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APPLICATION OF INDIRECT POTENTIOMETRIC DETECTION WITH A METALLIC COPPER ELECTRODE TO ION CHROMATOGRAPHY OF TRANSITION METAL IONS

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SUMMARY

A metallic copper electrode is applied to the indirect detection of some transition metal ions separated by ion chromatography. This separation may be accomplished by cation exchange using an eluent consisting of ethylenediammonium ions and a copper complexing ligand such as oxalate, citrate, or tartrate. Alternatively, anionic metal complexes formed with ligands such as oxalate or citrate may be separated by anion-exchange chromatography. In both methods, detection is based on an increase in the potential of the copper electrode resulting from a decreased concentration of the eluent ligand (*i.e.* oxalate, citrate etc.), when a metal ion is eluted. Cation-exchange chromatography is the more successful approach and theoretical electrode response characteristics are presented for this method. Experimental calibration plots confirm theoretical predictions and show that for small amounts of injected solute, a linear relationship exists between peak height and the amount of injected solute. When larger solute amounts are used, the injected amount is proportional to $1 - 10^{-H/S}$, where H is the peak height and S is the Nernstian slope. Retention data and sample chromatograms are given, and these indicate that the major limitation of potentiometric detection with a metallic copper electrode is the selection of mobile phase conditions which provide both good separation and sensitive electrode response.

INTRODUCTION

In the determination of inorganic cations by high-performance liquid chromatography (HPLC), various spectrophotometric and electrochemical methods of detection can be employed[1]. Transition metal ions are particularly suited to spectrophotometric detection using post-column reaction with reagents such as pyridylazoresorcinol (PAR)[2–5], arsenazo III[6] or dithizone[7]. Alternatively, transition metal

ions may be detected by such electrochemical methods as coulometry at controlled potential[8,9], conductivity measurements[10] and amperometry using various designs of working mercury electrodes[11–14].

In contrast, potentiometric detection has not been widely applied in the determination of inorganic cations. Deelder et al.[15] have used a flow-through cell fitted with a non-selective cationic membrane for detection of lithium and sodium, but the sensitivity obtained was very poor. More sensitive potentiometric detection was recently reported for monovalent cations using ion-selective membrane electrodes[16]. On the basis of flow-injection measurements, indirect detection of transition metal ions and lanthanide ions has been suggested[17], but no HPLC data has been reported.

For some time, we have been investigating the use of a metallic copper electrode as a potentiometric detector for liquid chromatography and flow-injection analysis. This electrode has been shown to respond directly to such species as amino acids[18], organic acids[19,20] and inorganic anions[21,22], and has also been used for the indirect detection of some inorganic anions[22] and alkaline earth ions[23,24]. Calibration relationships exhibited for these species have been found to be dependent on the mode of detection applicable to each species. In this paper, we report the indirect potentiometric detection of transition metal ions, with particular emphasis on theoretical and practical interpretation of the response characteristics of the metallic copper indicator electrode.

THEORY

Fundamental to the functioning of a metallic copper electrode as a potentiometric sensor in the indirect detection of metal ions is a dependence of its potential on the presence in solution of complexing agents which bind cuprous or cupric ions. As we have shown for a variety of organic[20] and inorganic[21] ligands, the electrode potential is related to the stoichiometry and stability of the complexes formed and also to the valency of the complexed copper ions. When in a given range of total ligand concentration the formation of a single copper complex predominates, the relationship between the potential of a metallic copper electrode and the total ligand concentration can be Nernstian and for the formation of a 1:1 complex with cupric ions, is given by[21]:

$$E = A - \frac{RT}{2F} \ln \frac{C_L^0}{\alpha_{L(H)}} \tag{1}$$

where A is constant, C_L^0 is the total ligand concentration, $\alpha_{L(H)}$ is the side-reaction coefficient for protonation of the ligand L, F is the Faraday constant, and R and T are the gas constant and temperature, respectively. The relationship in eqn. 1 is limited in the negative potential direction to the value where even in the absence of oxygen, an important role is played by the possible decomposition of solvent when the stability of the complex formed is high, due to the following reaction:

$$Cu^0 + 2H_2O + L^{2-} \rightarrow CuL + 2OH^- + H_2 \tag{2}$$
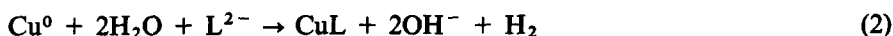
This process appears to be responsible for limited Nernstian functioning of this detection method for ligands forming strong copper complexes[21].

The relationship in eqn. 1 is the basis for indirect detection of metal ions. In previously reported[18] flow-injection studies on inorganic cations, samples containing a cation at a concentration of C_M^0 were injected into a stream of ligand solution of total concentration C_L^0. Taking into consideration dilution expressed by the dispersion coefficient D and assuming a 1:1 complex between M and L, the concentration C_L of ligand approaching the detector is given by:

$$C_L = C_L^0 - C_M^0/D \tag{3}$$

If the complex formed (i.e. ML) is not very stable, then dissociation of this complex must also be considered and eqn. 3 now becomes:

$$C_L = C_L^0 - \frac{C_M^0}{D} + \frac{C_M^0}{K_{ML}' \cdot C_L \cdot D} \tag{4}$$

where K_{ML}' is the conditional formation constant of the complex ML.

The peak height H under flow-injection conditions is given by[23]:

$$H = \frac{RT}{2F} \ln \left(1 - \frac{C_M^0}{C_L^0 \cdot D} \right) \tag{5}$$

This relationship applies to stable ML complexes and is based on eqn. 3 above; a more complicated relationship is involved if eqn. 4 is to be considered for less stable ML complexes. One can expect that eqn. 5 will be valid for chromatographic measurements at short retention times, where peak broadening does not significantly influence peak height potential value. According to the above equation, a linear relationship can be expected between C_M^0 and the term $1 - 10^{-H/S}$ (where $S = RT/2F$), provided that the eluent ligand is present in excess over the dispersed sample; that is $C_L^0 > C_M^0 D$.

At very low concentrations of metal ions in the injected samples, eqn. 5 may be expanded as a series to give:

$$H = -\frac{RT}{2F} \left[-\frac{C_M^0}{C_L^0 \cdot D} - \frac{1}{2} \left(\frac{C_M^0}{C_L^0 \cdot D} \right)^2 - \frac{1}{3} \left(\frac{C_M^0}{C_L^0 \cdot D} \right)^3 - \ldots \right] \tag{6}$$

When $C_L^0 \gg C_M^0$, this equation simplifies to:

$$H = \frac{RT}{2FC_L^0 D} C_M^0 \tag{7}$$

The peak height therefore depends inversely on the ligand concentration in the eluent and the dispersion, and a linear relationship between peak height and C_M^0 is predicted for low concentrations of injected metal ion. This relationship has previously been observed for ion chromatography of alkaline earth ions[24]. In both eqns.

5 and 7, the term C_M^0 may be replaced with N_M, the amount of injected metal ion, without alteration to either equation.

EXPERIMENTAL

Instrumentation

The HPLC equipment consisted of a Waters Assoc. (Milford, MA, U.S.A.) Model M45 solvent pump and Model U6K injector. The potentiometric flow-through detector incorporating a copper wire electrode and silver–silver chloride reference electrode has been described previously[18]. This detector was connected to a Radiometer (Copenhagen, Denmark) PHM 62 pH/millivolt meter interfaced to a Houston Instruments (Austin, TX, U.S.A.) Omniscribe recorder. The columns used were a Wescan (Santa Clara, CA, U.S.A.) low-capacity silica-based cation-exchange column (Type 269-004, 250 × 4.6 mm I.D.), a Nucleosil (Macherey-Nagel, Düren, F.R.G.) Type 10.SA (300 × 4.0 mm I.D.) and a Vydac 302 IC 4.6 (Separations Group, Hesperia, CA, U.S.A.) low-capacity anion exchanger, 250 × 4.6 mm I.D. All parts of the chromatographic system in contact with the eluent were either stainless steel or polypropylene. Prior to use, the copper wire electrode was removed from the cell, briefly immersed in concentrated nitric acid and then rinsed with distilled water. The detector cell was then reassembled and eluent was pumped through the cell until a stable baseline potential was obtained.

Reagents

The reagents used were citric acid from E. Merck (Darmstadt, F.R.G.), (+)-tartaric acid and oxalic acid from Ajax Chemicals (Sydney, Australia). Ethylenediamine and metal nitrates were obtained from May and Baker (Dagenham, U.K.) except for uranyl nitrate from Hopkin and Williams (Chadwell Heath, U.K.), chromic nitrate from BDH (Poole, U.K.) and manganese nitrate from Merck (Darmstadt, F.R.G.). Ferrous sulphate was obtained from BDH (Boronia, Australia). All these reagents were used without further purification.

Procedure

Eluent solutions were prepared by dissolution of an appropriate amount of organic acid and ethylenediamine in distilled and deionized water and the pH was adjusted with 2 M sodium hydroxide solution. The exact concentrations and pH values for the eluents used are provided in the figure captions. Eluents were filtered through a 0.45-μm membrane filter and degassed before use.

RESULTS AND DISCUSSION

Eluent composition

In the chromatographic methods described in this paper, the eluent contains a ligand which forms complexes with copper and also with the injected metal ions which are to be separated. The principles of electrode response given in the Theory section show that the concentrations of both the injected metal ion and the eluent ligand play a major role in the application of indirect potentiometric detection to transition metal ions. The concentration of the eluent ligand also determines to a

large extent the chromatographic behaviour of metal ions. Using conductivity detection, Sevenich and Fritz[10] have shown that an increase in eluent ligand concentration favours faster elution of metal ions. Clearly, the stabilities of the complexes formed between metal ions and the eluent ligand also affect retention behaviour, and in addition, the eluent pH must be considered in determining the degree of complexation of the solute metal ions. The eluent ligand, mobile phase conditions and the column used must therefore be selected with both separation and detection in mind.

In the preliminary stages of this study, we have considered tartrate, citrate, oxalate, maleate, fumarate, iminodiacetate and nitrilotriacetate as eluent ligands. All of these species form stable or moderately stable complexes with cupric ions, except for fumarate which strongly binds cuprous ions. Table I shows retention times obtained on a Nucleosil column for several transition metal ions using different ligands at the same concentration and pH, together with a fixed concentration of ethylenediammonium ions (en^{2+}) added as the competing cation in the ion-exchange process. Also shown are calculated values of side-reaction coefficients, $\log \alpha_{M(L)}$, which illustrate that decreased retention times were observed for metal ions forming stable complexes with the eluent ligand.

TABLE I

RETENTION TIMES (min) OBTAINED FOR THE NUCLEOSIL COLUMN WITH VARIOUS ELUENT LIGANDS

Eluents contained 5 mM ligand and 5 mM ethylenediamine at pH 4.5. A flow-rate of 2 ml/min was used. Calculated values of $\log \alpha_{M(L)}$, based on stability constants taken from ref. 26, are shown in brackets.

Metal ion	Oxalate	Citrate	Tartrate	Fumarate
Pb^{2+}	1.7 (1.7)	1.9 (1.6)	3.1 (0.8)	7.2 (−*)
Zn^{2+}	1.6 (1.9)	2.1 (1.3)	4.1 (0.5)	10.2 (−*)
Ni^{2+}	1.7 (2.8)	1.8 (1.7)	3.4 (0.2)	
Co^{2+}	1.7 (1.6)	2.2 (1.3)	6.6 (0.2)	
Cd^{2+}	3.3 (0.5)	5.7 (0.4)	7.5 (−*)	

* No stability constants were found.

The retention times obtained were strongly dependent on the nature of the cation added to the mobile phase to participate in the ion-exchange process. Lithium, sodium and ethylenediammonium cations were studied and the efficiency with which these ions eluted sample cations was $en^{2+} > Na^+ > Li^+$.

Ion-exchange capacity of the column

Taking into account the observed retention times, the sensitivity of detector response and the shapes of the recorded peaks, it was evident that the ion-exchange capacity of the Nucleosil column was too large for many of the metal ions examined. To obtain workable retention times, a relatively high concentration of eluent ligand was required, however this resulted in poor detection sensitivity (see Theory section). For this reason, additional studies were carried out using a Wescan 269-004 column, which was packed with a cation-exchange material of low capacity (ca. 0.1 mequiv./g). Schematic representations of retention times and peak magnitudes ob-

tained with the Nucleosil and Wescan columns, using citrate or tartrate as the eluent ligand and ethylenediammonium ions as competing cations, are given in Figs. 1 and 2, respectively. The effects of changing either the eluent ligand concentration or the ethylenediamine concentration are evident from these figures.
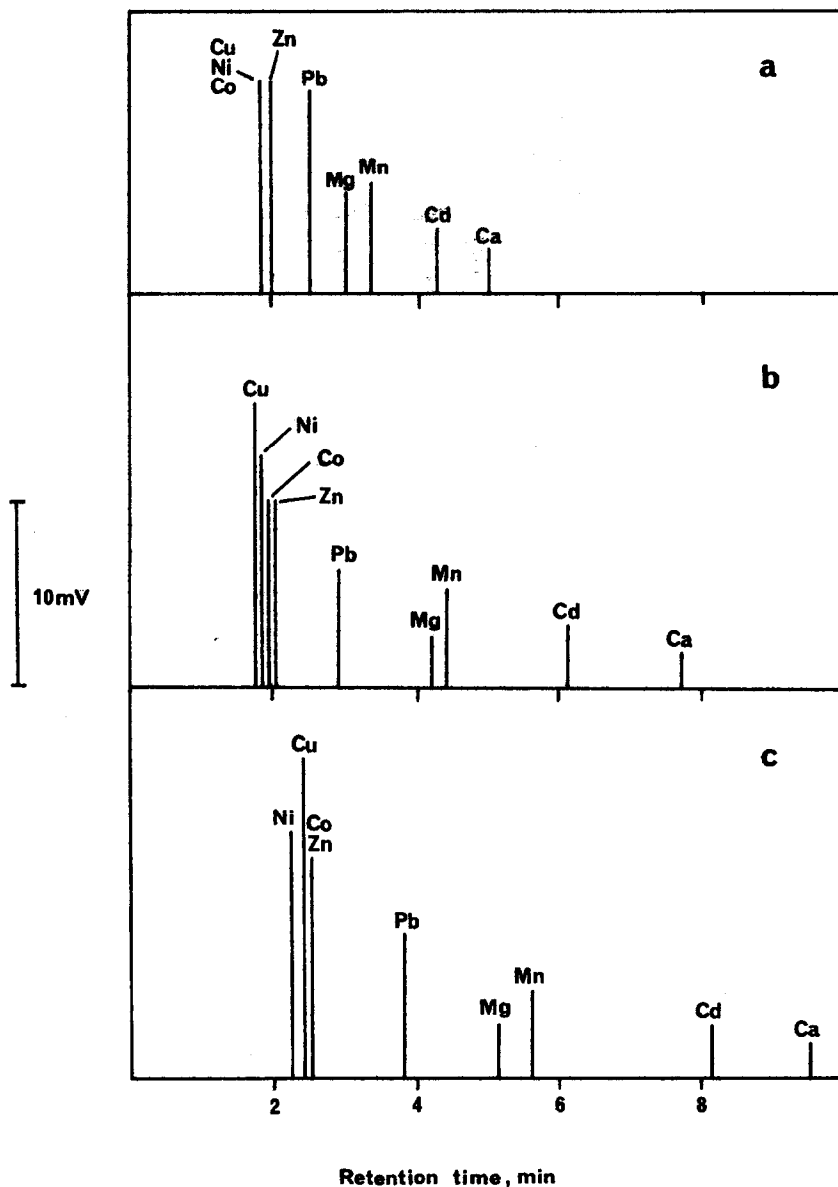

Fig. 1. Schematic presentation of experimentally obtained retention times and peak heights using a Wescan 269-004 column at a flow-rate of 0.4 ml/min for injections of 25 nmol of metal ions. Eluents: a, 1 mM citrate, 1 mM ethylenediamine, pH 4.6; b, 1 mM citrate, 0.5 mM ethylenediamine, pH 4.6; c, 0.5 mM citrate, 0.5 mM ethylenediamine, pH 4.6.
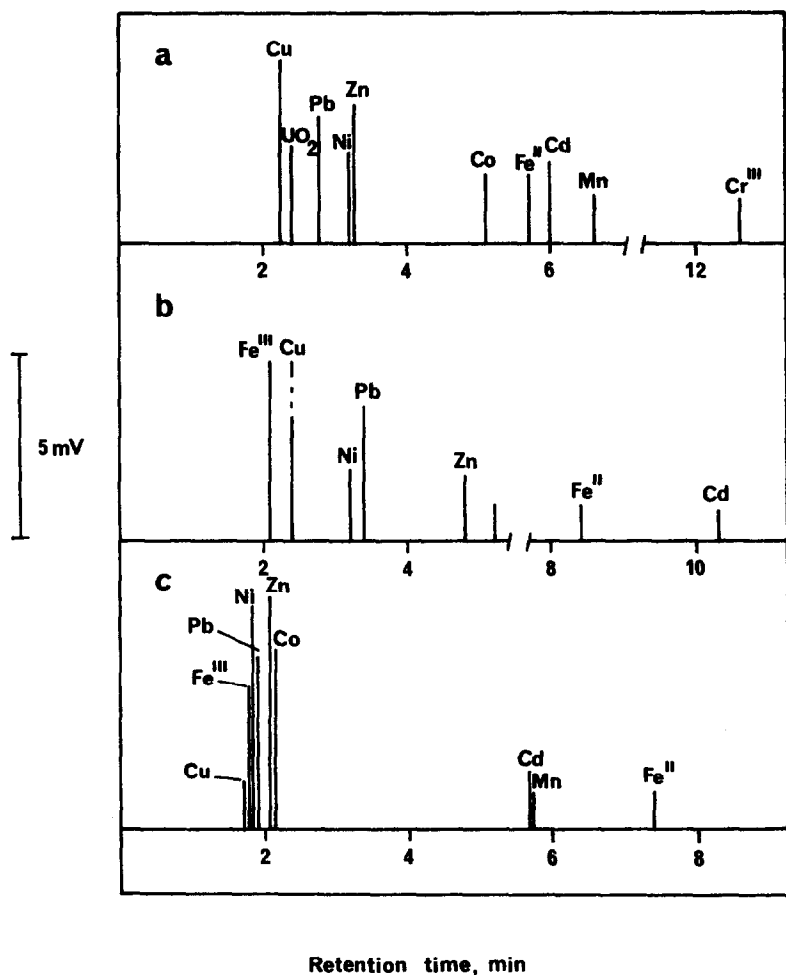
Retention time, min

Fig. 2. Schematic presentation of experimentally obtained retention times and peak heights using a Nucleosil 10SA column at a flow-rate of 2 ml/min. Eluents: a, 5 mM tartrate, 7.5 mM ethylenediamine, pH 4.5; b, 5 mM citrate, 5 mM ethylenediamine, pH 4.0; c, 5 mM citrate, 5 mM ethylenediamine, pH 4.5. Injected amounts: 250 nmol (a), 100 nmol (b and c).

Calibration relationships

Eqns. 5 and 7 in the Theory section suggest that when indirect potentiometric detection of metal ions with a metallic copper electrode is used, the observed peak height should be a linear function of the concentration of the injected metal ion C_M^0 (or the amount of injected metal ion N_M), when this concentration is low. Negative deviations from the above linear relationship are likely if broad peaks are produced, or if the complex formed between the metal ion and the eluent ligand has low stability. In these cases, best results should be obtained using peak area measurements instead of peak height. Larger amounts of the injected metal ion should be linearly related to the function $1 - 10^{-H/S}$ (see eqn. 5).

The results obtained in this study confirm these predictions. Measurements made with the Nucleosil column using early eluting (UO_2^{2+}) and late eluting (Co^{2+} and Mn^{2+}) ions showed a linear relationship between peak height and the injected amount of metal ion, provided the peak height was less than about 1 mV (Fig. 3a). When larger peaks were included, the calibration plot for uranyl ion showed a positive deviation from linearity, whilst those for cobalt and manganous ions showed negative deviations. In the case of uranyl ion, a plot of peak height *versus* $1 - 10^{-H/S}$ was linear, as predicted by eqn. 5 (Fig. 3b), whereas for cobalt and manganous ions, a plot of peak area *versus* the injected amount of metal ion was linear (Fig. 3c), in accordance with the above discussion. Detection limits calculated from Fig. 3 were 9, 13 and 34 nmol for uranyl, cobalt and manganous ions, respectively.
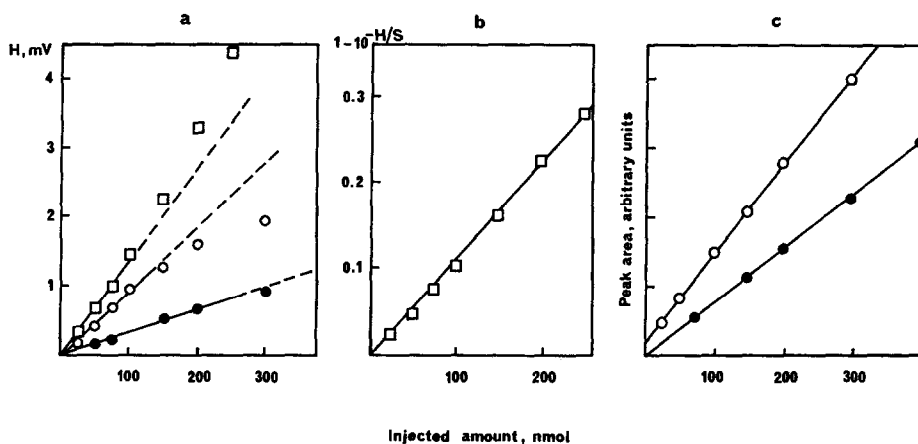

Fig. 3. Calibration plots for uranyl ($\square$), cobalt(II) ($\bigcirc$) and manganese(II) ($\bullet$) ions obtained using a Nucleosil column with 5 m*M* tartrate and 7.5 m*M* ethylenediamine at pH 4.0 (Co^{2+}; UO_2^{2+}) or 4.5 (Mn^{2+}) as eluent. The flow-rate was 2 ml/min.

Similar results were obtained with the Wescan column, however the linearity of plots of peak area *versus* the injected amount of metal ion extended to higher values of peak potential. This is illustrated for nickel and manganous ions in Fig. 4, from which calculated detection limits were 0.3 and 1.7 nmol, respectively.

Examples of separations
        The requirements for the mobile phase composition to provide both adequate separation and suitable detector response imposes considerable restriction on the selection of the mobile phase. Figs. 5 and 6 illustrate some typical separations and these figures show that good resolution has not been achieved for some metals. Two distinct and reproducible peaks were obtained for iron(III) (see Fig. 6) and a possible explanation for this is that one of these peaks was due to elution of an irreversible hydroxocomplex either present in the original iron(III) sample or formed during the chromatographic separation. It is noteworthy that only a single peak was observed for chromium(III) (see Fig. 2) when this species is also known to form hydroxocomplexes, but this may perhaps be attributed to the fact that chromium(III) hydroxo-
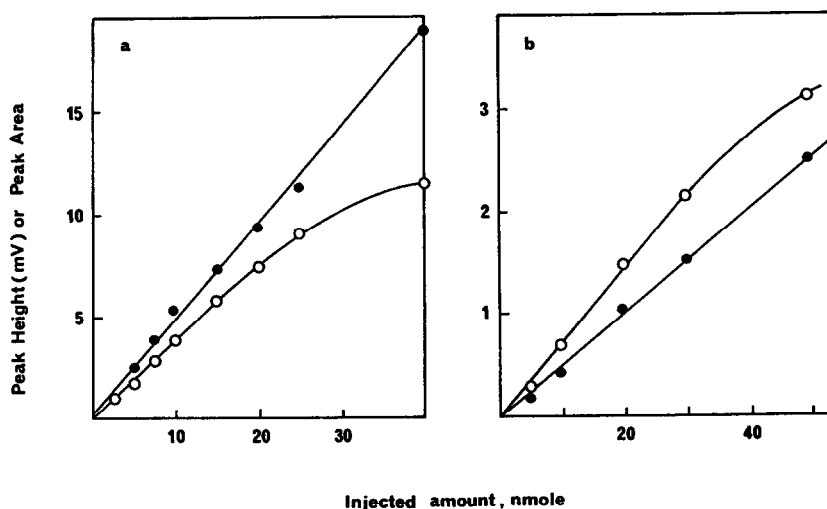
Fig. 4. Relationship between peak height ($\bigcirc$) or peak area ($\bullet$) (expressed in arbitrary units) and the injected amount of Ni^{2+} (a) and Mn^{2+} (b). Eluent: 0.5 mM citrate, 0.5 mM ethylenediamine, pH 4.5. Flow-rate: 1 ml/min. Column: Wescan 269-004.
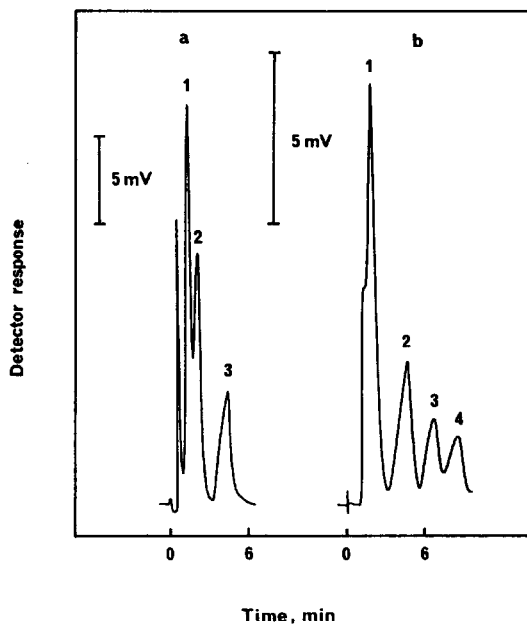
Fig. 5. Chromatograms obtained using the Wescan column under the following conditions: (a) eluent: 0.5 mM citrate, 0.5 mM ethylenediamine, pH 4.6; flow-rate, 1 ml/min; sample volume, 75 μl; injected amounts: 37 nmole of Cu^{2+} and Pb^{2+}, 75 nmol of Cd^{2+}; peak identities: 1 = Cu^{2+}, 2 = Pb^{2+}, 3 = Cd^{2+}. (b) Eluent: 1 mM citrate, 0.5 mM ethylenediamine, pH 4.6; flow-rate, 0.4 ml/min; sample volume, 25 μl; injected amounts, 25 nmol; peak identities: 1 = Zn^{2+}, 2 = Mn^{2+}, 3 = Cd^{2+} and 4 = Ca^{2+}.
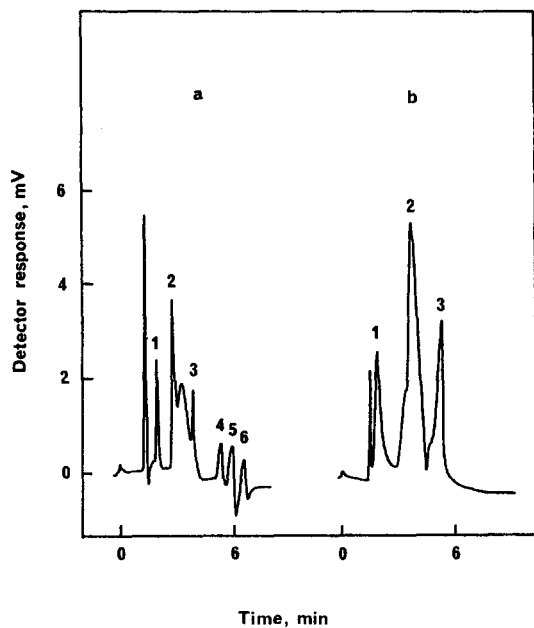
Fig. 6. Chromatograms obtained using the Nucleosil column under the following conditions: (a) eluent: 5 mM tartrate, 7.5 mM ethylenediamine, pH 4.0; flow-rate, 2 ml/min; sample volume, 25 μl; injected amounts: UO_2^{2+} and Pb^{2+} 150 nmol, Zn^{2+}, Co^{2+} and Cd^{2+} 100 nmol, and Mn^{2+} 250 nmol; peak identities: 1 = UO_2^{2+}, 2 = Pb^{2+}, 3 = Zn^{2+}, 4 = Co^{2+}, 5 = Cd^{2+}, 6 = Mn^{2+}. (b) Eluent: 5 mM tartrate, 20 mM ethylenediamine, pH 4.5; flow-rate, 2 ml/min; sample volume, 25 μl; injected amounts, 125 nmol. Peak identities: 1 and 2 = Fe^{3+}, 3 = Cr^{3+}.

complexes are weaker than those of iron(III). The chromatograms obtained with the Nucleosil column (Fig. 6) suffer from an interfering system peak of unknown origin which renders separation of a large group of metal ions difficult. It is of course possible to adjust mobile phase conditions so that no metal ion coelutes with the system peak, however this invariably detracts from resolution between the metal ions themselves.

Detection of copper ions with a citrate eluent containing ethylenediammonium ions was especially sensitive, as shown in Fig. 7, where a detection limit of 7 pmole was observed. Under the conditions used, the citrate was strongly protonated, leading to a small conditional formation constant for the copper(II)–citrate complex. It is therefore likely that the electrode response was due to direct sensing of uncomplexed copper(II) ions and this suggestion was supported by the fact that a plot of peak height *versus* the amount of injected copper showed Nernstian behaviour (measured slope = 29.6 mV per decade).

Separation of metal ions on an anion-exchange column

A further possibility investigated in this study was the formation of anionic metal complexes and their separation using anion-exchange chromatography. The eluent ligands used were oxalic acid (H_2Ox) and citric acid (H_4Cit). Divalent metal ions form mainly neutral (MOx) or anionic $[M(Ox)_2]^{2-}$ complexes with oxalate[26]
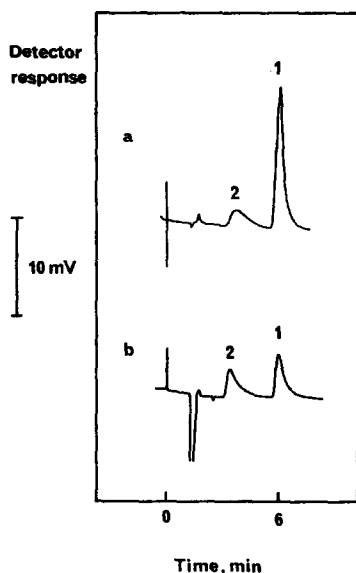
Fig. 7. Chromatograms obtained with the Nucleosil column for injection of 120 μl of 0.1 mM cupric nitrate solution (a) and 100 μl tap water (b) showing the copper peak (1) and a "system" peak (2). Eluent: 5 mM citrate, 5 mM ethylenediamine, pH 3.0. Flow-rate: 2 ml/min.

and neutral (MH_2Cit) or anionic ($MHCit^-$) complexes with citrate[26]. With both ligands, a variety of complexes having different charges are formed at different pH values, and thus prediction of retention behaviour is difficult. In general, the elution order of metal ions from a low capacity anion-exchange column (Vydac 302 IC) was the reverse to that obtained on the cation exchange columns described earlier. This is illustrated in Table II, which compares retention times obtained on cation- and anion-exchange columns, using citrate eluents. Similar results were observed for oxalate eluents.

TABLE II

RETENTION TIMES (min) FOR THE ELUTION OF TRANSITION METAL IONS OBTAINED WITH ANION- AND CATION-EXCHANGE COLUMNS

The eluent for the Nucleosil 10.SA column was 5 mM citrate and 5 mM ethylenediamine. The eluents for the Vydac 302 IC 4.6 column were 20 mM citrate (A) and 5 mM citrate (B). For all eluents: pH 4.5; flow-rate, 2 ml/min.

Ion	Nucleosil 10.SA (cation exchanger)	Vydac 302 IC 4.6 (anion exchanger)	
		A	B
Cu^{2+}	1.8	25	60
Pb^{2+}	1.9	2.9	4.5
Zn^{2+}	2.1	7.0	16.6
Cd^{2+}	5.7	2.4	3.6
Mn^{2+}	5.7	2.1	3.1

In view of the facts that citrate eluents gave best sensitivity and oxalate eluents gave shorter retention times for strongly retained metal ions such as Cu^{2+}, Zn^{2+}, Ni^{2+} and Co^{2+}, eluents containing mixtures of these ligands were studied. Retention times and peak magnitudes obtained for two different mixed eluents are schematically represented in Fig. 8. Increased concentration of the eluent ligand resulted in a decrease in retention times and the same effect was caused by raising the eluent pH, although different metal ions showed varying responses to changes in eluent pH. The electrode response mechanism which operates in this case is identical to that operating in the cation-exchange mode discussed earlier. That is, complexation of the eluent ligand by the eluted metal ion causes a localised decrease in free ligand concentration, leading to an increase in the copper concentration at the electrode surface, and hence a potential change. A typical separation of transition metal ions by anion-exchange is illustrated in Fig. 9. The peak for nitrate ion in this chromatogram results from the fact that the metal ion solutions were prepared from nitrate salts and we have previously shown that electrode response for nitrate can be expected under the mobile phase conditions used[22].
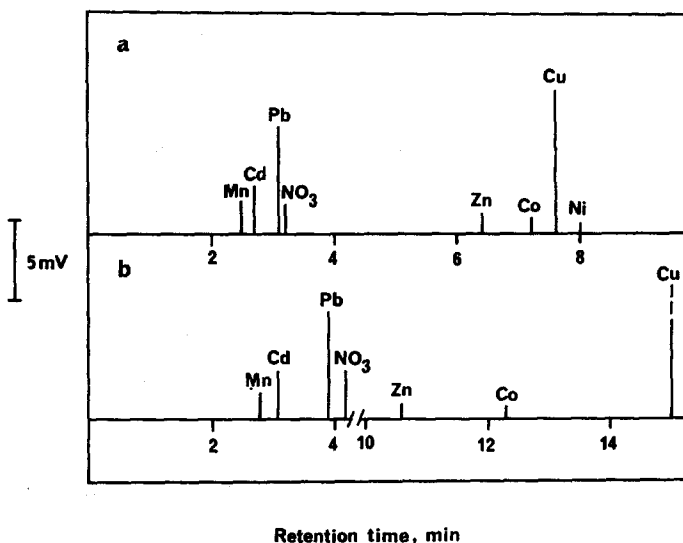

Fig. 8. Schematic presentation of experimentally obtained retention times and peak heights using a Vydac column at pH 4.5 and a flow-rate of 2 ml/min. Eluents: (a) 10 mM citrate and 10 mM oxalate, (b) 5 mM citrate and 5 mM oxalate. Injected amounts, 250 nmol of each component.

CONCLUSIONS

This study has shown that indirect potentiometric detection of transition metal ions with a metallic copper electrode was applicable to cation- or anion-exchange chromatography. When cation-exchange separation was employed, detection sensitivity was highest when columns of low ion-exchange capacity were used. Experimentally observed calibration plots have been shown to agree closely with the the-
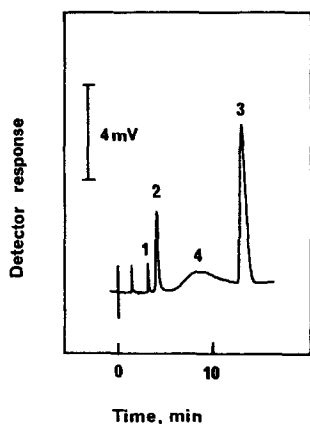
Fig. 9. Chromatogram obtained with a Vydac column for a mixture of copper and lead nitrates. Eluent: 5 mM citrate, 5 mM oxalate, pH 5.5. Flow-rate, 2 ml/min. Sample volume, 10 μl. Injected amounts, 50 nmol. Peak identities: 1 = NO_3^-, 2 = Pb^{2+}, 3 = Cu^{2+}, 4 = system peak.

oretical electrode response in which a linear relationship between peak height and the amount of injected solute was predicted for small amounts of solute, whilst for larger amounts, a more complex relationship was predicted. The chromatograms presented show that only poor separations have been achieved and this reflects the difficulties encountered in selection of a mobile phase composition suitable both for chromatographic separation and sensitive detection. Nevertheless, the results obtained clearly indicate the utility of potentiometry for the detection of transition metal ions.

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