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CHEMISTRY

# ION-SELECTIVE ELECTRODES

Arthur Covington

C



CHEMISTRY CASSETTE

## CHEMISTRY CASSETTES

General Editor:  
Peter Groves  
The University of Aston in Birmingham

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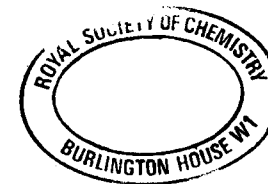
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## ACKNOWLEDGEMENT

The information provided in many of the frames of this workbook is derived from A K Covington (editor): Ion-Selective Electrode Methodology by permission of CRC Press Inc., Boca Raton, Florida, USA.



# 1

## TOPICS TO BE COVERED

### Part I

- a) Electroactive materials
- b) Classification of ion-selective electrodes
- c) Construction of ion-selective electrodes
- d) Gas sensors
- e) Enzyme electrodes

### Part II

- a) Selectivity and interferences
- b) Determination of selectivity coefficients
- c) Measurements by
  - i) direct potentiometry
  - ii) known increment methods
  - iii) potentiometric titrations

### Part III

- Some important ion-selective electrodes
  - i) fluoride
  - ii) nitrate
  - iii) calcium
  - iv) potassium

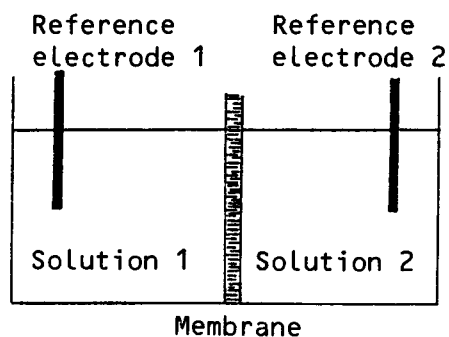
Appendix I Conventional electrode classification

Appendix II Ionic strength

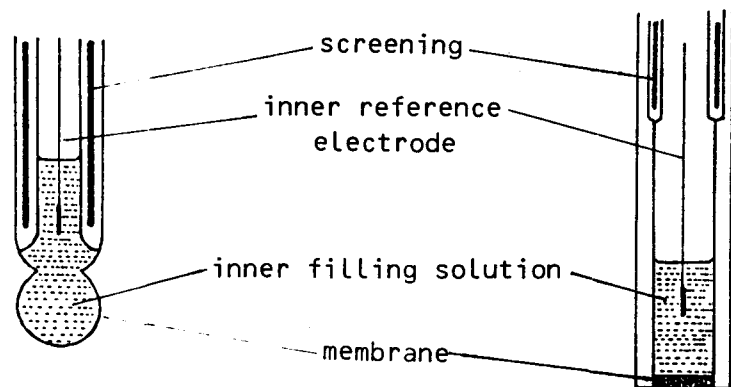
Appendix III Exercises

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SCHEMATIC OF ION-SELECTIVE ELECTRODE CELL

3

GLASS ELECTRODE COMPARED WITH A SOLID STATE TYPE ION-SELECTIVE ELECTRODE

Glass electrode

Solid state type  
ion-selective electrode

4

ELECTROACTIVE MATERIALS

- i) Glass
- ii) Insoluble inorganic salts
- iii) Organic ion-exchangers, chelating agents, ionophores

(for examples see frames 9-11)

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ELECTRODE FORMS

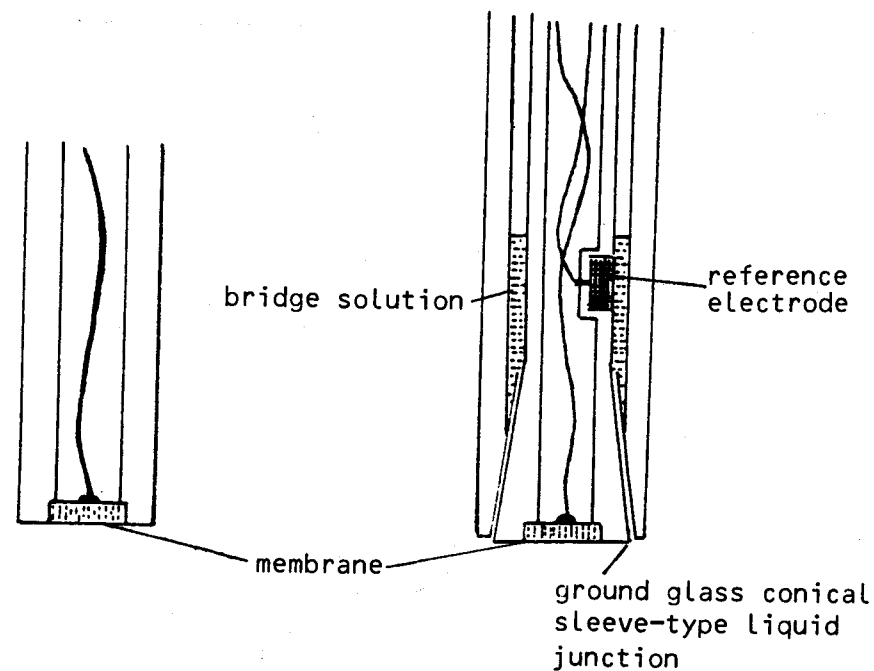
## Solid membranes

- a) Homogeneous (single phase)  
e.g. glass, a single crystal, polycrystalline material
- b) Heterogeneous (two phase)  
e.g. some glasses, insoluble materials in PVC and silicone rubber

## Liquid membranes

- a) Unsupported e.g. capillary tube
- b) Supported e.g. cellulose ester, porous glass, porous carbon
- c) Gelled e.g. in PVC

6

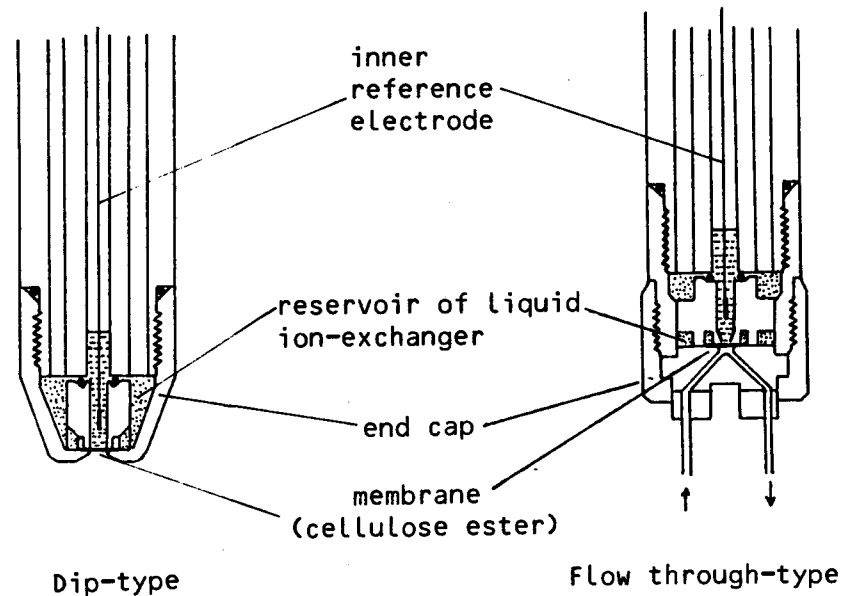
ALL-SOLID STATE TYPE ION-SELECTIVE ELECTRODES

Single electrode

Combination electrode

7

## TWO TYPES OF LIQUID ION-EXCHANGE ION-SELECTIVE ELECTRODES

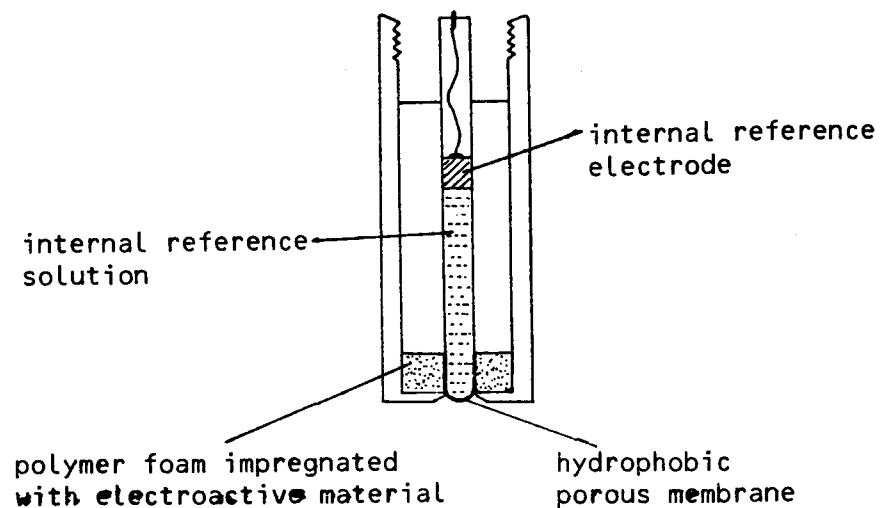


Dip-type

Flow through-type

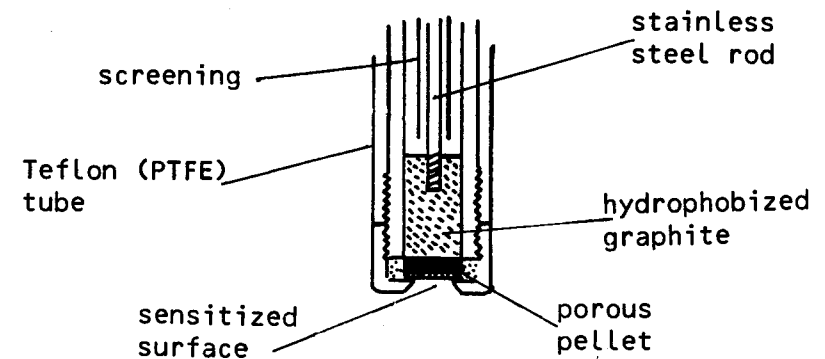
8

## WICK-TYPE REPLACEABLE ELEMENT LIQUID ION EXCHANGE ELECTRODE



9

## IMPREGNATED GRAPHITE ELECTRODE



10

## GLASS MATERIALS

H <sup>+</sup> -responsive	soda-lime silicates eg. Corning 015 glass
	lithia-baria-silicates
Na <sup>+</sup> -responsive	sodium aluminosilicates,
K <sup>+</sup> -responsive	lithium aluminosilicates
NH <sub>4</sub> <sup>+</sup> -responsive	
Redox responsive	lithium ferrisilicates

11

## INSOLUBLE INORGANIC SALT MATERIALS

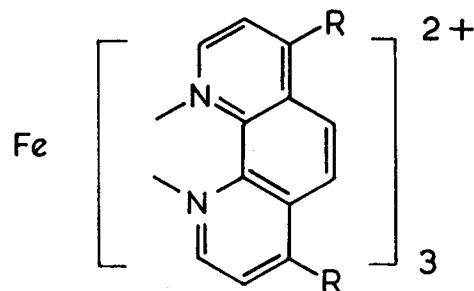
- a) Related to electrodes of the second kind
- Requirements: i) solubility less than  $10^{-6}$  mol dm<sup>-3</sup>  
ii) electrical conductivity
- Examples: silver chloride, silver bromide, silver iodide, lanthanum fluoride
- b) Related to electrodes of the third kind
- Examples:
- |  |                    |
|--|--------------------|
| CuS, Ag <sub>2</sub> S                         | copper electrode   |
| CuS, Ag <sub>2</sub> S, PbS, PbSO <sub>4</sub> | sulphate electrode |
| LaF <sub>3</sub> , CaF <sub>2</sub>            | calcium electrode  |

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ORGANIC ION-EXCHANGERS, CHELATING AGENTS AND IONOPHORES

a) Positively charged (anion-responsive)

e.g. tetraalkylammonium salts for  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$   
substituted o-phenanthroline salts for  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$



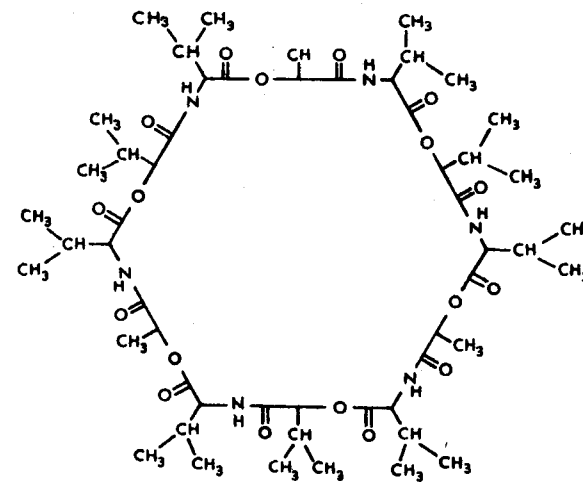
b) Negatively charged (cation-responsive)

e.g.  $[(\text{C}_{10}\text{H}_{21}\text{O})_2\text{PO}_2]\text{Ca}$  for calcium.  
potassium tetrakis(p-chlorophenyl)borate for potassium.

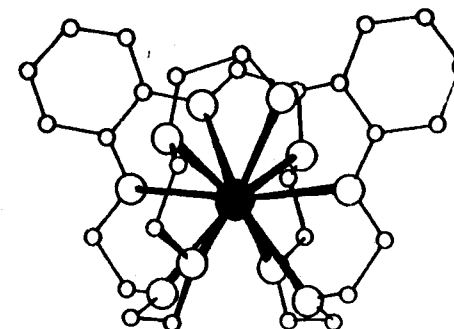
c) Neutral carriers (cation-responsive)

e.g. valinomycin, monactin for potassium, ammonium.  
polycyclic ethers (crowns) for sodium, potassium.  
synthetic ionophores for calcium, lithium, potassium.

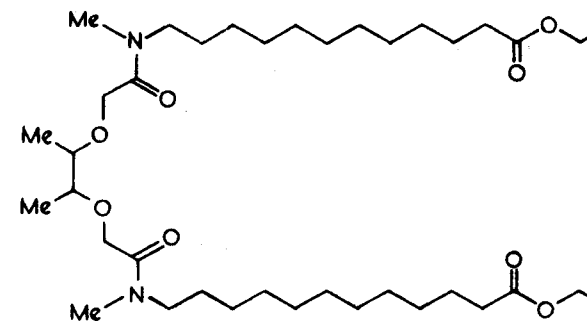
13



a) The naturally occurring macrocyclic antibiotic, valinomycin

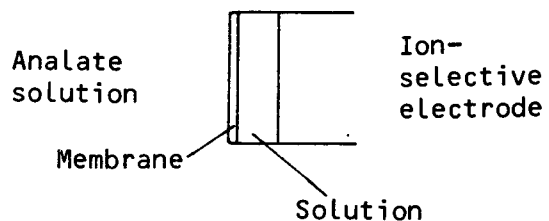


b) Dibenzo-30-crown-10 coordinating one potassium ion



c) A synthetic ionophore for calcium:  
N,N-di[(11-ethoxycarbonyl)undecyl]N,N 4,5-tetramethyl  
3,6 dioxaoctane diamide

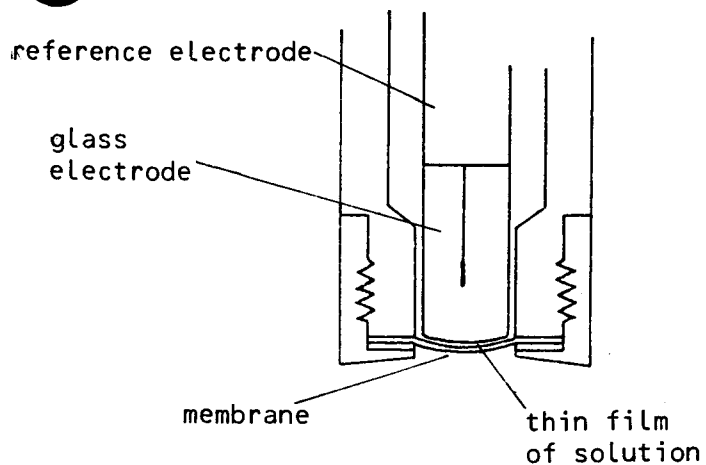
**14** SCHEMATIC OF DOUBLE MEMBRANE (SENSITIZED) ELECTRODES.  
GAS ELECTRODES OR ENZYME ELECTRODES



**15** GAS-SENSING ION-SELECTIVE ELECTRODE SYSTEMS

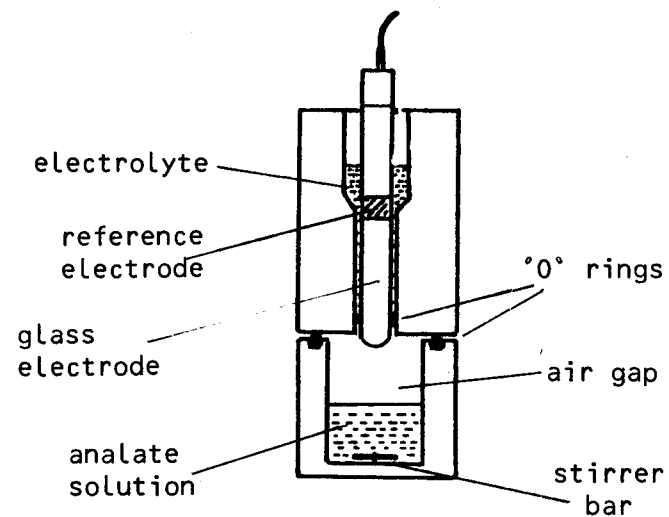
Gas	Reaction	Sensor
CO <sub>2</sub>	$\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^-$	H <sup>+</sup> -glass
NH <sub>3</sub>	$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$	H <sup>+</sup> -glass
NO <sub>2</sub>	$2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + \text{NO}_2^- + 2\text{H}^+$	H <sup>+</sup> -glass, nitrate
H <sub>2</sub> S	$2\text{OH}^- + \text{H}_2\text{S} \rightarrow \text{S}^{2-} + 2\text{H}_2\text{O}$	sulphide
HCN	$\text{Ag}(\text{CN})_2^- \rightarrow \text{Ag}^+ + 2\text{CN}^-$	sulphide, silver
Cl <sub>2</sub>	$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{ClO}^- + \text{Cl}^-$	H <sup>+</sup> -glass, chloride
HF	$\text{HF} \rightarrow \text{H}^+ + \text{F}^-$	fluoride
SO <sub>2</sub>	$\text{OH}^- + \text{SO}_2 \rightarrow \text{HSO}_3^-$	H <sup>+</sup> -glass

**16** GAS ELECTRODE



**17**

AIR GAP ELECTRODE



**18**

ENZYME ELECTRODES

Enzyme	for determination of	Sensor
urease	urea	NH <sub>4</sub> <sup>+</sup> -glass
penicillinase	penicillin	H <sup>+</sup> -glass
α-glucosidase	amygdalin	CN <sup>-</sup> -(Ag <sub>2</sub> S) electrode

## PRINCIPAL ION-SELECTIVE ELECTRODE SYSTEMS

Ion	Material/form
H <sup>+</sup>	glass/bulb
Li <sup>+</sup>	glass/bulb
Na <sup>+</sup>	glass/bulb; glass/disc
K <sup>+</sup>	glass/bulb; valinomycin/L(diphenylether) or PVC or SR; potassium tetrakis (p-chlorophenyl)borate/L
NH <sub>4</sub> <sup>+</sup>	glass/bulb; monactin-monactin/L(diphenylether)
Ca <sup>2+</sup>	calcium di-n-decylphosphate/L(di(n-octylphenyl)phosphonate) or PVC; thenoyltrifluoroacetone/PVC; CaF <sub>2</sub> -LaF <sub>3</sub> /disc; calcium(di-n-octylphenyl) phosphate/G(di(n-octylphenyl)phosphonate); SSL
Ca <sup>2+</sup> /Mg <sup>2+</sup>	calcium di-n-decylphosphate/L(decanol)
Ba <sup>2+</sup>	nonylphenoxypolyethyleneoxyethanol/L
Cu <sup>2+</sup>	Ag <sub>2</sub> S + CuS/disc or SR; Cu <sub>1.7</sub> S/disc; CuS/G; chalcogenide glass/disc; (R-S-CH <sub>2</sub> COO) <sub>2</sub> Cu/L
Fe <sup>3+</sup>	chalcogenide glass/disc
Ag <sup>+</sup>	glass/bulb; Ag <sub>2</sub> S/disc
Zn <sup>2+</sup>	ZnSe + Ag <sub>2</sub> S/disc
Mn <sup>2+</sup>	MnSe + Ag <sub>2</sub> S/disc
Cd <sup>2+</sup>	CdS + Ag <sub>2</sub> S/disc
Ni <sup>2+</sup>	NiSe + Ag <sub>2</sub> S/disc
Pb <sup>2+</sup>	PbS + Ag <sub>2</sub> S/disc or SR; (R-S-CH <sub>2</sub> COO) <sub>2</sub> Pb/L
F <sup>-</sup>	LaF <sub>3</sub> /single crystal or SR
Cl <sup>-</sup>	AgCl + Ag <sub>2</sub> S/disc; AgCl/SR; AgCl + Ag <sub>2</sub> S/G; Hg <sub>2</sub> Cl <sub>2</sub> + HgS/disc; dimethyldistearylammonium chloride/L
Br <sup>-</sup>	AgBr + Ag <sub>2</sub> S/disc; AgBr/SR; AgBr + Ag <sub>2</sub> S/G
I <sup>-</sup>	AgI + Ag <sub>2</sub> S/disc; AgI/SR; I <sub>2</sub> /G(CCL <sub>4</sub> )
S <sup>2-</sup>	Ag <sub>2</sub> S/disc; Ag <sub>2</sub> S/SR; Ag <sub>2</sub> S/G
ClO <sub>4</sub> <sup>-</sup>	Fe(II) tris(substituted 1,10-phenanthroline)perchlorate/L; tetra-n-heptylammonium perchlorate/L
NO <sub>3</sub> <sup>-</sup>	Ni(II) tris(substituted 1,10-phenanthroline)nitrate/L or PVC; tridodecylhexadecylammonium nitrate/L or PVC
BF <sub>4</sub> <sup>-</sup>	Ni(II) tris(substituted 1,10-phenanthroline)fluoroborate/L
SCN <sup>-</sup>	AgSCN + Ag <sub>2</sub> S/disc; AgI/SR
SO <sub>4</sub> <sup>2-</sup>	PbSO <sub>4</sub> + PbS + Ag <sub>2</sub> S + Cu <sub>2</sub> S/disc
CO <sub>3</sub> <sup>2-</sup>	Tri(n-octyl)methylammonium chloride/L(trifluoroacetyl-p-butylbenzene)

### Key

L, liquid ion-exchange form; G, graphite Selectrode®;  
 SR, silicone rubber heterogeneous membrane; PVC, polyvinyl chloride membrane;  
 SSL, specially synthesized ligand.

## THE NERNST EQUATION

$$E = \text{constant} \pm \frac{RT}{nF} (\ln 10) \log c_i$$

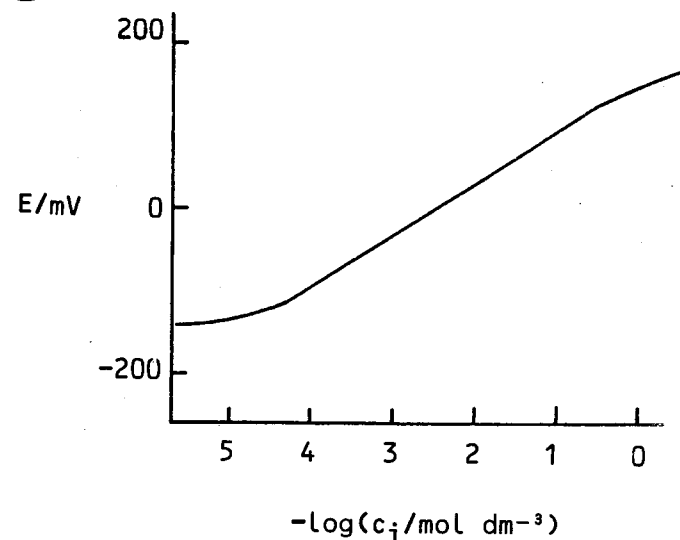
where E is potential  
 R is the gas constant  
 T is the absolute temperature  
 F is the Faraday constant  
 n is equal to the charge on ion i \*  
 c<sub>i</sub> is the concentration of the ion i

By convention the + sign refers to cation-responsive electrodes and the - sign to anion-responsive electrodes.

c<sub>i</sub> should really be replaced by the effective ionic concentration of the ion (its activity) but often ion-selective electrodes are used under conditions where changes in activity effects are made small by working in the presence of an added inert electrolyte.

\* For a conventional electrode it is the number of electrons appearing in the electrode reaction.

## CALIBRATION CURVE





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SELECTIVITY AND INTERFERENCES

Nicolsky-Eisenman equation:

$$E = \text{constant} \pm 59.16 \log(c_i + k_{ij}c_j) \quad \dots (1)$$

for  $i, j$  singly charged ions at  $25^\circ\text{C}$  where  $k_{ij}$  is the selectivity coefficient.

$$E = \text{constant} \pm \frac{59.16}{2} \log(c_i + k_{ij}c_j^2) \quad \dots (2)$$

for  $j$  singly charged and  $i$  doubly charged.

eg.  $k_{\text{CaNa}} = 0.001$  means that the electrode is 1000 times more responsive to calcium ions than to sodium; or, in other words, that it can tolerate about 1000 times higher concentration of sodium ions than calcium without suffering interference.

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SEPARATE SOLUTION METHOD FOR DETERMINING SELECTIVITY COEFFICIENTS

If measurements are made in two solutions, each containing only one of the ions

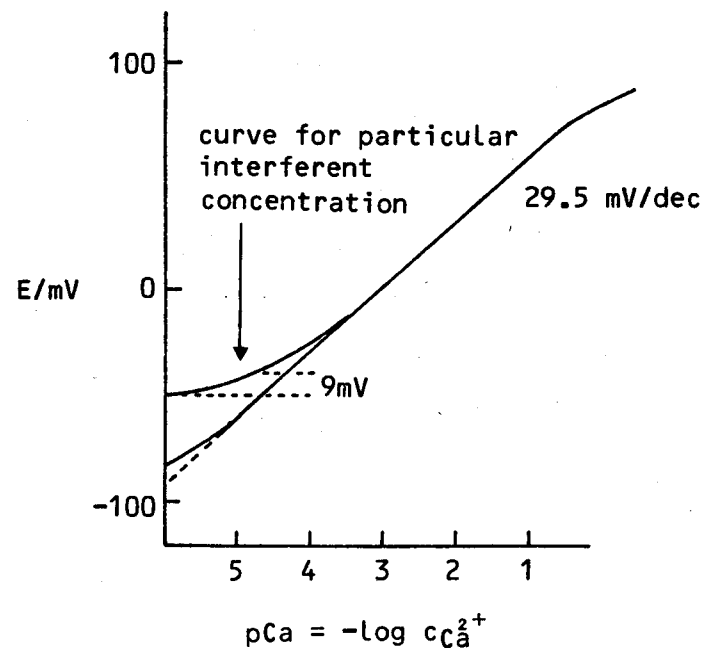
eg.  $c_i = 0.1$ ;  $c_j = 0.1 \text{ mol dm}^{-3}$ , then

$$E_i - E_j = \pm 59.16 \log k_{ij}c_j/c_j = \pm 59.16 \log k_{ij}$$

where  $E_i$  is the reading of potential in the solution containing  $i$  only

and  $E_j$  is the reading of potential in the solution containing  $j$  only

24

SELECTIVITY COEFFICIENT DETERMINATION BY THE MIXED SOLUTION METHOD: E.G. INTERFERENCE ON A CALCIUM ELECTRODE

25

SELECTIVITY DETERMINATION  
BY THE MIXED SOLUTION METHOD

a) Constant Level of interfering ion j

For i, j singly charged

$$E_i = \text{constant} \pm 59.16 \log c_i$$

$$E_{i(j)} = \text{constant} \pm 59.16 \log (c_i + k_{ij}c_j)$$

$$\text{So, } \Delta E = E_{i(j)} - E_i = \pm 59.16 \log (c_i + k_{ij}c_j)/c_i$$

From the results (see frame 24) find the condition  $\Delta E = 0$ , that is, the value of  $c_i$ , called  $c_{i(j)}$ , which has the same value of potential as the horizontal limit in the presence of a fixed concentration of interfering ion j.

Under these conditions  $c_i \ll k_{ij}c_j$  and hence

$$k_{ij} = c_{i(j)}/c_j = \frac{\text{value of } c_i \text{ for horizontal Limit}}{\text{value of fixed concentration of j}}$$

If the horizontal limit is difficult to detect exactly, it may be possible to locate it by extrapolating the calibration slope to a point  $k \log 2$  or 18 mV below the mixed response line. For a divalent-responsive electrode the value is half this, that is 9 mV as shown on frame 24.

---

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SELECTIVITY DETERMINATION BY  
THE MIXED SOLUTION METHOD

b) Constant level of primary ion

This is essentially the opposite of the previous method. A calibration graph is first constructed with varied interferent ion j and then repeated with the addition of a fixed high concentration of primary ion i.

For i, j singly charged

$$E_j = \text{constant} \pm 59.16 \log c_j$$

$$E_{j(i)} = \text{constant} \pm 59.16 \log (c_j + k_{ji}c_i)$$

$$\text{So } \Delta E = E_{j(i)} - E_j = \pm 59.16 \log (c_j + k_{ji}c_i)/c_j$$

and as before the condition  $\Delta E = 0$  is found, the value of  $c_{j(i)}$  which has the same potential as the horizontal limit in the presence of primary ion.

Under these conditions  $c_j \ll k_{ji}c_i$ , and hence

$$k_{ji} = c_{j(i)}/c_i = 1/k_{ij}$$

This method sometimes has to be used when it is not possible to use the first mixed solution method: for instance, hydrogen ion interference may be done in this way. A disadvantage is that the electrode may not show theoretical slope in the presence of interfering ion j alone. Some interfering ions exhibit irreversible and time dependent effects on electrodes.

---

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### SELECTIVITY COEFFICIENTS $k_{ij}$ FOR SOME IMPORTANT ELECTRODE SYSTEMS (MANUFACTURERS' DATA)

Electrode	Interferences
Ca <sup>2+</sup> (Beckman)	Fe <sup>2+</sup> 5, Cu <sup>2+</sup> 0.33, Mg <sup>2+</sup> 0.9, Ba <sup>2+</sup> 0.1
Ca <sup>2+</sup> (Corning)	Mg <sup>2+</sup> 0.01, Ba <sup>2+</sup> 0.01, Ni <sup>2+</sup> 0.01, Na <sup>+</sup> 10 <sup>-3</sup>
Ca <sup>2+</sup> (Orion)	Zn <sup>2+</sup> 3.2, Fe <sup>2+</sup> 0.80, Pb <sup>2+</sup> 0.63, Cu <sup>2+</sup> 0.27, Mg <sup>2+</sup> 0.01, Ba <sup>2+</sup> 0.01, Na <sup>+</sup> 1.6x10 <sup>-3</sup>
Ca <sup>2+</sup> (Philips)	Zn <sup>2+</sup> 5.0-0.9, Fe <sup>3+</sup> 0.45, Cu <sup>2+</sup> 0.07, Mg <sup>2+</sup> 0.032, Ba <sup>2+</sup> 0.02
Ca <sup>2+</sup> +Mg <sup>2+</sup> (Beckman)	Zn <sup>2+</sup> 1.0, Ba <sup>2+</sup> 1.0, Na <sup>+</sup> 0.01, K <sup>+</sup> 0.01
Ca <sup>2+</sup> +Mg <sup>2+</sup> (Orion)	Zn <sup>2+</sup> 3.5, Fe <sup>2+</sup> 3.5, Cu <sup>2+</sup> 3.1, Ba <sup>2+</sup> 0.94, Na <sup>+</sup> 0.01
NO <sub>3</sub> <sup>-</sup> (Beckman)	ClO <sub>4</sub> <sup>-</sup> 100, NO <sub>2</sub> <sup>-</sup> 0.045, Cl <sup>-</sup> 0.01, SO <sub>4</sub> <sup>2-</sup> 10 <sup>-5</sup>
NO <sub>3</sub> <sup>-</sup> (Corning)	ClO <sub>4</sub> <sup>-</sup> 1000, Cl <sup>-</sup> 4x10 <sup>-3</sup> , SO <sub>4</sub> <sup>2-</sup> 10 <sup>-3</sup>
NO <sub>3</sub> <sup>-</sup> (Orion)	ClO <sub>4</sub> <sup>-</sup> 1000, NO <sub>2</sub> <sup>-</sup> 0.06, Cl <sup>-</sup> 6x10 <sup>-3</sup> , SO <sub>4</sub> <sup>2-</sup> 6x10 <sup>-4</sup>
ClO <sub>4</sub> <sup>-</sup> (Beckman)	I <sup>-</sup> 0.033, NO <sub>2</sub> <sup>-</sup> 0.005, SO <sub>4</sub> <sup>2-</sup> 10 <sup>-6</sup>
ClO <sub>4</sub> <sup>-</sup> (Corning)	I <sup>-</sup> 0.001, NO <sub>2</sub> <sup>-</sup> 0.001, SO <sub>4</sub> <sup>2-</sup> 0.001
ClO <sub>4</sub> <sup>-</sup> (Orion)	OH <sup>-</sup> 1.0, I <sup>-</sup> 0.012, NO <sub>2</sub> <sup>-</sup> 0.0015, SO <sub>4</sub> <sup>2-</sup> 1.6x10 <sup>-4</sup>
K <sup>+</sup> (Beckman)	Rb <sup>+</sup> 2.2, Cs <sup>+</sup> 0.5, NH <sub>4</sub> <sup>+</sup> 0.014, Na <sup>+</sup> 2x10 <sup>-4</sup> , Li <sup>+</sup> 3x10 <sup>-4</sup>
K <sup>+</sup> (Corning)	Rb <sup>+</sup> 10, Cs <sup>+</sup> 20, NH <sub>4</sub> <sup>+</sup> 0.023, Na <sup>+</sup> 0.012
K <sup>+</sup> (Philips)	Rb <sup>+</sup> 1.9, Cs <sup>+</sup> 0.38, NH <sub>4</sub> <sup>+</sup> 0.012, Na <sup>+</sup> 2.6x10 <sup>-4</sup> , Li <sup>+</sup> 2.1x10 <sup>-4</sup>
K <sup>+</sup> (Orion)	Rb <sup>+</sup> 2.2, Cs <sup>+</sup> 0.5, NH <sub>4</sub> <sup>+</sup> 0.05, Na <sup>+</sup> 0.09, Li <sup>+</sup> 0.03
NH <sub>4</sub> <sup>+</sup> (Philips)	K <sup>+</sup> 0.12, Rb <sup>+</sup> 0.043, Cs <sup>+</sup> 0.0048, Li <sup>+</sup> 0.0042, Na <sup>+</sup> 0.002
F <sup>-</sup> (Beckman)	OH <sup>-</sup> 0.1
F <sup>-</sup> (Orion)	OH <sup>-</sup> 0.1

28

### RANGES OF EMF CHANGE FOR ION-SELECTIVE ELECTRODES

From

$$E = E^0 \pm \frac{RT}{nF} \ln 10 \log(c_i / \text{mol dm}^{-3}) \text{ (see frame 20)}$$

then, taking a difference

$$\frac{\Delta E}{\text{mV}} = \pm \frac{59}{n} \Delta \log(c_i / \text{mol dm}^{-3})$$

So, for  $c_i = 10^{-1}$  to  $10^{-5}$  mol dm<sup>-3</sup>,  $\Delta \log c_i = 4$ 

$$\text{and } \Delta E = \pm \frac{59}{n} \times 4 \text{ mV}$$

or 236 mV for a singly charged ion but 118 mV for a doubly charged ion.

In contrast, for pH measurements, the normal range of hydrogen ion concentration is  $10^0$  to  $10^{-14}$ , so  $\Delta \log c_i = 14$  and  $n = 1$ .

$$\text{So, } \Delta E = 59 \times 14 = 826 \text{ mV.}$$

29

### SOME USEFUL BRIDGE SOLUTIONS FOR DOUBLE JUNCTION REFERENCE ELECTRODES

Solution	Use
Lithium trifluoroacetate (5 mol dm <sup>-3</sup> )	K <sup>+</sup> , ClO <sub>4</sub> <sup>-</sup>
Potassium nitrate (saturated)	Cl <sup>-</sup>
Ammonium nitrate (3 mol dm <sup>-3</sup> )	K <sup>+</sup>
Tetramethylammonium chloride (3 mol dm <sup>-3</sup> )	K <sup>+</sup>
Potassium sulphate (saturated)	NO <sub>3</sub> <sup>-</sup>

30

### METHODS OF USING ION-SELECTIVE ELECTRODES

#### a) Direct potentiometry

2.0 mV error in E leads to 7.5% error in concentration. Useful at low concentration level in same way as flame photometry. Must add reagents to complex interferences.

#### b) Known increment

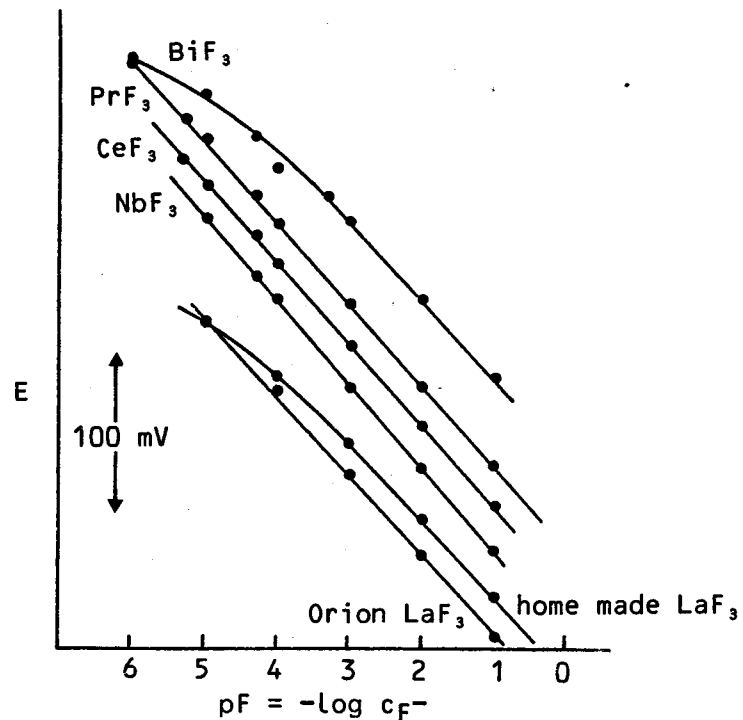
- i) known addition (spiking)
- ii) known subtraction (add reagent which complexes with sensed ion)
- iii) analate addition
- iv) analate subtraction.

#### c) Potentiometric titration

Offers increase in accuracy over direct potentiometry and known increment methods because change in potential is greater in the vicinity of the end point than between the two solutions. The electrode used may respond to the sample or to the titrant.

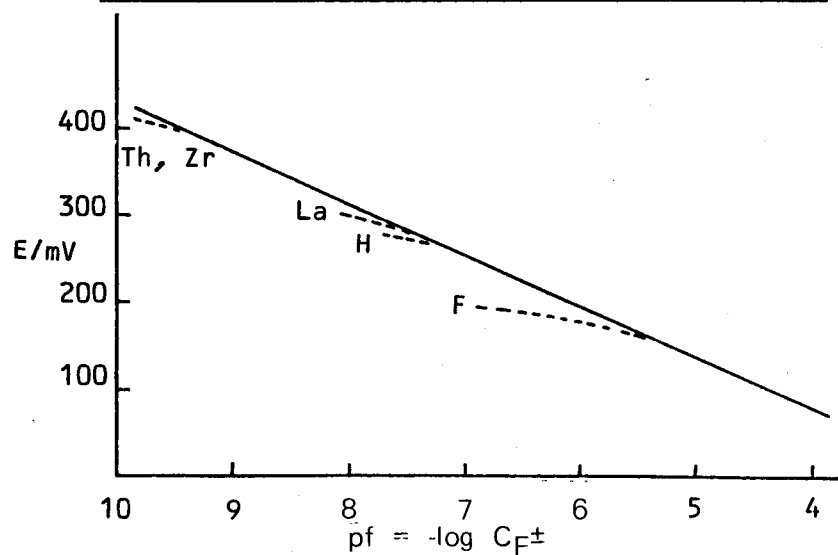
31

CALIBRATION CURVES FOR SOME RARE EARTH FLUORIDES AND BISMUTH FLUORIDE ELECTRODES



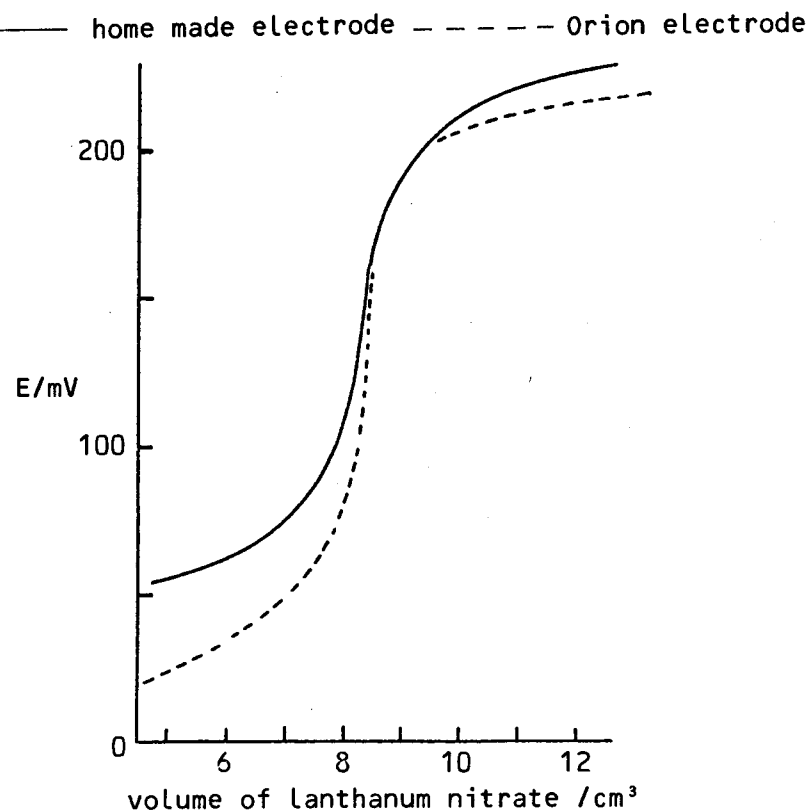
32

CALIBRATION CURVE FOR LANTHANUM FLUORIDE ELECTRODES DOWN TO LOW LEVEL FLUORIDE USING SOLUTIONS CONTAINING FLUORIDE COMPLEXES



33

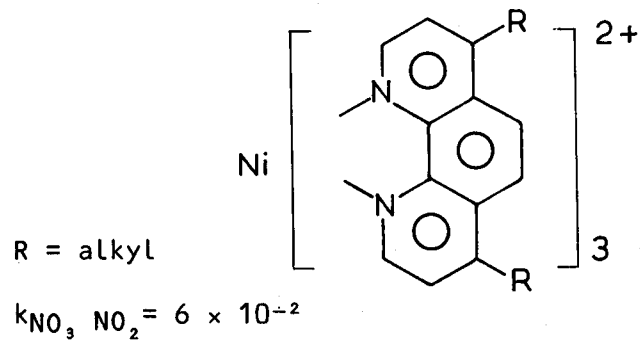
POTENTIOMETRIC TITRATION OF FLUORIDE WITH LANTHANUM NITRATE



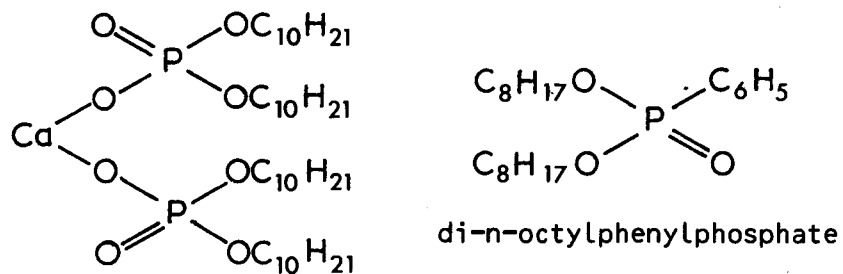
34

NITRATE ION-SELECTIVE ELECTRODE

Substituted o-phenanthroline nickel salt in a nitroaromatic solvent



35

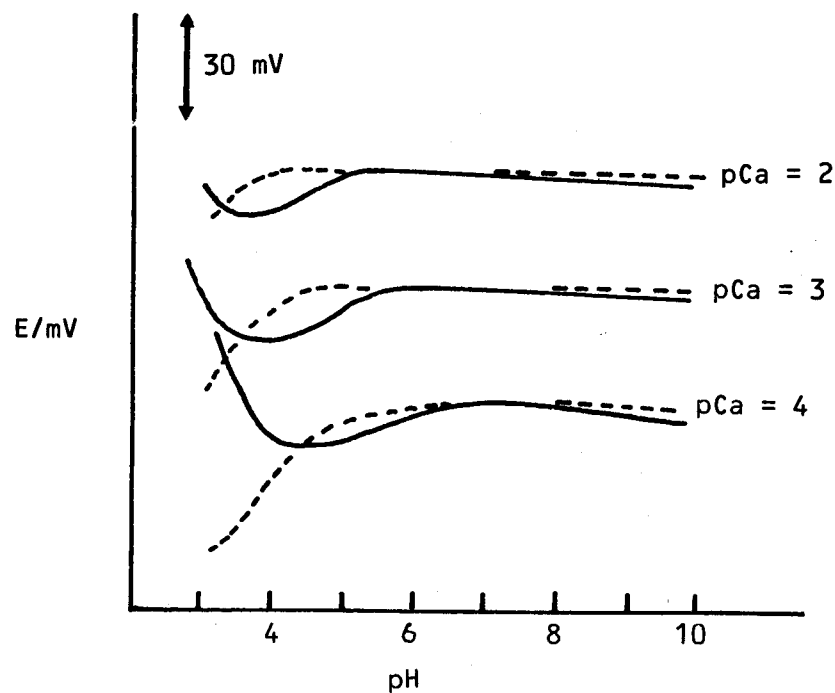
CALCIUM ION-SELECTIVE ELECTRODE

Calcium bis(di-n-decyl)phosphate

36

EFFECT OF pH ON TWO CALCIUM ION-SELECTIVE ELECTRODES

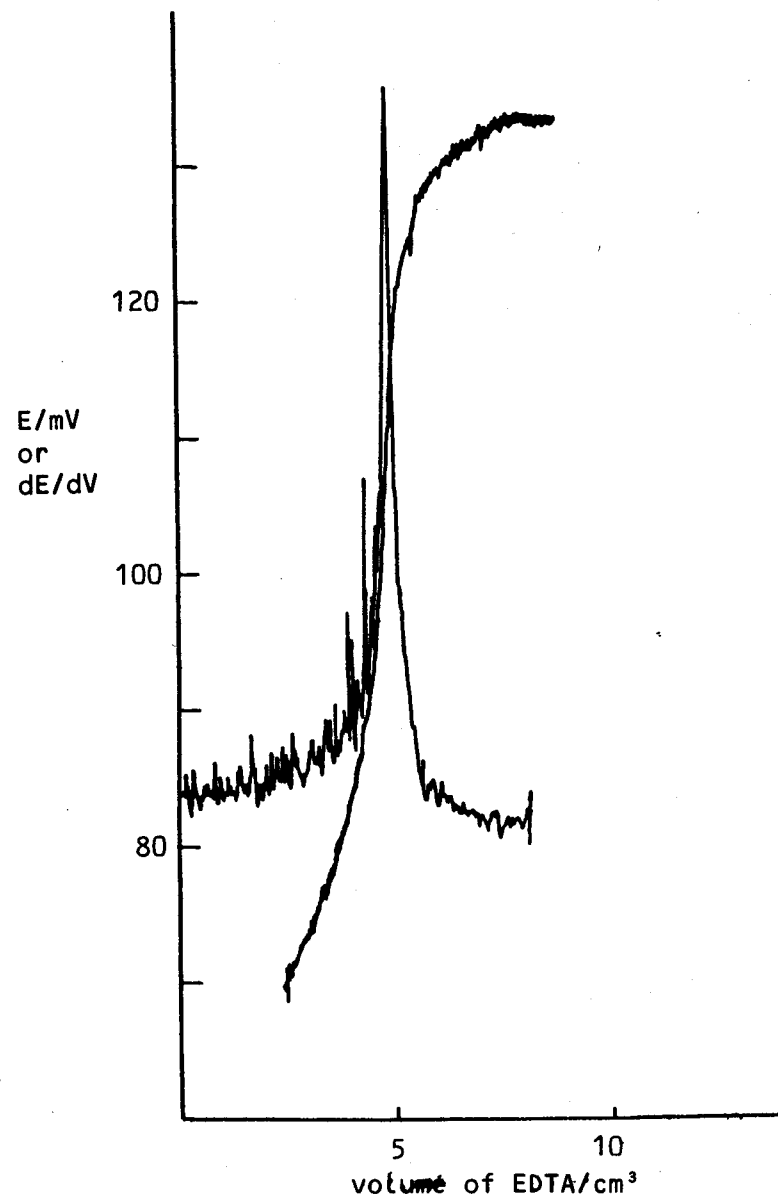
———— calcium bis(di-n-decyl)phosphate  
 - - - - - calcium bis(di-n-octyl)phosphate

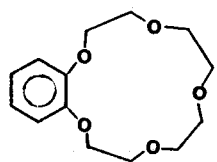


37

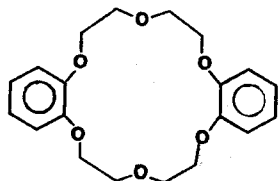
POTENTIOMETRIC TITRATION OF 0.01 mol dm<sup>-3</sup> CALCIUM CHLORIDE WITH 0.01 mol dm<sup>-3</sup> EDTA AT pH 10 USING A CALCIUM ION-SELECTIVE ELECTRODE

The differential titration curve dE/dV is also shown.

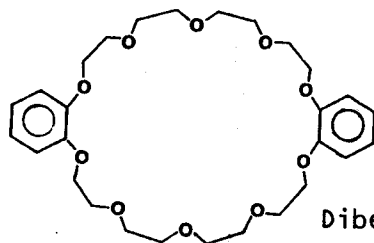




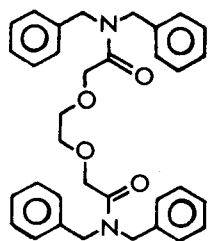
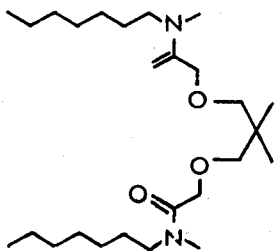
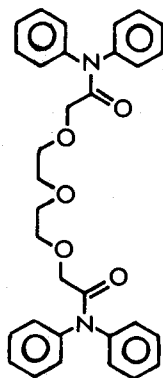
Benzo-15-crown-5



Dibenzo-18-crown-6



Dibenzo-30-crown-10

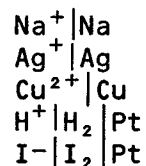
for Na<sup>+</sup>for Li<sup>+</sup>for Ba<sup>2+</sup>

- P L Bailey: Analysis with Ion-Selective Electrodes, Heyden, London, 1976.
- A K Covington (editor): Ion-Selective Electrode Methodology, Vol I & II, CRC Press, Boca Raton, Florida, 1979.
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- R A Durst (editor): Ion-Selective Electrodes, National Bureau of Standards Spec. Publ. No. 314, US Government Printing Office, 1969.

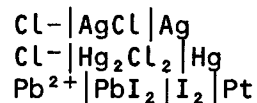
## APPENDIX I

Conventional electrodes may be classified into first, second and third kinds:

Electrodes of the First Kind\* consist of an element (metal or non-metal) in contact with one of its ions. Examples are

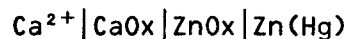


An Electrode of the Second Kind\* is basically one of the first kind to which an insoluble salt of the element has been added. Examples are:



in which a cation reversible electrode is converted to an anion reversible electrode as in the first two examples, or, more rarely, as in the last example, an anion reversible into a cation reversible.

An Electrode of the Third Kind\* is somewhat of an academic curiosity in that a second less insoluble salt is added, converting the electrode back to its original cation (or anion) function. An example is



where Ox = oxalate

\* In accordance with international convention the electrode schemes are written for electrodes placed on the right hand side of the cell scheme.

## APPENDIX II IONIC STRENGTH

The ionic strength  $I$  is defined by

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

where  $c_i$  is the concentration of the ionic species  $i$

$z_i$  is the charge or valence of ionic species  $i$ .

For example, for calcium chloride,  $\text{CaCl}_2$ , of concentration  $c$

$$I = \frac{1}{2}(2^2 \cdot c + 2c \cdot 1^2) = 6c/2 = 3c.$$

Now try it for  $\text{CuSO}_4$ ,  $\text{LaCl}_3$ ,  $\text{Na}_2\text{SO}_4$ .

## APPENDIX III EXERCISES

### Problem 1

In an experiment with a liquid ion-exchanger type nitrate ion-selective electrode the following calibration results were obtained at 25°C.

$\text{NaNO}_3 / \text{mol dm}^{-3}$	$E/\text{mV}$
$10^{-5}$	216
$10^{-4}$	224
$10^{-3}$	172
$10^{-2}$	101
$10^{-1}$	45
$10^0$	-8

Determine the slope of the calibration curve, and the limit of the detection.

In a further experiment to determine the selectivity coefficient for nitrate in the presence of chloride, the following results were obtained in solutions of sodium nitrate containing  $0.5 \text{ mol dm}^{-3}$  sodium chloride:

$\text{NaNO}_3 / \text{mol dm}^{-3}$	$E/\text{mV}$
$10^{-5}$	122
$10^{-4}$	125
$10^{-3}$	123
$10^{-2}$	100
$10^{-1}$	47

Determine the selectivity coefficient  $k_{\text{NO}_3, \text{Cl}}$  graphically.

### Problem 2

In experiments with two liquid ion-exchanger electrodes:

A - calcium selective

B - calcium + magnesium selective ("water hardness" electrode)

the following results were obtained for calibration in calcium chloride solutions.

Ca <sup>2+</sup> conc. / mol dm <sup>-3</sup>	E/mV	
	A	B
10 <sup>-5</sup>	-74	-38
10 <sup>-4</sup>	-46	-27
10 <sup>-3</sup>	-16	-12
10 <sup>-2</sup>	16	14
10 <sup>-1</sup>	46	43
10 <sup>0</sup>	77	75

Determine the calibration slope and range of each electrode.

In further experiments in calcium chloride + 0.4 mol dm<sup>-3</sup> magnesium chloride solutions the following results were obtained:

Ca <sup>2+</sup> conc. / mol dm <sup>-3</sup>	E/mV	
	A	B
10 <sup>-5</sup>	4	55
10 <sup>-4</sup>	4	54
10 <sup>-3</sup>	7	53
10 <sup>-2</sup>	24	53
10 <sup>-1</sup>	47	58
10 <sup>0</sup>	77	77

Determine the selectivity coefficient  $k_{CaMg}$  of each electrode. Is the "water hardness" electrode equally selective towards calcium and magnesium?

### Problem 3

A fluoride ion-selective electrode was used to determine the fluoride content of a solution by the known addition method as follows. Five increments of a 0.1 cm<sup>3</sup> 0.02 mol dm<sup>-3</sup> sodium fluoride solution were added to 100 cm<sup>3</sup> of sample solution. The volume change could therefore be neglected. The potential readings were 97.0 mV before addition, then successively 88.5, 82.5, 78.0, 74.1 and 70.4 mV at 25°C.

Casting the Nernst equation (frame 20) in the form:

$$E = \text{const.} - 59 \log c$$

into  $10^{-E/59} = \text{const.} \times c$

shows that the antilog  $-E/59$  is proportional to concentration. Plot  $10^{-E/59}$  against the added fluoride concentration of the sample after each addition. Determine the original fluoride concentration of the sample from the negative value on the added concentration axis for which  $10^{-E/59} = 0$ . This corresponds to the amount of fluoride increments to be added to a blank to obtain the sample solution. (The blank often contains an inert electrolyte to keep activity coefficients at least approximately constant.)

This can be justified as follows

$$10^{-E/59} = \text{const.} \times (c_x + nc_s)$$

where  $c_x$  is the unknown fluoride concentration and  $c_s$  the incremental concentration of fluoride. The left hand side is zero when

$$c_x = -xc_s$$

where  $x$  is the number of increments of  $c_s$  necessary to produce the sample from a blank solution. This is an example of a Gran plot. Special semi-antilog paper can be used which avoids the need to calculate exponentials. It is a fairly easy matter to make volume corrections, and modified semi-antilog paper is also available which allows correction to be made automatically.



APPENDIX IV ANSWERS TO PROBLEMS

Problem 1

58 mV/dec. ;  $10^{-4}$  mol dm<sup>-3</sup>

$\text{KNO}_3$  Cl =  $1.2 \times 10^{-2}$

Problem 2

A. 30.8 mV/dec. ;  $10^0 - 10^{-4}$  mol dm<sup>-3</sup>.

B. 30.0 mV/dec. ;  $10^0 - 10^{-2}$  mol dm<sup>-3</sup>.

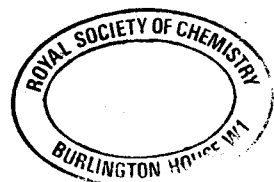
A.  $k_{\text{Ca Mg}} = 2.2 \times 10^{-2}$ .

B.  $k_{\text{Ca Mg}} = 6.8 \times 10^{-1}$ .

No, value should be 1.0.

Problem 3

$5.6 \times 10^{-5}$  mol dm<sup>-3</sup>.



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