liquid chromatography (HPLC) has received increased attention over recent years and when compared with most conventional spectroscopic methods, HPLC offers the considerable advantage of allowing a number of cations to be determined in a single run. This approach has been successfully used for the determination of alkali metal and ammonium ions[1], alkaline earth metal ions[1,2], transition metal ions[2–5] and lanthanides[2,6]. These methods have been based on ion-exchange or ion-pairing separation techniques, coupled with conductivity[1,2], coulometric[3] or spectrophotometric detection [4–6]. In the latter case, detection was accomplished by a post-column reaction system wherein coloured metal complexes were formed. An important disadvantage of such a post-column reaction detector is the band broadening which inevitably results in the mixing coil.

We have previously described a potentiometric HPLC detector based on an active copper surface as the sensing electrode[7]. This device was originally applied to the direct detection of copper complexing ligands such as amino acids, but we also recently reported its application in flow-injection analysis to the indirect detection of cations in a suitable carrier[8]. The aim of this communication is to indicate the utility of potentiometric detection in cation chromatography as an alternative to presently used detection methods.

EXPERIMENTAL

The HPLC equipment consisted of a Kortec (Sydney, Australia) K35 pump, an Altex (Berkely, CA, U.S.A.) Model 905-42 sample injection valve fitted with a 20-μl loop and a Wescan (Santa Clara, CA, U.S.A.) low-capacity silica-based cation-exchange column (Type 269-004, 250 × 4.6 mm I.D.). The potentiometric flow-through detector incorporating a metallic copper electrode has been described previously[8]; this detector was connected to a Radiometer (Copenhagen, Denmark) PHM 62 pH/millivolt meter, interfaced to a Houston Omniscribe (Houston, TX, U.S.A.)

Model EB 5117-5-S recorder, set on the 10-mV range. All fittings in contact with the eluent were either stainless-steel or polypropylene. All chromatograms were obtained at room temperature.

Reagents used were ethylenediamine (May and Baker, U.K.), diethylenetriamine (Hopkin and Williams, U.K.), L-glutamic acid (Koch-Light, Colnbrook, U.K.), citric acid (BDH, Sydney, Australia) and tartaric acid (Standard Laboratories, Melbourne, Australia). These reagents were used without further purification. Eluents were prepared in distilled and deionised water and were filtered through a 0.45-μm membrane filter and degassed before use. The pH of each eluent was adjusted with nitric acid or sodium hydroxide. Stock solutions of alkaline earth metal ions were prepared from analytical grade nitrates and were diluted as required.

RESULTS AND DISCUSSION

Principle of operation

The fundamental feature of a metallic copper electrode which enables it to be used for potentiometric detection of cations is its sensitivity to the presence of copper complexing ligands[7-9]. The electrode potential of the copper electrode is dependent on the concentration of ligand present in the test solution. Thus when a metal ion which forms a complex with the ligand is added to the test solution, the potential of the copper electrode alters in response to the changed concentration of ligand. This concept has been employed for the determination of metal ions by flow-injection analysis, using EDTA as ligand[8].

To be applicable to cation chromatography, this approach requires that a li-
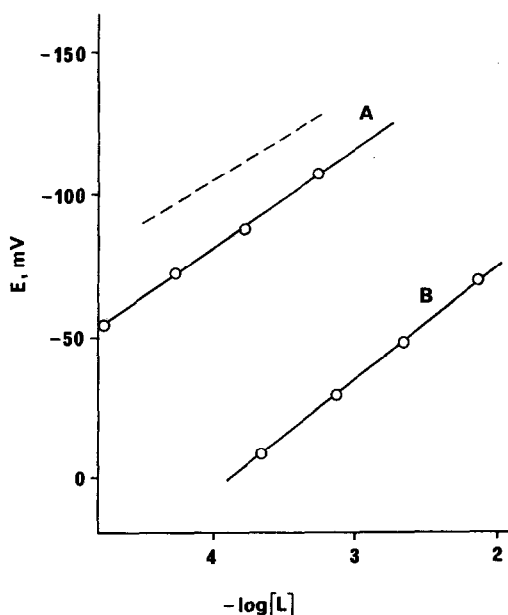

Fig. 1. Copper electrode potential under continuous flow conditions as a function of free ligand concentration for citrate (A) and tartrate (B). The broken line indicates the theoretical divalent Nernstian slope.

gand capable of complexing both copper and the ions to be determined be present in the mobile phase. The ligand selected should form a strong complex with copper ions, since the stability of the copper–ligand complex governs the available range of electrode potential changes to be used for detection of metal ions. It is not essential for the metal ions to be determined to also form strong complexes with the ligand, since as discussed previously[8], the stoichiometry of the complex plays the most significant role. In general, it is desirable to maintain the ligand concentration at the lowest possible level, since this improves the sensitivity of the electrode towards metal cations.

Application to cation-exchange chromatography

　　The presence of a complexing agent in the eluent of a cation-exchange system has a marked effect on the separation process. Sevenich and Fritz[2] have shown that the adjusted retention time for a particular metal ion is inversely proportional to the extent to which the cation is complexed by the ligand in the mobile phase. This complexation is designated by the side-reaction coefficient, $\alpha_{M(L)}$, for a metal ion M and a ligand L. When the ligand forms very strong complexes with metal ions, or if excessive concentrations of ligand are used, very short retention times result. These factors are of great importance when low-capacity ion-exchange columns are used.

　　Satisfactory separation of alkaline earth ions by ion-exchange, coupled with potentiometric detection using a copper electrode is therefore most likely to be successful with low concentrations of a ligand which forms a strong complex with copper ions, but complexes only weakly with alkaline earth ions. These requirements are filled by tartrate and citrate in weakly acidic solution, and by glutamate in weakly alkaline solution. Fig. 1 shows the dependence of the copper electrode potential value under continuous flow conditions on the logarithm of free ligand concentration for tartrate and citrate at pH 4.6. The values of free ligand concentration were calculated using tabulated values of the acid dissociation constants for the ligands concerned[10]. Although no measurements were made with glutamate as ligand, the similarity of

TABLE I

VALUES OF SIDE-REACTION COEFFICENTS ($\alpha_{M(L)}$) FOR ALKALINE EARTH METAL IONS

Conditions as used for chromatographic separation (calculated using constants from ref. 10).

	Ligand		
	Tartrate	*Citrate*	*Glutamate*
pH	4.6	4.6	7.6
Total ligand concentration C_L, M	0.002	0.002	0.1
Free ligand concentration (L), M	$1.5 \cdot 10^{-3}$	$1.2 \cdot 10^{-4}$	$8.4 \cdot 10^{-4}$
$\alpha_{Mg\ (L)}$	1.04	1.24	1.07
$\alpha_{Ca\ (L)}$	1.10	1.02	1.02
$\alpha_{Sr\ (L)}$	1.10	1.01	1.02
$\alpha_{Ba\ (L)}$	1.06	1.01	1.02

stability and acid dissociation constants between glutamate, tartrate and citrate suggests that a similar response of the copper electrode can be expected.

Table I gives the calculated values of the side-reaction coefficients, $\alpha_{M(L)}$, for alkaline earth ions in the presence of tartrate, citrate or glutamate, under the conditions indicated. The values of the side-reaction coefficients are very small and suggest that even at maximum, only about 20% of the metal ions are complexed. It should be emphasized that the values given in Table I are approximate only because of the difference in reaction conditions used here to those used for the determination of the stability constants, but the calculated $\alpha_{M(L)}$ values permit an estimate of the magnitude of the expected electrode potential to be made. For example, if the free ligand concentration and the metal ion concentration are both 1 mM, and 10% binding by the ligand is assumed, then the copper electrode will show a potential increase of 1.4 mV after addition of the metal ion. At higher ligand concentrations, this potential change would be less and at lower ligand concentrations, a greater potential change would be expected. Experimentally determined retention times and observed potential changes were in good agreement with those calculated from Table I. In the tartrate medium, highest sensitivity was obtained for calcium, whereas magnesium gave best results with citrate. For glutamate, magnesium and strontium produced larger potential changes than calcium or barium.

Other eluent parameters

In addition to the complexing ligand discussed in the preceding section the eluent necessarily contains a competing cation to participate in the ion-exchange
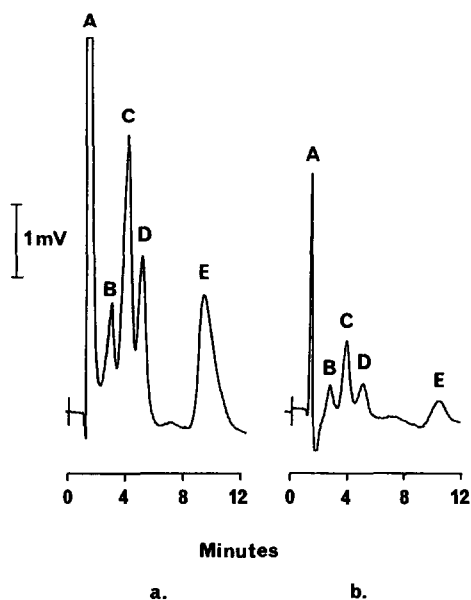

Fig. 2. Potentiometric detection of alkaline earth ions after ion-exchange separation using 20-μl sample injection. Conditions: Wescan cation-exchange column; eluent 1 mM tartrate + 1 mM diethylenetriamine at pH 4.6; flow-rate 0.3 ml/min. Peak identities: (A) solvent, (B) Mg, (C) Ca, (D) Sr, (E) Ba at 100 ppm (a) and 20 ppm (b).
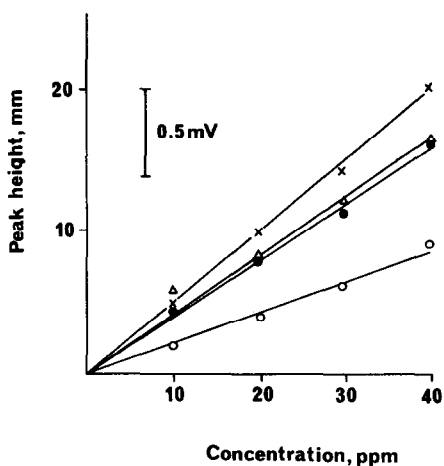
Fig. 3. Calibration plots for Mg (○), Ca (×), Sr (●) and Ba (△). Conditions are as given in Fig. 2, except that 0.5 mM diethylenetriamine and a flow-rate of 1 ml/min were used.

process. An increase in the concentration of this cation results in a decrease in observed retention times of eluted cations. In our initial work using sodium or potassium salts of the ligands studied, relatively long retention times and poor peak shape resulted, together with small detector signal values. Addition of 2 mM ethylenediamine (En) or diethylenetetramine (Den) resulted in improved peak shape and increased sensitivity. When Den was used in the mobile phase, the detector response to barium and strontium was superior to other eluents.

The mobile phase flow-rate was varied over the range 0.3–1.0 ml/min in order to observe the effect on peak shape, resolution and detector signal. No significant effects were noted, as illustrated by the calculated values of resolution for the least resolved peak pair (calcium and strontium) which were 0.87, 0.84 an 0.80 for flow-rates of 0.3, 0.5 and 1.0 ml/min, respectively.·

Fig. 2 shows chromatograms obtained for mixtures of magnesium, calcium barium and strontium (at 100 ppm and 20 ppm levels), with 1 mM tartrate and 1 mM Den as eluent. Using this eluent, calibration curves were prepared over the concentration range 0–40 ppm and as shown in Fig. 3, a linear relationship between peak height and concentration was observed. Similar results were obtained with citrate and glutamate eluents.

Potentiometric detection using a metallic copper electrode provides an alternative to conductivity or post-column reaction detection methods in ion chromatography applied to the determination of alkaline earth ions. It is expected that use of a higher capacity ion-exchange column would permit stronger complexing ligands to be used in the mobile phase, leading to improved detection limits. When suitable ligands are selected, potentiometric detection should be applicable to many other metal ions.

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