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ION CHROMATOGRAPHY OF INORGANIC ANIONS WITH POTENTIOMETRIC DETECTION USING A METALLIC COPPER ELECTRODE

P. R. HADDAD* and P. W. ALEXANDER

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

and

M. TROJANOWICZ

Department of Chemistry, University of Warsaw, Warsaw (Poland)

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SUMMARY

The determination of inorganic anions by ion chromatography with potentiometric detection using a metallic copper indicator electrode is described. The electrode response to inorganic anions can result from consumption of cuprous and cupric ions in the diffusion layer at the electrode surface, from production of copper ions due to oxidation of metallic copper, or as a result of displacement of a copper-complexing ligand from the eluent by an eluted non-complexing inorganic anion. The first possibility is exemplified by the determination of cyanide, chloride, bromide, iodide and thiocyanate, whereas the second possibility is illustrated by the determination of iodate, bromate and chlorate. An example of the indirect detection method is the determination of nitrite, nitrate and sulphate, using sodium tartrate as eluent. Calibration data for all of the above detection methods are provided and are interpreted in terms of theoretical response equations. Detection limits are also presented and are shown to be strongly dependent on the chromatographic conditions used and on the electrode response mechanism applicable to each anion.

INTRODUCTION

The intensive development over recent years of ion chromatographic (IC) techniques for the determination of inorganic anions has resulted from a lack of other instrumental methods suitable for the simultaneous determination of several components in a single run. IC has been the subject of two monographs^{1,2}, several reviews (e.g. refs. 3 and 4) and many original research papers. A significant trend in the development of IC methods is the investigation of new, sensitive and universal methods of detection. The most widely applied detection method in IC is conductivity detection, which exploits differences in equivalent conductivity between components of the mobile phase and eluted ions. In contrast, electrochemical methods, and in particular potentiometric detection, have been used relatively infrequently.

For potentiometric detection, the most commonly employed indicator electrodes are ion-selective membrane electrodes; however, these are too selective in response to be applicable to the detection of a large number of anions. Nevertheless, applications of this approach for the determination of several ions have been reported using non-selective cationic or anionic ion-exchange membrane electrodes⁵, a pH glass electrode for detection of anions of weak acids by mobile phase pH changes⁶ and a silver wire electrode coated with a sparingly soluble silver salt for detection of halides and thiocyanate⁷. Indirect potentiometric methods using chloride⁸ or copper-membrane⁹ ion-selective electrodes have been applied to the measurement of a deficit of chloride or cupric ions in the eluent, caused by the eluted ions.

For some time, we have been examining the use of a metallic copper indicator electrode for potentiometric detection in flow injection analysis and liquid chromatography. Electrochemical studies on the corrosion of copper have been the subject of numerous publications, *e.g.* on the effects of dissolved oxygen¹⁰, aliphatic diamines¹¹ and amino acids¹². In these papers, it has been shown that voltage changes occur at a metallic copper electrode in an electrochemical cell when the electrode is exposed to corrosion agents, with the electrode potential being dependent on the concentration of these corrosion agents. There appears to be no reports on the possible use of such effects in a liquid chromatography detector.

We have designed a potentiometric detector based on a metallic copper indicator electrode¹³, and this device has been reported as a detector for amino acids¹⁴, other organic acids¹⁵ and alkaline earth metal ions¹⁶. In this paper, the application of this detector is extended to include detection of inorganic anions in IC. Three distinct electrode response mechanisms are identified and a theoretical relationship between electrode potential and the amount of injected solute is derived.

THEORY

The potentiometric response of a metallic copper electrode in contact with a mobile phase depends on several factors, including the presence of ligands which complex cuprous or cupric ions, the pH of the solution and the oxygen content of the solution. At a constant flow-rate, the introduction of a species that binds copper ions results in a decrease in the electrode potential. When an injected ligand, *L*, forms a 1:1 complex with cupric ions (of stability constant β_1) that is significantly more stable than complexes formed by the components of the mobile phase, and when the free ligand concentration greatly exceeds β_1^{-1} , then the height (*H*) of the recorded peak is given by¹⁷:

$$H = A + 0.029 \log \frac{C_L}{\alpha_{L(H)} D} \quad (1)$$

where C_L is the total ligand concentration in the injected sample, $\alpha_{L(H)}$ is the side-reaction coefficient, which describes the extent of ligand protonation, *D* is the dispersion factor, which determines the decrease in total ligand concentration during transport of the injected sample through the chromatographic system, and *A* is a constant depending on the stability of copper complexes formed by the solute ligand

and by components of the mobile phase. This equation may be rewritten in terms of the number of moles N of the injected ligand L as:

$$H = B + 0.029 \log N \quad (2)$$

where B is a constant.

If a single stable compound (either a soluble complex or precipitate) is formed by the solute ligand L with cuprous or cupric ions, then a linear relationship between H and $\log N$ will be observed, with Nernstian slope. When several complexes are formed in comparable amounts, then a more complex relationship between H and $\log N$ can be expected.

The above Nernstian relationship is also not followed for very small concentrations of injected ligand. The observed peak height is dependent on the difference in copper complexation strength between the mobile phase components and the injected ligand, and this can be expressed in terms of side-reaction coefficients for the mobile phase $\alpha_{\text{Cu}^{\text{II}}(\text{B},\text{OH})}$ and for the ligand $\alpha_{\text{Cu}^{\text{II}}(\text{L})}$. Here the mobile phase is assumed to contain a buffer B and hydroxide as copper reactive species. We have previously shown¹⁷ that the peak height can be expressed as:

$$H = \frac{RT}{2F} \ln \frac{\alpha_{\text{Cu}^{\text{II}}(\text{L})} + \alpha_{\text{Cu}^{\text{II}}(\text{B},\text{OH})} - 1}{\alpha_{\text{Cu}^{\text{II}}(\text{B},\text{OH})}} \quad (3)$$

This equation may be simplified when:

$$\alpha_{\text{Cu}^{\text{II}}(\text{L})} \gg \alpha_{\text{Cu}^{\text{II}}(\text{B},\text{OH})} - 1 \quad (4)$$

or

$$\alpha_{\text{Cu}^{\text{II}}(\text{B},\text{OH})} \approx 1 \quad (5)$$

to give

$$H = C + \frac{RT}{2F} \ln \alpha_{\text{Cu}^{\text{II}}(\text{L})} \quad (6)$$

where C is a constant.

Assuming a 1:1 complex between the ligand L and copper, then:

$$\alpha_{\text{Cu}^{\text{II}}(\text{L})} = 1 + \beta_1[\text{L}] \quad (7)$$

Substituting into equation (5) gives:

$$H = E + \frac{RT}{2F} \ln \left(\frac{1}{\beta_1} + [\text{L}] \right) \quad (8)$$

where E is a constant. The logarithmic component of eqn. 8 may be expanded as a series to give:

$$\ln\left(\frac{1}{\beta_1} + [L]\right) = \ln\frac{1}{\beta_1} + 2 \left[\frac{[L]}{\frac{2}{\beta_1} + [L]} + \frac{1}{3} \left(\frac{[L]}{\frac{2}{\beta_1} + [L]} \right)^3 + \frac{1}{5} \left(\frac{[L]}{\frac{2}{\beta_1} + [L]} \right)^5 + \dots \right] \quad (9)$$

When the term $\left(\frac{[L]}{\beta_1} + [L] \ll 0.5\right)$ (that is when $[L] \ll \frac{2}{\beta_1}$), then the higher terms of the above series may be neglected. This condition applies for very low ligand concentrations. Eqn. 9 now reduces to:

$$\ln\left(\frac{1}{\beta_1} + [L]\right) \approx \ln\frac{1}{\beta_1} + \beta_1[L] \quad (10)$$

Taking into account the dispersion factor D and allowing for protonation of the ligand, eqn. 8 now becomes:

$$H = \text{constant} + \frac{RT\beta_1}{2FD\alpha_{L(H)}} [L] \quad (11)$$

which may be rewritten in terms of the number of moles (N) of the injected ligand L as:

$$H = \text{constant} + \frac{RT\beta_1}{2FD\alpha_{L(H)}} N \quad (12)$$

The value of the constant in this equation depends on the value of $\alpha_{Cu^{II}(B,OH)}$ and approaches zero at low complexation by the eluent components.

Hence at very low concentrations of the injected ligand, a linear relationship between the peak height and the total ligand concentration is predicted. The slope of this relationship is a function of the stability of the complex formed and the dispersion in the chromatographic system. We have previously observed such a linear relationship for injections of low concentrations of organic acids¹⁵.

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 previously¹⁸. This detector was connected to a Radiometer (Copenhagen, Denmark) PHM62 pH/millivolt meter, interfaced to a Houston

Instruments (Austin, TX, U.S.A.) Omniscrite recorder. The column used was 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 attained.

Reagents

The reagents used were obtained from Ajax Chemicals (Sydney, Australia) except sodium iodate from Merck (Darmstadt, F.R.G.), potassium bromate from Whiffen and Sons (London, U.K.), and potassium iodide and potassium cyanide from May and Baker (Dagenham, U.K.). All reagents were used without further purification. Stock solutions of the anions used were prepared in distilled water which had been further purified on a Millipore (Bedford, MA, U.S.A.) Milli-Q water purification system.

Procedure

Sodium tartrate eluent solutions were prepared by dissolution of an appropriate amount of tartaric acid in distilled and deionized water and the pH was adjusted with 2 M sodium hydroxide solution. Potassium orthophosphate eluent solutions were prepared by dissolution of appropriate amounts of potassium dihydrogen orthophosphate and the pH was adjusted with 1 M potassium 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- μ m membrane filter and degassed before use.

RESULTS AND DISCUSSION

Direct detection based on consumption of copper ions

Fig. 1 shows the separation of a mixture of halides, cyanide and thiocyanate, using ion-exchange chromatography with sodium tartrate as eluent and potentiometric detection. The peaks are displayed in the positive direction according to the arbitrary convention adopted in our previous work¹⁵, that is, a positive peak corresponds to a decrease in free copper ion concentration. Previous flow-injection analysis studies¹⁷ have indicated that the electrode response to halides and thiocyanate results from the formation of a precipitate with cuprous ions at the electrode surface, whereas electrode response to cyanide results from the formation of a 1:2 complex with cuprous ions.

Calibration plots for bromide and iodide are shown in Fig. 2, in which the peak height (H) is plotted against N (Fig. 2a) and $\log N$ (Fig. 2b), where N is the amount of the injected anion (nmole). Fig. 2a shows that the linear dependence of H on N predicted in eqn. 12 may be approximated only at the lowest amounts of injected ligand tested. A wider range of linearity was obtained for the semilogarithmic calibration plot (Fig. 2b), in accordance with eqn. 2. The experimentally obtained slopes shown in Fig. 2b are much lower than Nernstian, which suggests that there

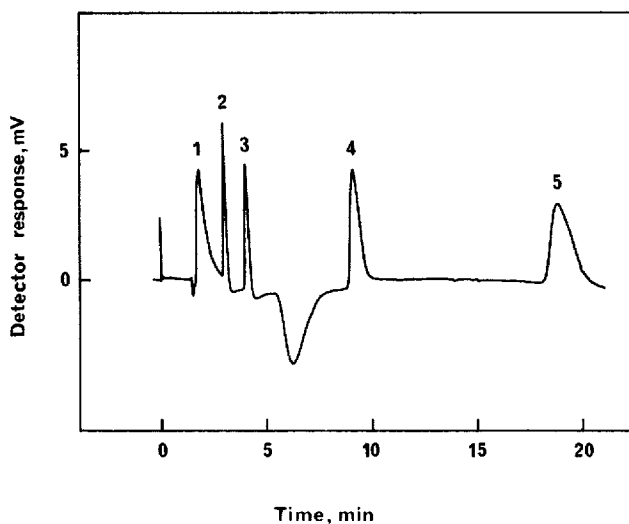


Fig. 1. Chromatogram of a mixture of cyanide (1), chloride (2), bromide (3), iodide (4) and thiocyanate (5), obtained using 40 mM sodium tartrate (pH 3.2) as eluent. Conditions: column, Vydac 302 IC; flow-rate, 2 ml/min; injection volume, 10 μ l. Injected amounts: CN^- , 0.8; Cl^- , 80; Br^- , 10; I^- , 0.4; SCN^- , 0.4 nmol.

is a significant contribution from other factors not considered in the theoretical treatment presented earlier.

Detection limits for the anions shown in Fig. 1 were determined by calculating the anion concentration which would give a 0.3 mV potential change (*i.e.* corresponding to a signal-to-noise ratio of 3.0) and the results are given in Table I. These detection limits must be interpreted in terms of the eluent used (since the electrode

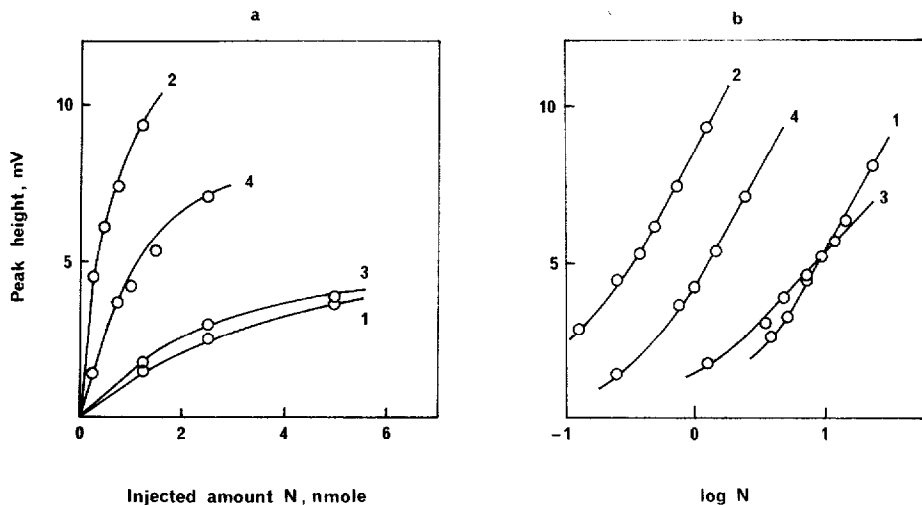


Fig. 2. Calibration plots for bromide (1), iodide (2), iodate (3) and bromate (4). Conditions as for Fig. 1.

TABLE I

RETENTION TIMES AND ESTIMATED DETECTION LIMITS FOR THE ION CHROMATOGRAPHIC DETERMINATION OF INORGANIC ANIONS USING POTENTIOMETRIC DETECTION WITH A METALLIC COPPER INDICATOR ELECTRODE

Anion	Eluent	Retention time (min)	Limit of detection	
			nmol injected	ppm*
Cl ⁻	40 mM	2.9	2	0.7
Br ⁻	sodium	4.1	0.3	0.2
I ⁻	tartrate,	9.2	0.02	0.03
CN ⁻	pH 3.2	1.8	0.04	0.01
SCN ⁻		18.8	0.04	0.03
ClO ₃ ⁻		4.0	9	7.5
BrO ₃ ⁻		2.8	0.05	0.06
IO ₃ ⁻		2.2	0.3	0.5
HCO ₃ ⁻	10 mM	2.8	27	16
NO ₂ ⁻	sodium	3.9	5	2.3
NO ₃ ⁻	tartrate,	6.0	50	32
SO ₄ ²⁻	pH 3.2	12.4	94	92

* For a sample injection volume of 100 μ l.

signal is dependent on the complexation strengths of both the eluent and the solute anion) and also in terms of the proportion of solute ligand that is present in the deprotonated form. With regard to the first point, use of phosphate at pH 4.3 as eluent with an aminopropyl column gave a 10–40 fold improvement in detection

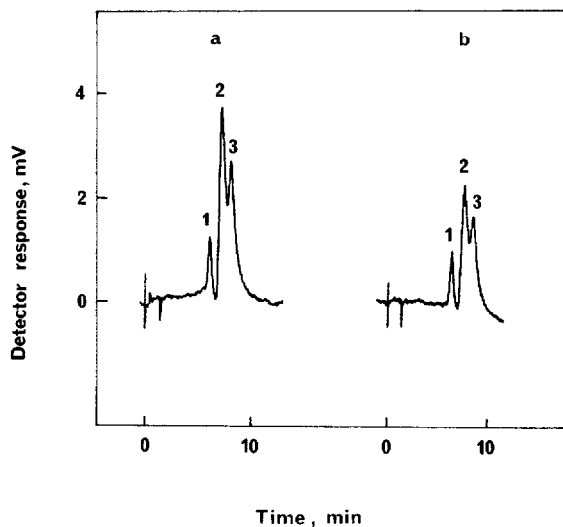


Fig. 3. Chromatogram of a mixture of chloride (1), iodide (2) and thiocyanate (3) obtained using 7 mM potassium orthophosphate (pH 4.3) as eluent. Conditions: column, laboratory-packed aminopropyl silica column (250 \times 4.6 mm I.D.); flow-rate, 2 ml/min. Injected amounts: (a) Cl⁻, 5; I⁻, 0.25; SCN⁻, 0.05 nmol. (b) Cl⁻, 500; I⁻, 25; SCN⁻, 5 pmol. Injection volume, 5 μ l.

limits for iodide and thiocyanate compared with the values shown in Table I; however, separation was much poorer. This is shown in Fig. 3, which also illustrates that the water used for sample preparation contained a significant background concentration of chloride, since the chloride peak was approximately the same for both dilutions of the sample tested.

The second point mentioned above can be illustrated by reference to cyanide, since the detection limit indicated in Table I refers to the total concentration of cyanide injected, when in fact only a very small amount (*ca.* 0.0001%) of this remains in the deprotonated form at pH 3.2. Under the conditions used, the electrode response results from reaction of copper ions with hydrogen cyanide and so a different detection limit can be expected from that which would apply at a higher eluent pH where copper ions would react with free cyanide ion.

It is noteworthy that the separation shown in Fig. 1 was strongly dependent on the condition of the column used. We have observed that the Vydac 302 IC column has a relatively short lifetime when tartrate was used as the mobile phase, with consistent peak shape and retention times recorded for only the first 100 injections made. Similar results for the same type of column have been recently reported by Willison and Clarke¹⁹.

Direct detection based on oxidation of metallic copper

In the previous section, the detection of inorganic anions was based on complexation and precipitation reactions, which caused a decrease in the concentration of copper ions in the diffusion layer at the electrode surface, resulting in a positive peak. Alternatively, anions that can oxidise metallic copper can be detected by the increase in copper ion concentration at the electrode surface, and should produce negative peaks. This type of electrode response is illustrated in Fig. 4, which shows the separation of chlorate, bromate and iodate using ion-exchange chromatography

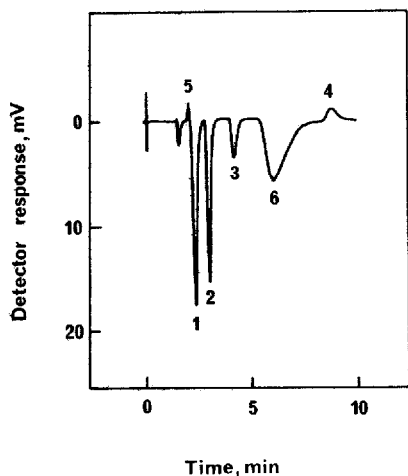
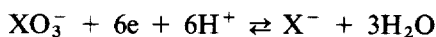


Fig. 4. Chromatogram of a mixture of iodate (1), bromate (2) and chlorate (3) obtained using 40 mM sodium tartrate (pH 3.2) as eluent. Other recorded peaks are hydrogen carbonate (5), traces of iodide (4) and "system" peak (6). Conditions: column, Vydac 302 IC; flow-rate, 2 ml/min; injection volume, 50 μ l. Injected amounts: IO_3^- , 100 nmol; BrO_3^- , 10 nmol; ClO_3^- , 0.5 μ mol.

with potentiometric detection. The chromatogram shows the expected negative peaks for the oxidising ions, together with two small positive peaks corresponding to hydrogen carbonate present in the injected sample and a trace amount of iodide present in the reagents.

Calibration plots for bromate and iodate are included in Fig. 2 and detection limits are listed in Table I. The comments made in the previous section regarding the shapes of the calibration plots and their relationship to theoretical prediction are also applicable to bromate and iodate; however, there is a need for explanation of the large differences in the detection limits obtained for the three oxidising anions tested. Oxidation potential values for the half-reaction of each anion according to the scheme:

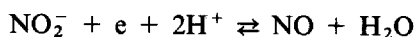


are 1.45, 1.44 and 1.08 V, where X is chloride, bromide and iodide, respectively²⁰. Taking into account complexation of the halide produced in the above reaction with cuprous ions, and using known values of solubility products²¹, formal potential values $E'_{\text{XO}_3^-, \text{CuX}}$ can be calculated as 1.52 V for chlorate and bromate and 1.20 V for iodate. This explains the low detection limit for bromate in comparison to iodate, but suggests that chlorate and bromate should have equivalent detection limits, which is not observed in practice (Table I). The high detection limit measured for chlorate, despite its high formal potential, may be attributed to its slow reaction rate in dilute solution²⁰.

Indirect detection

A further possibility studied in this work was the indirect detection of certain anions that do not bind copper ions and do not oxidise metallic copper. In this approach, the eluent contains a copper-complexing ligand and the electrode will respond to the decreased concentration of this ligand which accompanies elution of the solute anion. Under these conditions, the copper ion concentration in the diffusion layer at the electrode surface will increase, so a negative peak can be expected in accordance with our arbitrary convention¹⁵. This concept has already been applied for the separation and detection of anions of various organic acids, using a metallic copper electrode as a potentiometric detector¹⁵.

A chromatogram showing the ion-exchange separation of nitrite, nitrate, sulphate and weakly complexing hydrogen carbonate, using 10 mM tartrate at pH 3.2 as eluent, is given in Fig. 5. Under these conditions, the nitrate peak coelutes with a small, negative "system" peak, however the directions of all peaks in the chromatogram are in accordance with theoretical prediction. Calibration plots for the well-resolved nitrite and sulphate peaks are shown in Fig. 6 and the estimated detection limits are included in Table I. The calibration plots show that a linear relationship between peak area and the amount of injected anion was applicable under the conditions used. Table I indicates that nitrite gave a much larger electrode response than nitrate or sulphate, and this is attributed to some oxidation of metallic copper by nitrite according to the half-reaction



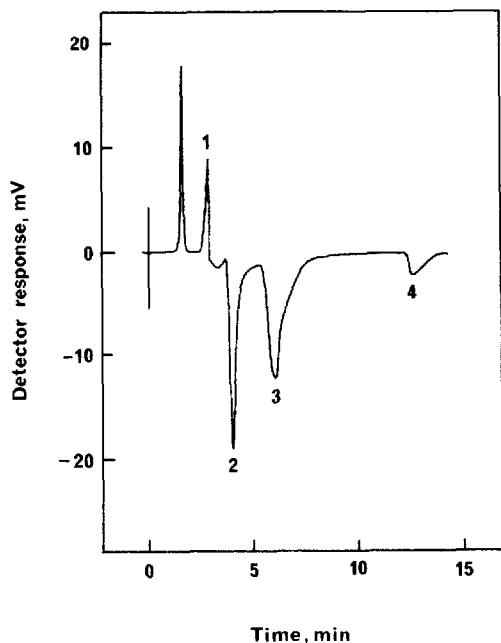


Fig. 5. Chromatogram of a mixture of hydrogen carbonate (1), nitrite (2), nitrate (3) and sulphate (4) obtained using 10 mM sodium tartrate (pH 3.2) as eluent. Conditions: column, Vydac 302 IC; flow-rate, 2 ml/min; injection volume, 100 μ l; injected amount, 1 μ mol of each component.

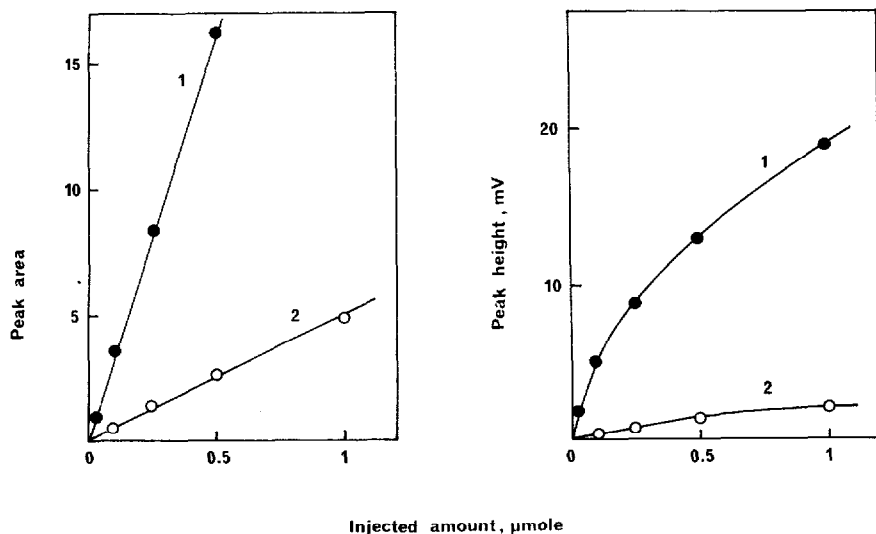


Fig. 6. Calibration plots for nitrite (1) and sulphate (2). Conditions as for Fig. 5.

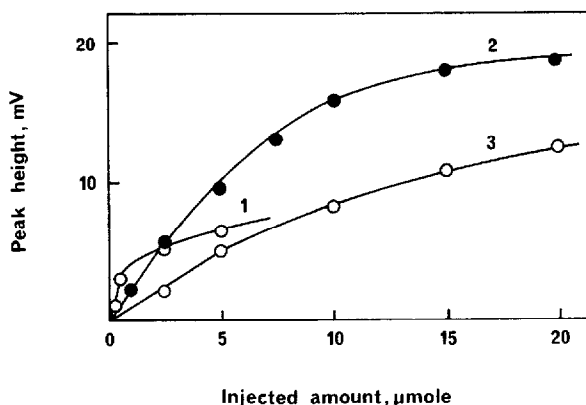


Fig. 7. Calibration plots for nitrate obtained using 10 mM (1), 20 mM (2) and 40 mM (3) sodium tartrate (pH 3.2) as eluent with a Vydac 302 IC column at a flow-rate of 2 ml/min.

which has a standard potential of 1.0 V (ref. 20).

The detection limits obtained in the indirect potentiometric detection method are strongly dependent on the concentration of the ligand present in the mobile phase. When the concentration of the injected non-complexing ligand in the dispersed sample band equals the concentration of the eluent ligand, then the measured peak height is the difference between the electrode potential value in the eluent and in the dispersed solution of the non-complexing ligand. Higher concentration of injected ligand will therefore produce no further increase in peak height and the calibration curve can be expected to show a plateau. For lower concentrations of injected ligand, the peak height will depend on sample concentration and the slope of the calibration plot (and hence the sensitivity of response) will increase as the eluent ligand concentration is lowered. These relationships are shown for nitrate at three different tartrate concentrations in Fig. 7. The values of the side-reaction coefficients, $\alpha_{\text{Cu}^{\text{II}}(\text{tart})}$, are 3.7, 6.5 and 12 for 10, 20 and 40 mM tartrate, respectively, at pH 3.2. Detection limits estimated from the short linear parts of the calibration plots in Fig. 7 were 50, 150 and 300 nmol of injected nitrate for 10, 20 and 40 mM tartrate eluents, respectively.

CONCLUSIONS

The application of potentiometric detection with a metallic copper indicator electrode to IC of inorganic anions has been shown to be based on three possible response mechanisms. The measured potential change can result from consumption of cuprous or cupric ions in the diffusion layer at the electrode surface, from oxidation of metallic copper, or in an indirect mode where solute anions that do not interact with copper displace a copper-complexing ligand from the mobile phase during elution. The third response mechanism is characterised by poor sensitivity and requires careful optimisation of the chromatographic conditions. The results obtained for the former two response mechanisms demonstrate that, for some of the anions tested, potentiometric detection with a metallic copper electrode gives comparable or better sensitivity than conductivity or UV absorbance detection. Further-

more, it also appears that this form of potentiometric detection may be applicable to many other anions, *e.g.* those containing phosphorus or sulphur.

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