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**SPECIAL ISSUE**  
**THEORY AND APPLICATIONS OF ION-SELECTIVE ELECTRODES:**  
**PART II**  
by J. KORYTA

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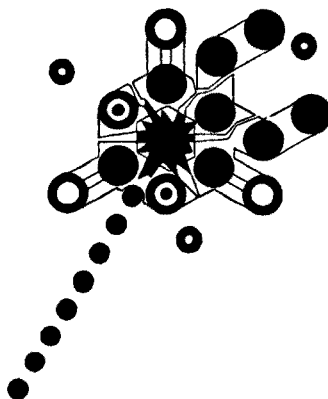
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Proceedings of the Third International Symposium held in Amsterdam, September 7 - 9, 1976

C. E. ROLAND JONES and CARL A. CRAMERS (*Editors*)

This symposium is particularly noteworthy because of the emphasis given to the newly emergent technique of pyrolysis/mass spectrometry. The large number of papers devoted to this technique at the meeting are an indication of the impetus which this recent development has given to analytical pyrolysis.

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edited by **LARRY KEVAN**, Professor of Chemistry, Wayne State University, Detroit, Michigan and **BRIAN WEBSTER**, Lecturer in Theoretical Chemistry, Glasgow University, Great Britain.

**1976 xiv+360 pages US \$57.50/Dfl. 150.00 ISBN 0-444-41412-6**

Six contributions of an experimental character and three of a theoretical nature describe the current state of research on solvated electrons. Where appropriate, comparisons are made with anion-solvation phenomena. The main aim is to define more closely the nature of electron-solvent interactions. The book discusses the notable experimental achievements which have recently been made in this field. The techniques covered include photoemission spectroscopy, fast photo-absorption methods and methods for measuring excess electron mobilities. The considerable degree of interplay which exists between theory and observation is made apparent. When studied as a whole, it is hoped that the various experimental and theoretical methods will be seen to have a strong underlying unity, with the directions of advance clearly delineated.

**CONTENTS:** Chapters 1. Theoretical studies of electron-solvent interactions: solved and unsolved problems (*N.R. Kestner*). 2. Ground states of excess electrons in liquids and glasses: magnetic resonance studies (*R. Catterall*). 3. Excited states of excess electrons studied by fast photoabsorption methods (*D.C. Walker*). 4. Continuum transitions of excess electrons studied by photoelectron emission spectroscopy (*P. Delahay*). 5. Dynamics of electron-solvent interactions (*A. Mozumder*). 6. Formation mechanisms and primary reactions of excess electrons in condensed polar media (*H.B. Steen*). 7. Electron migration in liquids and glasses (*W.F. Schmidt*). 8. Calculations of anion-solvent interactions (*P. Schuster*). 9. Spectroscopic studies of monatomic anion-solvent interactions (*M.C.R. Symons*). Index.

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## REVIEW

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# THEORY AND APPLICATIONS OF ION-SELECTIVE ELECTRODES PART II\*

JIRÍ KORYTA

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Opletalova 25, 110 00 Prague 1 (Czechoslovakia)*

(Received 17th December 1976)

## SUMMARY

This review on ion-selective electrodes is arranged in the same way as Part I. The substantial growth of the whole subject is emphasized. Progress in theory centres on the mechanism of the response of both solid and liquid membrane systems and on the theory of response times. The technology section stresses the importance of plastic film membranes. Many new applications of the fluoride and other electrodes are listed. Applications in medicine and biology emphasize the importance of ionized serum calcium and intra- and extra-cellular potassium determinations. Research trends are outlined. Over 1250 references, including material published in 1976, are presented.

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In 1972 ion-selective electrodes were still regarded as an interesting novelty in the laboratory but they have now become an indispensable tool for solving various analytical problems. Part I of *Theory and Applications of Ion-Selective Electrodes* [1] covered the literature to the beginning of 1972; it included a survey of the theory of glass electrodes together with the basic facts about glass electrodes sensitive to cations other than hydronium, and dealt in some detail with the general properties of neutral ion-carriers. The present review covers papers published before about mid-1976. Glass electrodes are not discussed except for some chalcogenide glasses (p. 40), and neutral ion-carriers are described only in connection with their functions in ion-selective electrodes. Even so, the number of references exceeds 1200, and only a small fraction of these are papers published before 1972 and omitted in Part I. The subject is treated in an order similar to that used previously. First, progress in the theory is dealt with, then some points common to all ion-selective electrodes are characterized, and finally new information on the basic properties of the various types of electrodes, together with their analytical applications, is reviewed.

During the past few years, several symposia on ion-selective electrodes have been organized and the proceedings published [2-6]. The theory and applications of ion-selective electrodes have been dealt with in four books [7-10] and three other books contain comprehensive chapters on the subject [11-13]. Periodic reviews have been published by Buck [14, 15]. Numerous general reviews have appeared in international and national journals and other periodicals [16-55]. Specialized reviews [56-125] have dealt with topics including mechanistic aspects [103, 106], analytical applications [72, 84, 87, 115, 119], process control and monitoring [64-66, 82, 96, 110, 111], low-level measurements [69], chromatographic detectors [101], organic [80, 122] and pharmaceutical analysis [75, 97, 98, 102, 118], air pollution [83], water quality and pollution control [56, 59, 68, 73, 81, 85, 86, 88-80, 95, 96, 100, 105, 108, 109, 112-114, 117, 120, 125], sea-water analysis [58, 63, 123-125], soil science [62, 71], industrial applications [60, 79, 94], ferrous metallurgy [76], metal finishing [70, 116, 121], beet sugar industry [77], food [92], toxicology and industrial hygiene [61], clinical analysis [68, 74, 104, 107], enzymology [91] and precipitate-based ion-selective electrodes [99].

The nomenclature of ion-selective electrodes was not standardized until the Commission on Analytical Nomenclature of the IUPAC Analytical

Chemistry Division made tentative recommendations in 1975 [126]. In this provisional nomenclature, important terms concerning ion-selective electrodes and their analytical application are defined. This terminology will be used in the present review, except for the symbol  $k_{A,B}$  for the selectivity coefficient; the symbol  $K_{A,B}^{Pot}$  used in Part I will be retained. Some of the definitions proposed are, however, operational only, e.g. those for detection limit and response time, and the authors of original papers will sometimes use alternative definitions better suited to their particular purposes. Some topics, such as methods for determining selectivity coefficients, are perhaps more appropriate to a monograph than to basic nomenclature. Some recommendations concerning publication of ion-selective electrode data have been made by Moody and Thomas [127].

Various types of ion-selective electrodes are manufactured by the firms listed in Part I and new developments will be found in the commercial literature. More recently, Polymetron AG, Hombrechtikon (Switzerland) have produced "Sensotrodes" for  $F^-$ ,  $Cl^-$ ,  $Ag^+$  and  $Cu^{2+}$ , and EDT Research, London, also have electrodes available. The properties of Soviet ion-selective electrodes produced by Gomelskii ZIP [40] are listed in Table 1. The publication of a useful periodical, Orion Research Newsletter, Specific Ion Electrode Technology [128] was discontinued in 1974 and replaced by catalogues containing abstracts of published papers. Czechoslovak ion-selective electrodes CRYTUR have been reviewed [129].

#### A. THEORY OF MEMBRANE POTENTIALS

The theory of membrane processes including those that occur in ion-selective electrodes has been reviewed by Buck [130], who attempted to bring out the links between electrode kinetics and membrane processes. Starting with qualitative and quantitative electrostatic features of interfaces

TABLE 1

Ion-selective electrodes manufactured by Gomelskii ZIP [40]

Ion	Membrane composition	Resistance ( $M\Omega$ )
$F^-$	$LaF_3$ crystal membrane	0.03–1.5
$Cl^-$	$AgCl$ crystal membrane	0.03–1.5
$Br^-$	—	0.03–1.5
$Ca^{2+}$	PVC membrane	0.03–1.5
$Mg^{2+}$	PVC membrane	0.03–1.5
$Cu^{2+}$	Polycrystalline membrane	0.02–0.2
$Pb^{2+}$	—	1.0–4.0
$K^+$	PVC membrane	2.5–10
$NO_3^-$	PVC membrane	2.5–10
$SO_4^{2-}$	PVC membrane	2.5–10
$S^{2-}$	$Ag_2S$ membrane	—
$S^{2-}$	Glass covered with $Ag_2S$	—

between a solid and a liquid electrolyte and between two liquid electrolytes, he dealt with various methods of describing membrane transport, and with ion-exchanging sites (site free membranes, fixed site and mobile site membranes) in different membranes including thin bilayer lipid membranes and thick membranes; he then discussed the time-dependent behaviour of membranes and, finally, ion-selective electrodes. Systems in a steady state (zero-current) and systems under current flow were discussed. Two reviews by Lakshminarayanaiah also dealt with progress in the theory of membrane systems [33].

(i) *Solid-state membranes [131–142]*

Recent work on the theory of solid-state membranes has been connected mainly with the influence of defects in the solid phase on electrochemical behaviour and with so far unelucidated problems of “all-solid-state” membranes. Morf et al. [142] dealt with silver halide and silver sulfide electrodes, particularly with the influence of silver defects on the dependence of the electrode potential on the activity of the potential-determining ions and on the detection limit. In a somewhat simplified way, their basic idea is that the concentration of silver ions in the vicinity of the membrane is given, in case of selectivity for silver ions, by the sum of the concentrations of silver ions added to the solution,  $[Ag^+]_{add.}$ , of those formed by dissolution of the membrane,  $[Ag^+]_{diss.}$ , and of those transferred to the solution from defective silver atoms,  $[Ag^+]_{def.}$ :

$$[Ag^+]_s = [Ag^+]_{add.} + [Ag^+]_{diss.} + [Ag^+]_{def.} \quad (1)$$

The solubility product  $P_{Ag_zX}$  depends on the total concentration of silver ions at the membrane surface and on the concentration of the anion  $X^{2-}$  formed by dissolution of the membrane,  $[X]_{diss.}$

$$P_{Ag_zX} = [Ag^+]_s^z [X]_{diss.} = [Ag^+]_s^z \{z[Ag^+]_s - z[Ag^+]_{add.} - z[Ag^+]_{def.}\} \quad (2)$$

To avoid the clumsy algebra connected with a cubic equation in the case of a silver sulfide electrode, the problem will be restricted to the halide case ( $z = 1$ ). Equation (2) then yields

$$[Ag^+]_s = \frac{1}{2} \{ [Ag^+]_{add.} + [Ag^+]_{def.} + \{ ([Ag^+]_{add.} + [Ag^+]_{def.})^2 + 4P_{AgX} \}^{\frac{1}{2}} \} \quad (3)$$

For  $[Ag^+]_{def.}^2 \gg 4P_{AgX}$ , the potential of the ion-selective electrode (with a dilute solution) is given by

$$E_{ise} = E_{Ag^+/Ag}^0 + (RT/F) \ln [Ag^+]_s = E_{Ag^+/Ag}^0 + (RT/F) \ln ([Ag^+]_{add.} + [Ag^+]_{def.}) \quad (4)$$

The detection limit is given by the quantity  $[Ag^+]_{def.}$ .

For  $[Ag^+]_{def.}^2 \ll 4P_{AgX}$ , the electrode potential depends on  $[Ag^+]_{add.}$  in the usual way:

$$E_{\text{ise}} = E_{\text{Ag}^+/\text{Ag}}^0 + (RT/F) \ln \left\{ \frac{1}{2} [\text{Ag}^+]_{\text{add.}} + ([\text{Ag}^+]_{\text{add.}}^2 + 4P_{\text{AgX}})^{\frac{1}{2}} \right\} \quad (5)$$

with the detection limit  $(P_{\text{AgX}})^{\frac{1}{2}}$ .

For an anion response, eqn. (2) is modified to the form

$$P_{\text{Ag}_2\text{X}} = ([\text{Ag}^+]_{\text{def.}} + [\text{Ag}^+]_{\text{diss.}})^z [\text{X}]_s = ([\text{Ag}^+]_{\text{def.}} + [\text{X}]_s - [\text{X}]_{\text{add.}})^z [\text{X}]_s \quad (6)$$

It should be noted that  $[\text{Ag}^+]_{\text{diss.}}$  may also be negative. On solving eqn. (6) for  $z = 1$ , then for  $[\text{X}]_{\text{add.}} - [\text{Ag}^+]_{\text{def.}} \gg 2(P_{\text{AgX}})^{\frac{1}{2}}$ :

$$E_{\text{ise}} = E_{\text{Ag}^+/\text{Ag}}^0 + (RT/F) \ln P_{\text{AgX}} - (RT/F) \ln ([\text{X}]_{\text{add.}} - [\text{Ag}^+]_{\text{def.}}) \quad (7)$$

while for  $[\text{Ag}^+]_{\text{def.}} - [\text{X}]_{\text{add.}} \gg 2(P_{\text{AgX}})^{\frac{1}{2}}$ :

$$E_{\text{ise}} = E_{\text{Ag}^+/\text{Ag}}^0 + (RT/F) \ln ([\text{Ag}^+]_{\text{def.}} - [\text{X}]_{\text{add.}}) \quad (8)$$

Morf et al. [142] tested their theory experimentally with satisfactory results. But according to Crombie et al. [134] the detection limit of the  $\text{Ag}_2\text{S}$  ion-selective electrode is determined solely by the solubility of  $\text{Ag}_2\text{S}$ . However, Buck [130] pointed out that the effect ascribed to silver defects might be caused by soluble silver salts originally adsorbed in the membrane material during its preparation and then slowly leached from it. Buck and Shepard [132] showed that solid-state ion-selective electrodes with an internal reference electrode have a response similar to that of the corresponding electrode of the second kind. However, in some cases, the all-solid-state ion-selective electrodes behave differently. This depends on the degree of saturation of the membrane material, for example, in the case of silver halides, with silver. This saturation, which corresponds to a rather low silver concentration, is usually achieved with a silver contact sealed to the membrane. Such electrodes have standard potentials identical to those of the corresponding second-kind electrodes. The electrodes with an inner conducting contact made of a material nobler than silver (graphite, Pt, Hg) may attain standard potentials, in the case of the response to silver ions, between the standard potential of the silver electrode  $E_{\text{Ag}^+/\text{Ag}}^0$  and the value  $E_{\text{Ag}^+/\text{Ag}}^0 + (RT/F) \ln K_0(\text{AgX})$ , where  $K_0(\text{AgX})$  is the formation constant of  $\text{AgX}$  at an activity  $\bar{a}(\text{AgX})$  in the membrane material (referred to pure  $\text{AgX}$ ) from silver at an activity  $a(\text{Ag})$  and chlorine at an activity  $a(\text{X}_2)$ ,

$$K_0(\text{AgX}) = \bar{a}(\text{AgX})/a(\text{Ag}) a(\text{X}_2)^{\frac{1}{2}}. \quad (9)$$

An analogous situation arises with chalcogenide ion-selective electrodes as pointed out by Koebel [137]. The standard potentials of these electrodes are determined by the activity of metal or sulfur in the membrane material. When silver metal is used as a direct contact material, the activity of silver in the  $\text{Ag}_2\text{S}$  component is equal to unity, and the  $\text{Ag}_2\text{S}$  ion-selective electrode then has properties identical with those of a silver or silver sulfide first- or second-kind electrode, respectively, according to the solution in contact. The standard potential of pellet electrodes based on a  $\text{Ag}_2\text{S}$ —MS mixture is

based on the solubility products of both sulfides (ref. 1, p. 368). Electrodes with a solid conductor different from silver, e.g. graphite, behave in another way (cf. [143]).

Let us consider the cell [137]



where  $\delta$  defines the excess of silver in the silver sulfide. The e.m.f. of cell (10) is given by the difference of the electrochemical potentials of the electrons in the chemically identical graphite contacts 4' and 4. Since silver sulfide shows a definite electronic conductivity, there is a contact equilibrium of electrons on the phase boundary between 3 and 4. Thus, on the basis of the usual procedure of characterizing the equilibrium between phases in contact by means of the electrochemical potentials of the components present in these phases (see e.g. [144]), we obtain  $\mu_{\text{Ag}}^{(3)} - \mu_{\text{Ag}}^0 = -F E$ , where  $\mu_{\text{Ag}}^0$  is the standard chemical potential of silver metal and  $\mu_{\text{Ag}}^{(3)}$  is the chemical potential of silver in the silver sulfide. This equation holds if there is no diffusion potential in the silver sulfide phase (as discussed in Part I) and if redox systems are absent from phase 2 (i.e. the transport number of  $\text{Ag}^+$  in phase 2 is equal to unity). If cell (10) has a silver contact instead of graphite, the value of  $\delta$  corresponds to saturation of  $\text{Ag}_2\text{S}$  with Ag and the silver activity in  $\text{Ag}_{2+\delta}\text{S}$  is equal to unity. Then  $\mu_{\text{Ag}}^{(3)} = \mu_{\text{Ag}}^0$  and the e.m.f. is equal to zero. The standard potential of the silver sulfide ion-selective electrode is equal to that of the silver electrode,  $E_{\text{ise}}^0 = E_{\text{Ag}^+/\text{Ag}}^0 = + 0.799 \text{ V vs. NHE}$ .

In contrast, if silver sulfide is in equilibrium with elemental sulfur (e.g. when silver sulfide is prepared in oxidizing conditions), then

$$\mu_{\text{Ag}}^{(3)} = 0.5 \mu_{\text{Ag}_2\text{S}}^0 - 0.5 \mu_{\text{S}}^0 \quad (11)$$

Here the standard potential chemical  $\mu_{\text{Ag}_2\text{S}}^0$  is used, because the deviation  $\delta$  from stoichiometry is small. By definition  $\mu_{\text{S}}^0 = 0$ . Thus  $\mu_{\text{Ag}}^{(3)} = 0.5 \mu_{\text{Ag}_2\text{S}}^0 = 0.5 \Delta G_f^{298} = 39\,160 \text{ J mol}^{-1}$ , and the e.m.f. of cell (10) is equal to 0.203 V. The resulting standard potential of the ion-selective electrode is then 1.002 V. The values 0.799 V and 1.002 V represent the lower and higher limits for the standard potential in contact with an "inert" conductor such as carbon. The e.m.f. of a cell of the type



can be discussed in an analogous way [137]. It should be emphasized that this procedure cannot be applied to membrane materials which show only ionic conductivity.

The theory of the cyanide ion-selective electrode has been presented [131, 135] in a way almost identical to that worked out in Part I, p. 336 (cf. [138]) based on Jaenicke's analysis of silver halide dissolution in complexing media [136]. Mascini [140] has deduced a simple expression

for the pH-dependence of the potential of the cyanide electrode which coincides with eqn. (123) of Part I, where identical diffusion coefficients are assumed for  $\Gamma^-$ ,  $\text{CN}^-$  and  $\text{Ag}(\text{CN})_2^-$ . This equation described his experimental results satisfactorily. The response of the cyanide electrode in the presence of metal ions has been discussed in a similar manner [141].

The transient behaviour of solid-state ion-selective electrodes [133] has been studied galvanostatically in order to measure the exchange current density in these systems (for basic definitions, see ref. 144). In all-solid-state systems containing  $\text{Ag}_2\text{S}$ , the rate-determining process is confined to the membrane—Ag boundary, as the ion exchange at the solution-membrane interface is quite rapid. Since this is also the case in sulfide solutions, Cammann and Rechnitz [133] concluded that the process taking place at this boundary is



where  $\text{Ag}_0^+$  denotes an interstitial silver ion.

For a  $\text{LaF}_3$ -membrane electrode, the standard exchange current density was found to be about  $10^{-5} \text{ A cm}^{-2}$  and the charge transfer coefficient  $\alpha = 0.65$  [133]. The hydroxide interference is probably not due to incorporation of  $\text{OH}^-$  into the  $\text{LaF}_3$  lattice but is connected with a chemical reaction of the type



However,  $\text{La}^{3+}$  does not take part in the charge transfer. The very general theory of small-signal frequency response of binary electrolytes [139] may, perhaps, find some application in the solid-state membrane field.

#### (ii) Liquid membranes with dissolved ion-exchangers [145–156]

The theory of this type of ion-selective electrode has been reviewed [153, 155]. Although the main results of the theory (see Part I, p. 348) have already been confirmed basically, considerable effort has since been devoted to investigations of the relationship between the extraction parameters (i.e. solvent-dependent, site-independent and simultaneously solvent- and site-dependent characteristics) of various ions and their electrode behaviour [145–147, 150–156]. Solvent-dependent effects are operative only with rather highly polar membrane solvents like aromatic nitro compounds. The degree of ion-pairing is then negligible and the selectivity coefficient is given by the relationship

$$K_{\text{JK}}^{\text{Pot}} = k_{\text{K}}/k_{\text{J}} = \exp [(\Delta G_{\text{tr,J}}^{0,\text{W}\rightarrow\text{M}} - \Delta G_{\text{tr,K}}^{0,\text{W}\rightarrow\text{M}})/RT] \quad (15)$$

where  $k_{\text{J}}$  and  $k_{\text{K}}$  are the partition coefficients of the ions J and K between the membrane solvent and water, and  $\Delta G_{\text{tr,J}}^{0,\text{W}\rightarrow\text{M}}$  and  $\Delta G_{\text{tr,K}}^{0,\text{W}\rightarrow\text{M}}$  are the standard Gibbs energies of transfer of these ions from water to the membrane solvent

$$k_{\text{K}} = \exp (-\Delta G_{\text{tr,K}}^{0,\text{W}\rightarrow\text{M}}/RT) \quad (16)$$



Neither the partition coefficients nor the standard Gibbs energies of individual ions are accessible to direct measurement. The partition coefficient of a salt, KA, can be described by

$$k_{KA} = \exp [ - (\Delta G_{tr,K}^{0,W \rightarrow M} + \Delta G_{tr,A}^{0,W \rightarrow M}) / RT ] \quad (16a)$$

hence it is a matter of establishing a suitable convention by which scales of standard Gibbs energies for individual cations and anions can be elaborated [157, 158]. However, eqn. (15) is valid irrespective of the scale chosen since there is a difference of standard Gibbs transfer energies on the right-hand side.

Scholer and Simon [154] determined selectivity coefficients for a number of organic and inorganic cations with an ion-selective electrode based on sodium tetraphenylborate dissolved in 2-nitro-*p*-cymene. Figure 1 demonstrates the complete agreement of their results with theory when the logarithms of selectivity coefficients were plotted against  $k_K/k_J$  estimated by Rais for the system nitrobenzene—water [159].

Baum [146] obtained values for selectivity coefficients of various choline esters determined with an electrode based on acetylcholine tetra(*p*-chlorophenyl) borate in 3-*o*-nitroxylyene. A linear dependence with the theoretical slope was obtained by plotting the logarithms of those coefficients vs. the standard Gibbs energies of transfer of those ions from water to ethanol. This result is somewhat surprising because the standard Gibbs transfer energies are given by the difference of Gibbs energies of solvation in those particular solvents. The solvation effects in nitroxylyene and in ethanol seem not to be identical. Similar results [146] for amino acids obtained with an electrode based on a quaternary amine surfactant in higher alcohols as solvents were treated in the same way, whereas James et al. [150] considered a strong association in analogous systems. They studied extraction of the ion pair of tetrahexylammonium and iodide from water into *n*-pentanol, *n*-hexanol and *n*-decanol characterized by the extraction constant

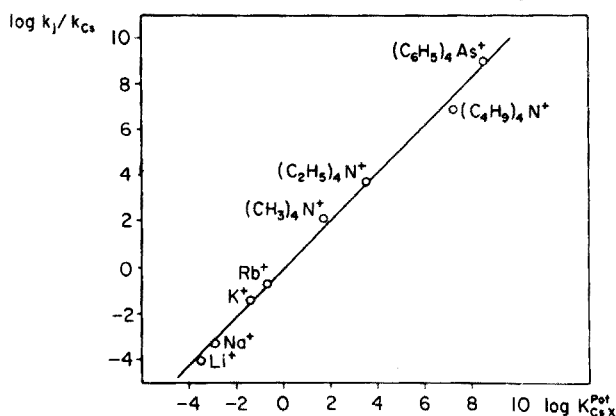
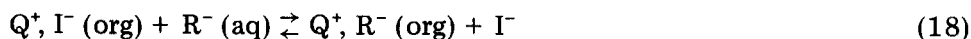


Fig. 1. Correlation of the observed selectivity constants  $K_{Cs,j}^{Pot}$  with the ratio of partition coefficients  $k_j/k_{Cs}$  [154].

$$K_{\text{extr}} = K_{Q^+, I^-} \cdot k_{Q^+, I^-} = \frac{[Q^+, I^-]_{\text{org}}}{[Q^+]_{\text{aq}} [I^-]_{\text{aq}}} \quad (17)$$

where  $K_{Q^+, I^-} = [Q^+, I^-]_{\text{aq}} / [Q^+]_{\text{aq}} [I^-]_{\text{aq}}$  is the ion-pair formation constant for water and  $K_{Q^+, I^-}$  the partition coefficient of the ion pair  $Q^+, I^-$  between water and the organic solvent.

The competitive distribution



is characterized by the constant

$$K_{\text{CD}} = \frac{K_{Q^+, R^-} \cdot k_{Q^+, R^-}}{K_{Q^+, I^-} \cdot k_{Q^+, I^-}} = \frac{[Q^+, R^-]_{\text{org}} [I^-]_{\text{aq}}}{[Q^+, I^-]_{\text{org}} [R^-]_{\text{aq}}} \quad (19)$$

When the mobilities of  $Q^+, R^-$  and  $Q^+, I^-$  in the membrane phase are approximately the same and the ion pairing is strong (the dissociation constants of ion pairs in this system are about  $10^{-10}$ ), the selectivity coefficient should be equal to  $K_{\text{CD}}$  (cf. eqn. (96) of Part I for  $\tau = 1$  and  $U_{\text{JS}} = U_{\text{KS}}$ ). The competitive distribution constants and the selectivity coefficients for an ion-selective electrode with tetrahexylammonium iodide as ion exchanger in aliphatic alcohols are compared in Table 2.

The selectivity coefficients of a series of potential-determining ions should fulfil the relationship

$$K_{1n}^{\text{Pot}} = K_{12}^{\text{Pot}} K_{23}^{\text{Pot}} K_{34}^{\text{Pot}} \dots K_{n-1, n}^{\text{Pot}} \quad (20)$$

but this is often not confirmed experimentally, when some of these constants are much smaller than unity [151, 156]. In this case, if the membrane contains an ion for which it is much more selective than for another ion in the test solution, the ion present in the membrane dissolves in the test solution and the electrode responds only to this ion without influence from the weak interferant.

Sandblom and co-workers [145, 153] have extended the general theory of liquid-membrane ion-selective electrodes with charged mobile sites (Part I,

TABLE 2

Comparison of competitive extraction constants and selectivity coefficients for various amino acid-selective electrodes (in parentheses) [150]

Interfering anion	Tryptophan electrode $\log K_{\text{CD}}$ ( $\log K_{\text{JK}}^{\text{Pot}}$ )	Phenylalanine electrode $\log K_{\text{CD}}$ ( $\log K_{\text{JK}}^{\text{Pot}}$ )	Leucine electrode $\log K_{\text{CD}}$ ( $\log K_{\text{JK}}^{\text{Pot}}$ )	Methionine electrode $\log K_{\text{CD}}$ ( $\log K_{\text{JK}}^{\text{Pot}}$ )	Valine electrode $\log K_{\text{CD}}$ ( $\log K_{\text{JK}}^{\text{Pot}}$ )
Glycine	-1.52 (-1.8)	-1.61 (-1.4)	-1.11 (-1.2)	-0.61 (-0.8)	-0.54 (-0.9)
Alanine	-1.54 (-1.6)	-1.63 (-1.3)	-1.13 (-1.2)	-0.63 (-0.8)	-0.56 (-0.8)
Valine	-0.98 (-0.8)	-1.07 (-0.8)	-0.57 (-0.6)	-0.07 (-0.4)	
Leucine	-0.41 (-0.4)	-0.5 (-0.4)		+0.50	+0.57
Serine	-1.47 (-1.9)	-1.56 (-1.4)	-1.06 (-1.5)	-0.56 (-1.2)	-0.49 (-0.9)
Methionine	-0.91 (-0.8)	-1.0 (-0.7)	-0.50 (-1.5)		+0.07 (-0.1)
Phenylalanine	+0.09 (-0.1)		+0.50 (+0.2)	+1.0 (+0.4)	+1.07 (+0.4)
Tryptophan		-0.09 (-0.1)	+0.41 (+0.2)	+0.91 (+0.1)	+0.98 (+0.7)

p. 348), including the effects of "side reactions" in the membrane phase such as adduct formation and polymerization. They verified their theory, using tetraalkylammonium salts solutions in methylene chloride as membrane material. The selectivity properties were compared with the extraction parameters of the same system.

The phase boundary between two immiscible electrolyte solutions can be polarized in a way similar to the polarization of the interface between a metal electrode and an electrolyte solution if, under equilibrium conditions, one of the electrolytes predominates in one of the solvents and the other electrolyte in the second solvent [148, 149, 152]. Then, chronopotentiometry [148, 149] or polarography [152] can be used with such a system, and the half-wave potentials of ions present at low concentrations are, in the case of a rapid transfer of these ions between the two phases, closely related to standard transfer Gibbs energies. In this way the selectivity coefficients can be determined from eqn. (15).

*(iii) Liquid membranes with dissolved neutral carriers [160–172]*

Theoretical work on the membrane properties of neutral ion-carriers has mainly centred on bilayer lipid membranes, and has been reviewed [163, 167, 172]. Ion transport across such a membrane includes the transfer of ions, ion carriers and complexes of ions with ion carriers across the interface, and, possibly, volume reactions (dissociation and formation) of such complexes and, finally, the translocation of the complex and of the carrier across the interior of the membrane where two electrical diffuse double layers are super-imposed. However, the behaviour of the thick-membrane ion-selective electrodes has not yet been explained in full.

Lev et al. [168] investigated thick membranes containing valinomycin or nonactin dissolved in heptane. The membrane conductivity depends only slightly on the concentration of the salt present in the aqueous solution in contact with the membrane. The membrane potentials show somewhat better selectivity for  $K^+$  than lipid bilayer membranes. The resistance of a thick membrane is a linear function of the membrane thickness with a constant term corresponding to the surface resistance. The authors have elaborated a theory for ion transport across this type of membrane based on the Nernst–Planck equation with additional reaction-rate terms, but they were unable to deduce an explicit formula for the membrane potential.

The electroneutrality inside the membrane requires that the anions are extracted into the membrane together with the complexed cations. Accordingly, the  $\Delta\varphi_M - \log a$  dependence shows a maximum, and the electrode finally becomes responsive to anions. Boles and Buck [161] (see also [162]) worked out a theory of a thin lipid film accounting for anion solubilization in the membrane without any assumption of electroneutrality. This extension of the Ciani–Eisenman–Szabo theory (cf. ref. 99 of Part I) is, however, like the original theory, not directly applicable to ion-selective electrodes.

Let us consider a thick membrane with a dissolved ion carrier at a total concentration  $c_V^{\text{tot}}$  which is practically insoluble in the aqueous phase [169, 170]. The test solutions contain the salt JX at the activities  $a_J(1) \approx a_X(1)$ ,  $a_J(2) \approx a_X(2)$  (the symbols for individual parts of the membrane system are identical to those used in Part I, p. 332). At the interface, the Donnan equilibrium is established (eqn. (33) of Part I):

$$a_J(1)^2 = a_X(1)^2 = a_J(p) a_X(p) = \frac{C_J(p) C_X(p)}{k_J k_X} = \frac{C_{JV}(p) C_X(p)}{k_J k_X K_{JV} C_V(p)} \quad (21)$$

where  $a_J(p)$  and  $a_X(p)$  are the activities of hydrated ions  $J^+$  and  $X^-$  in the membrane,  $C_J(p)$  and  $C_X(p)$  the concentrations of these ions solvated by the membrane solvent,  $k_J$  and  $k_X$  their partition coefficients,  $K_{JV}$  the stability constant of the cation-carrier complex in the membrane, and  $C_V(p)$  the concentration of the free carrier at the interface between the membrane and the test solution. The concentration of free cations in the membrane is negligible. The extraction constant  $K_{\text{ex}}$  of the salt JX is given by the expression

$$K_{\text{ex}} = k_J k_X K_{JV} \quad (22)$$

The membrane potential  $\Delta\varphi_M$  is given by the sum of the Donnan potentials at both interfaces and by the diffusion potential in the interior of the membrane

$$\Delta\varphi_M = \Delta\varphi_D(1) + \Delta\varphi_L + \Delta\varphi_D(2) \quad (23)$$

For  $\Delta\varphi_D(1)$  (and analogously for  $\Delta\varphi_D(2)$ ) we have ( $C_X = C_{JV}$ )

$$\Delta\varphi_D(1) = \text{const} - (RT/F) \ln [c_X(1)/C_X(1)] = \text{const} + (RT/F) \ln C_V(p)^{\frac{1}{2}} \quad (24)$$

$$\Delta\varphi_D(2) = \text{const} - (RT/F) \ln C_V(q)^{\frac{1}{2}} \quad (25)$$

The diffusion potential is given by eqn. (41) of Part I

$$\Delta\varphi_L = \frac{U_+ - U_-}{U_+ + U_-} \frac{RT}{F} \ln \frac{C_X(p)}{C_X(q)} \quad (26)$$

where  $U_+$  and  $U_-$  are the mobilities of  $JV^+$  and  $X^-$ , respectively.

Addition of eqns. (25) and (26) gives

$$\Delta\varphi_M = \frac{U_+ - U_-}{U_+ + U_-} \frac{RT}{F} \ln \frac{a_J(1)}{a_J(2)} + \frac{2U_+}{U_+ + U_-} \frac{RT}{F} \ln \frac{C_V(p)^{\frac{1}{2}}}{C_V(q)^{\frac{1}{2}}} \quad (27)$$

If only a small fraction of V is bound in the complex, the second term on the right-hand side of eqn. (27) is equal to zero and the slope of the  $\Delta\varphi_M$ -log c dependence can attain any value between the Nernstian slope for cations and that for anions. If a considerable proportion of the carrier is fixed in the complex, then

$$C_V^{\text{tot}} = C_V(p) + C_{JV}(p) = C_V(p) + K_{\text{ex}}^{\frac{1}{2}} a_J(1) C_V(p)^{\frac{1}{2}} \quad (28)$$

giving

$$\Delta\varphi_M = \frac{U_+ - U_-}{U_+ + U_-} \frac{RT}{F} \ln \frac{a_J(1)}{a_J(2)} + \frac{2U_+}{U_+ + U_-} \frac{RT}{F} \times \ln \frac{[K_{ex} a_J(1)^2 + 4C_V^{tot}]^{\frac{1}{2}} - K_{ex}^{\frac{1}{2}} a_J(1)}{[K_{ex} a_J(2)^2 + 4C_V^{tot}]^{\frac{1}{2}} - K_{ex}^{\frac{1}{2}} a_J(2)} \quad (29)$$

For  $K_{ex} a_J(1)^2 \gg 4C_V^{tot}$ , the numerator of the last right-hand-side term in eqn. (29) approximates to  $1/(K_{ex}^{\frac{1}{2}} a_J(1))$ , and the dependence of the membrane potential on the logarithm of the mean activity of JX acquires a Nernstian slope for the anion.

Ryba and Petránek [170] have accounted for ion pairing in the membrane characterized by the constant  $K_{IP}$ . In their resulting equation, the  $K_{ex}$  terms in eqn. (29) are divided by  $(1 + K_{ex} K_{IP} a_J(1)^2)$  or  $(1 + K_{ex} K_{IP} a_J(2)^2)$ , respectively. Their experimental results with valinomycin and crown polyethers as  $K^+$ -carriers in the presence of chloride, perchlorate and picrate coincide remarkably with theory. However, the assumption that the anion mobility is negligibly small seems to be not fully justified.

An important improvement in the functioning of this type of ion-selective electrode was achieved by the introduction of a salt with a lipophilic anion like tetraphenylborate into the membrane as described by Morf et al. [169]. Morf et al. treated this case theoretically on the lines of the preceding case (eqns. (21)–(29)). However, a simpler description is possible by considering the system as containing an ionized cation-exchanger (Part I, p. 348). Let us assume that the lipophilic anion  $R^-$  is practically confined to the membrane and that the difference between the Gibbs standard energies of transfer of the anion in the test solution  $X^-$  and of  $R^-$  is large, so that an exchange of these anions is practically impossible. It is further assumed that the cations exist in the membrane practically only in the form of the complexes with the ion carrier V, and that the partition coefficients of the complexes of the cations  $J^+$  and  $K^+$  present in the test solutions,  $JV^+$  and  $KV^+$ , between water and the membrane are approximately equal ( $k_{JV} = k_{KV}$ ); the same holds for their mobilities in the membrane (see Part I, p. 393). The distribution coefficient of the ion carrier between water and the membrane  $k_V$  is very large, so that the equilibrium concentration of V in the test solution is very low.

In analogy to eqn. (78) of Part I, we have

$$\frac{a_J(1) K_{JV} (C_V - C_R) k_{JV}}{C_{JV}} = \frac{a_K(1) K_{KV} (C_V - C_R) k_{KV}}{C_{KV}}, \quad (30)$$

where  $k_{JV} = \exp [-(\mu_{JV}^0(m) - \mu_{JV}^0(1))/RT]$  and  $k_{KV} = \exp [-(\mu_{KV}^0(m) - \mu_{KV}^0(1))/RT]$ ;  $C_V$  is the overall concentration of the carrier in the membrane,  $C_R$  is the concentration of  $R^-$  in the membrane and  $K_{JV}$  is the stability constant of the complex  $JV^+$  in water. Neglecting the ion pairing in the membrane, the membrane potential  $\Delta\varphi_M$  can be obtained directly from eqn. (92) of Part I by putting  $U_J = U_K$ , and

$$k_J = \frac{K_{JV} (C_V - C_R) k_{JV}}{k_V} \quad (31)$$

$$k_K = \frac{K_{KV} (C_V - C_R) k_{KV}}{k_V} \quad (32)$$

so that

$$\Delta\varphi_M = \frac{RT}{F} \ln \frac{a_J(1) + (K_{KV}/K_{JV}) a_K(1)}{a_J(2) + (K_{KV}/K_{JV}) a_K(2)} \quad (33)$$

The Nernstian response of the electrode towards the ion  $J^+$  (if the second term in the numerator on the right-hand side of eqn. (33) can be neglected) originates in the fact that the concentration of  $JV^+$  in the membrane remains constant when  $a_J(1)$  increases. However, if the condition of a large difference in the Gibbs standard transfer energies of  $X^-$  and  $R^-$  is not fulfilled, the increase of  $a_J(1)$  is connected with the increase of  $C_{JV}$ , so that the increase in  $\Delta\varphi_M$  is smaller than would correspond to the Nernstian dependence, and finally, when the carrier is consumed, there is an anion response. This phenomenon was described by Morf et al. [169] by the equation (the terms related to the solution (2) have been included in the constant term)

$$\begin{aligned} \Delta\varphi_M = & \text{const} + \frac{U_+ - U_-}{U_+ + U_-} \\ & \times \frac{RT}{F} \ln \frac{a_J(1)^2}{[K_{ex} a_J(1)^2 (C_V^{tot} - \bar{C}_R) + \frac{1}{4}(\bar{C}_R + K_{ex} a_J(1)^2)^2]^{\frac{1}{2}} - \frac{1}{2}(\bar{C}_R - K_{ex} a_J(1)^2)} \\ & + \frac{RT}{F} \ln \frac{a_J(1)}{[K_{ex} a_J(1)^2 (C_V^{tot} - \bar{C}_R) + \frac{1}{4}(\bar{C}_R + K_{ex} a_J(1)^2)^2]^{\frac{1}{2}} + \frac{1}{2}(\bar{C}_R + K_{ex} a_J(1)^2)} \end{aligned} \quad (34)$$

The symbols in this equation were explained in connection with eqns. (21)–(27);  $\bar{C}_R$  is the average concentration of  $R^-$  in the membrane. This equation allows the course of the  $\Delta\varphi_M$ – $\log a_J(1)$  dependence on addition of a salt of  $R^-$  to be explained, including the position of the peak on this dependence.

The occurrence of fixed negative charges in the membrane as the cause of the Nernstian response of neutral carrier ion-selective electrodes to cations has been proposed by Kedem et al. [165, cf. 161, 171]. Boles and Buck [161] have discussed this alternative using the Teorell–Meyer–Sievers concept of a permselective membrane (see Part I, p. 343–344). Equations (51) and (54) of Part I can be applied directly to this case when eqn. (21) of the present review is used instead of eqn. (49) of Part I, and when some sign inversions are made, since the fixed ion was earlier considered as positive.

The fact that even membrane solvents alone may show some ion-selective properties has been already reported [refs. 264 and 499 of Part I]. Similar phenomena described recently [160, 164] are perhaps also due to fixed charges in the membrane. A lithium-selective electrode based on a Millipore

cellulose acetate filter soaked with n-decanol shows Nernstian response towards  $\text{Li}^+$  irrespective of whether the chloride, nitrate or sulfate salt or the hydroxide is used [164].

## B. THE TECHNOLOGY OF ION-SELECTIVE ELECTRODES

### (i) Construction [173–204]

The solid-state ion-selective electrodes include homogeneous as well as heterogeneous membrane systems. Among interesting developments in the former group is a split crystal electrode [203], which can be formed from a single-wafer thin-disc membrane by splitting so that two semicircular membranes are obtained which are then embedded together in one plastic bond. If they undergo uniform pretreatment, two sensors of identical behaviour are obtained (see Fig. 2). These electrodes are suitable for differential potentiometric titrations. A new type of solid-state electrode containing 1–50 mol % of gold powder has been described [190], but the advantage of this in comparison to conventional systems has still to be shown. Needle-shaped solid-state electrodes have been prepared by co-precipitation of  $\text{Ag}_2\text{S}$  with the sulfide of another metal or silver halide and subsequent pressing [179]; electrodes of the type  $\text{MS}/\text{Ag}_2\text{S}$  were examined for  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  and of the type  $\text{AgX}/\text{Ag}_2\text{S}$  for  $\text{S}^{2-}$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$  and  $\text{I}^-$ .

Recent developments in the field of precipitate-based heterogeneous membrane electrodes have been reviewed [99]. Liberti has reviewed methods for obtaining membranes with precipitates embedded in a polythene matrix. These electrodes show a high resistance towards most chemical agents, no leakage and a great mechanical strength [185]. Analogous electrodes can be prepared by cold polymerization with dental acrylic [201]. A comparison of  $\text{AgI}$  and  $\text{Ag}_2\text{S}$  ion-selective electrodes based on a silicone rubber matrix with pressed-pellet electrodes has shown the latter systems to have some advantages [176].

The properties of the Selectrode (Fig. 3) have been described in detail [195]. Electrodes of this type are produced by Radiometer (Types 3000–3004).

The liquid-membrane electrodes for practical use are now based mainly on plastic membranes containing the liquid ion-exchanger or ion-carrier solution as a plasticizer. Such systems were mentioned only briefly in Part I, p. 396, and also in connection with the work of Shatkay et al. in refs. 55, 292 and 597 of Part I [cf. 184a]. Those systems have been greatly improved by Moody et al. [188, cf. 178]. The ion-exchanger solution together with PVC is dissolved in tetrahydrofuran and poured into a glass ring resting on a sheet of plate glass. After two days of slow evaporation of the solvent, the membrane, which is several tenths of a millimeter thick, can be cut into discs which are then fixed to suitable PVC tubes. The ion-exchanger dispersion in such a membrane is shown in Fig. 4. The PVC tube closed by the membrane is then filled with a suitable inner electrolyte solution. A system with a graphite rod in direct contact with a membrane of this type

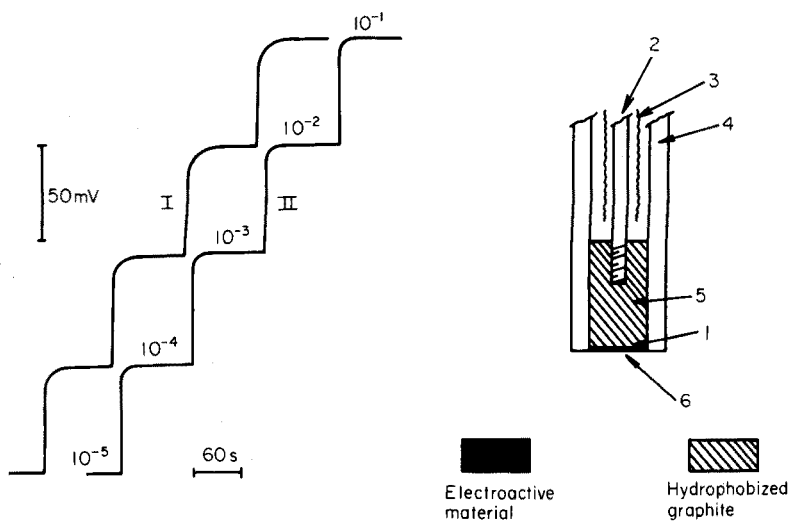


Fig. 2. Dynamic response of split AgI/Ag<sub>2</sub>S membranes I and II to decadic changes in iodide concentration [203].

Fig. 3. Růžička's Selectrode. 1 Membrane. 2 Stainless steel contact. 3 Screening. 4 Teflon tube. 5 Cylinder pressed from graphite hydrophobized by Teflon. 6 Sensitive surface.

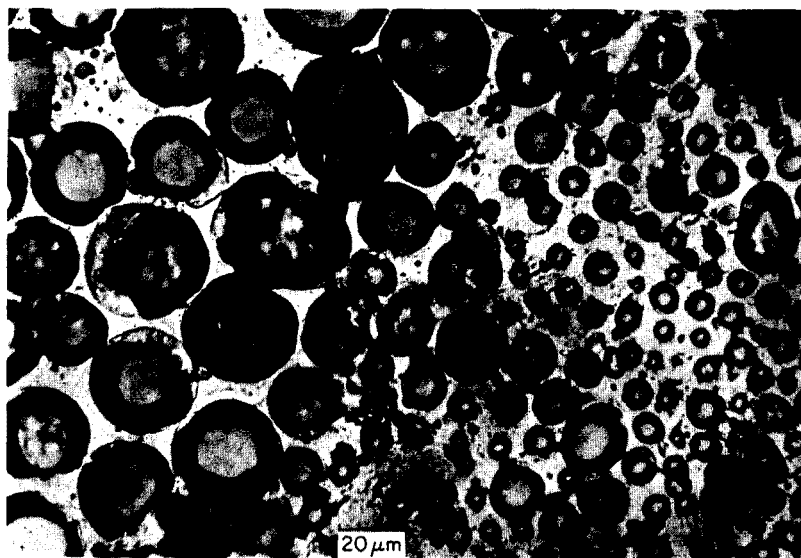


Fig. 4. Microphotograph of a polyvinyl chloride matrix membrane showing pores (dark circles) containing a solution of the calcium salt of didecylphosphoric acid in dioctylphenylphosphonate [843].



has also been proposed [174]. A review on solvent-polymer membranes including their applications for ion-selective electrodes has been published [202].

A Selectrode with a similar PVC membrane [180, 194] is shown in Fig. 5. In this case the membrane is in contact with the Teflon-graphite cylinder by means of a "reference layer" containing a mixture of Hg,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{CaSO}_4$  and saturated KCl solution in the case of a calcium-selective electrode [194].

Graphite paste electrodes were introduced to voltammetry by Adams [205]. Similar systems based on a mixture of graphite powder with a liquid ion-exchanger can function as membranes of ion-selective electrodes [173, 175, 196]. The construction of such electrodes is shown in Fig. 6. Graphite paste electrodes sensitive to  $\text{Cl}^-$  [196],  $\text{NO}_3^-$  [173, 196] and  $\text{Ca}^{2+}$  [196] have been prepared. A carbon paste electrode containing paraffin wax or Nujol with silver salt precipitates shows an appropriate response to halide and silver ions [187].

The coated-wire electrodes (see, e.g. [150a, 183, 184, 191]), have already been mentioned in Part I, p. 380. For an anion-selective coated-wire

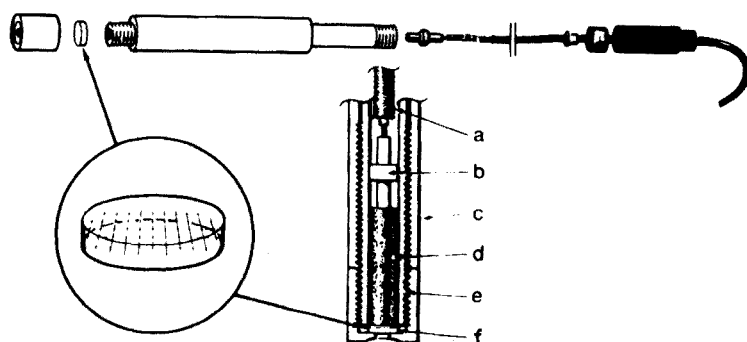


Fig. 5. A Selectrode with a PVC film membrane: (a) screening cable; (b) metallic contact; (c) outer tube made of Teflon; (d) cylinder of graphite hydrophobized by Teflon; (e) Selectrode body (Radiometer); (f) PVC membrane reinforced by a nylon net. The "reference layer" is situated between (d) and (f) [194].

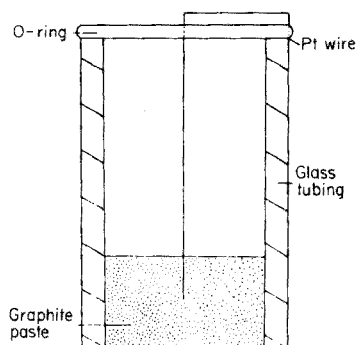


Fig. 6. An ion-selective graphite-paste electrode [196].

electrode [150a], a solution of Aliquat 336 S in 1-decanol is shaken with an aqueous solution of the sodium salt of the appropriate anion. A platinum wire electrode is dipped into a solution of PVC in cyclohexane, allowed to become almost dry, and then soaked with the decanol ion-exchanger solution. In another modification of the method, the electrode is directly covered with a PVC layer plasticized with the ion-exchanger solution. Such electrodes can be stored in air before use. Their selectivity differs somewhat from those of liquid-membrane electrodes. A coated-wire electrode sensitive to ionic surfactants has been prepared by solidification of the solution of the ion-exchanger zephiramine (tetradecyldimethylbenzylammonium dodecylbenzenesulphonate) on the surface of a platinum wire by addition of naphthalene [184].

A continuously renewing surface was accomplished in the dropping ion-selective electrode proposed by Skobets et al. [198, 199]. A Nernstian response of this system to  $\text{Br}^-$  [198] and  $\text{I}^-$  [199] was found in the concentration range  $10^{-1}$ — $10^{-6}$  M.

The potentiometric gas-sensing electrodes [192] are usually based on a microporous gas permeable hydrophobic membrane separating the analyzed liquid or gaseous medium from the ion-selective electrode, immersed into a suitable electrolyte solution (Fig. 7). The gas transported by diffusion through the membrane pores filled with air dissolves in the solution to form the ionic species determining the electrode potential. In addition to this type of membrane electrode, systems with homogeneous plastic films may be used, but the gas permeability across the most suitable material — silicone rubber — is still several orders of magnitude lower than with the Orion membrane.

Most of the gas-sensing electrodes contain glass electrodes as an internal sensor, thus being out of scope of the present review. Among these systems

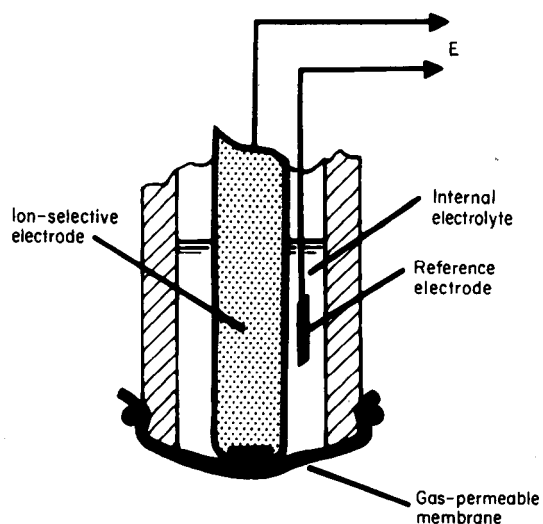


Fig. 7. The construction of a gas-sensing electrode (from Orion Research Newsletter 6 (1974)).

belong the most important sensors, the twenty year old  $\text{CO}_2$ -sensing electrode [206] and the Orion Research ammonia probe (Model 95-10). Internal  $\text{Ag}_2\text{S}$  electrodes are used for the  $\text{H}_2\text{S}$  and  $\text{HCN}$  sensors. In the latter system, the internal electrolyte contains the  $\text{Ag}(\text{CN})_2^-$  complex and the electrode is sensitive to the decrease of silver ion activity when the cyanide concentration increases. Gaseous chlorine or bromine decompose in an aqueous electrolyte to the  $\text{XO}^-$  and  $\text{X}^-$  species (X being the halogen). The change in  $\text{X}^-$  activity is then sensed with the appropriate ion-selective electrode [128, 192]. Alternative versions of ammonia-sensing electrodes have been based on shifting the equilibria of complexes of  $\text{Ag}(\text{I})$ ,  $\text{Cu}(\text{II})$  and  $\text{Hg}(\text{II})$  with ammonia and determining the change in metal ion activity with an ion-selective electrode [182]. In the "air-gap" electrode, the electrolyte solution on the electrode is separated by an air space from the test solution in a closed chamber [193]. Since 1970 attempts have been made to combine an ion-selective electrode with a MOSFET-type transistor. According to Bergveld [177], this ion-selective probe combines the field effect present in the metal oxide—semiconductor field-effect transistor with the ion-selective effect present in the electrical double-layer at the interface between the solution and the surface of a glass electrode. It was named ISFET (ion-selective field-effect transistor) by Bergveld. The ISFET is similar to a MOSFET except that the metal gate of the latter has been replaced by an ion-selective membrane which is in contact with the solution [186, 189, 204]. The electrical potential difference which develops at the membrane-solution interface as a result of the ion exchange has the same effect on the drain current of the transistor as the modulating electrical potential applied to the MOSFET metal gate. This was achieved by depositing a PVC-type  $\text{Ca}^{2+}$ - or  $\text{K}^+$ -selective membrane directly on the insulating layer of the transistor [189]. The advantage of this system is its small size, so that it may be used, for example, in physiological studies.

The details of a flow system for the study of fast reactions by means of solid-state ion-selective electrodes have been described by Thompson and Rechnitz [200]. Farney and McCoy [181] designed a flow-through electrode unit for determination of particulate atmospheric nitrate based on a nitrate ion-selective indicator electrode and a fluoride reference electrode. A combination ion-selective electrode with a gel-type reference electrode has also been described [197].

#### *(ii) Calibration [207—216]*

The necessity of conventional scales of ionic activity for standardization of ion-selective electrodes has been stressed by Bates and Robinson [210]: "The lack of consistent standards for the calibration of ion-selective electrodes, if long continued, promises to lead to chaos". Their report to the Commission on Electroanalytical Chemistry, Analytical Chemistry Division of IUPAC, was based on ref. 35 of Part I. In the same vein, Bates [209] listed ion-activity scales for calibration of ion-selective electrodes

with the help of hydration numbers of individual ionic species in unassociated species. Ionic activity scales for a mixture of two electrolytes with a common cation have been presented [215]. Bagg and Rechnitz [207] measured ionic activities at high ionic strengths with halide-selective electrodes which could be used up to 4–5 M solutions, except for the iodide electrode which worked only at concentrations lower than 0.5 M. Using the Bates–Staples–Robinson convention (ref. 35 of Part I), they determined ionic activity coefficients at concentrations as high as 6 M NaCl, 4 M KCl, 4 M KBr, 3 M KF and 1 M LiCl.

The metal buffers which were introduced by Schmid and Reilley [217], are suitable for calibration of copper- [211, 212], cadmium- [216] and lead- [213] selective electrodes.

Very dilute calibration solutions can be prepared in situ by the coulometric method based, for example, on reduction of the Ag/AgI electrode [208]. In another calibration method, the solution of the potential-determining ion is continuously diluted and the electrode potential is measured simultaneously [214].

### (iii) Selectivity coefficient [38, 218–221]

It is obvious that even in the ideal cases discussed in Part I the selectivity coefficients are functions of the ion activity coefficients and the ion mobilities within the membrane, and that, particularly in solid-state membranes, are strongly influenced by the presence of interfering ionic species. Thus, the values of selectivity coefficients determined by one of the three methods described in Part I, p. 359–360 (or by the modification of the Pungor method suggested in ref. 453 of Part I) are, in fact, only operational quantities. The values may differ considerably depending on the method of determination as discussed in detail by Moody and Thomas [10].

In addition to the influence of non-ideality of the membrane system, the fact that the selectivity coefficient depends on the concentration of potential-determining ions is clear from the theory which assumes an ideal behaviour of the membrane components. This is the case with the Sandblom–Eisenman–Walker theory of liquid membranes with a dissolved charged ion-exchanger (Part I, p. 348–350) where, in the final formula (eqn. 96) no constant term  $K_{ij}^{\text{Pot}}$  can be found. The dependence of the selectivity constant on the interferent concentration was predicted by Wuhrmann et al. [221] for the case of different charge numbers of the two ions which determine the membrane potential [cf. 218a]. The selectivity constant of ion-carrier electrodes is concentration-dependent when a lipophilic anion is dissolved in the membrane (see e.g. [38]). Buck [218] has suggested the term apparent selectivity constant  $K_{JK}^{\text{Pot}}$  (app.) defined by the equation

$$\ln K_{JK}^{\text{Pot}} (\text{app.}) = \ln \{ \exp [(E_{JK} - E_J)/S] - 1 \} - \ln a_K/a_J \quad (35)$$

where  $E_{JK}$  is the potential of the ion-selective electrode in the presence of

the ions  $J^+$  and  $K^+$  at activities  $a_K$  and  $a_J$ ,  $E_J$  the potential in the presence of the ion  $J^+$  alone at an activity  $a_J$ , and  $S$  is the slope of the  $E-\ln a_J$  dependence

$$E = E_0 + S \ln a_J \quad (36)$$

Equation (35) can be used only in the activity range where eqn. (36) is valid. In simple cases (rapid interfacial processes and simple diffusion potential in the membrane), the apparent selectivity coefficient is a function of the ratio  $a_K/a_J$  only, whereas in more complicated cases, it depends on the activity ratio as well as on the individual ionic activities.

*(iv) Response time [15, 222–230]*

Although the response time is undoubtedly one of the principal characteristics of an ion-selective electrode, a consistent theory pertaining to this phenomenon was, as pointed out recently by Shatkay [229], not available before 1975, with the notable exception of a paper by Markovic and Osburn [224]. Thus, on the whole, it was necessary to resort to semi-empirical interpolation formulae describing, sometimes quite satisfactorily, the potential–time dependence between the initial potential  $E_i$  and the steady-state potential  $E_{st}$ . These relationships are either exponential

$$E(t) = E_i + (E_{st} - E_i) \exp(-kt) \quad (37)$$

or hyperbolic

$$E(t) = E_i + (E_{st} - E_i) kt/(1 + kt) \quad (38)$$

where  $k$  is a constant.

Markovic and Osburn [224] suppose that a stagnant (hydrodynamic or Prandtl) layer remains at the surface of the electrode when the solution concentration is changed from  $c_1$  to  $c_2$ . Through this stagnant layer the solute is transported from the bulk (concentration  $c_2$ ) towards the surface (concentration  $c_1$ ). A similar stagnant layer is implicitly assumed in the theory of the cyanide electrode (Part I, p. 336) and the phenomenon has been discussed in greater depth, for example, in ref. 144. In the simplification used by Markovic and Osburn [224] (cf. [227], [229]) the concentration gradient in the Nernst layer (which is in fact narrower than the stagnant layer) is linear, so that the flux of solution is given by the expression

$$J(t) = -\frac{D(c_2 - c')}{\delta} \quad (39)$$

where  $D$  is the diffusion coefficient,  $c'$  the time-dependent concentration at the surface of the electrode and  $\delta$  the thickness of the Nernst layer. For the change of the average concentration  $c_{av}$  in the Nernst layer we have

$$\frac{d c_{av}}{dt} = \frac{J}{\delta} \quad (40)$$

Since

$$c_{av} = \frac{1}{2} (c_2 - c_1) \quad (41)$$

we immediately obtain the solution of the resulting differential equation [224, 228]

$$c' = c_1 + (c_2 - c_1) [1 - \exp(-2Dt/\delta^2)] \quad (42)$$

If the ion-selective electrode shows a Nernstian response, eqn. (42) leads to

$$E(t) = E_1 + (RT/F) \ln \{1 + [(c_2 - c_1)/c_1] [1 - \exp(-2Dt/\delta^2)]\} \quad (43)$$

or according to Morf et al. [227]

$$E(t) = E_{st} + (RT/F) \ln [1 - (1 - c_1/c_2) \exp(-t/\tau')] \quad (44)$$

where the time constant  $\tau'$  is given by the expression

$$\tau' \approx \delta^2/(2D) \quad (45)$$

On the basis of eqn. (44), the dynamic behaviour for the electrode will differ [227], depending on whether the concentration of solution (1) is increased or decreased.

An exponential interpolation formula like eqn. (37) follows from eqn. (43) only for small values of  $(c_2 - c_1)/c_1$ . A more elaborate treatment [224] supplies a result which, particularly for higher values of time, is not essentially different from eqn. (43). Unfortunately, the  $\text{Ag}_2\text{S}$  electrode in varying  $\text{AgNO}_3$  solutions shows a more complicated behaviour than that for which the simple formula (37) could be used, or than that predicted by eqn. (43); eqn. (38) or a sum of several exponentials gives a better fit [229]. A hyperbolic  $E-t$  dependence has also been found in a study of the fluoride-selective electrode in fast flow systems [225].

Rangarajan and Rechnitz [228] studied the response time by means of a flow-mixing method; the electrode was placed in a mixing chamber into which the electrolyte solution at alternate concentrations was introduced at different flow rates. The response time, defined as  $t_{95}$  (the time interval in which  $E(t)$  reaches 95% of the difference  $E_{st} - E_1$ , as shown in Fig. 8 [222], was then plotted against reciprocal flow-rate; remarkably enough, a constant value of extrapolated response time for an infinite flow rate was obtained independent of the ratio of the initial and final concentrations and even of the nature of the ion-selective electrode ( $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  electrodes were studied). It is, however, not clear how the authors compared their results with the Markovic-Osburn model [224].

In an interesting experimental approach to the response time, Lindner et al. [223] used a wall-jet flow of the electrolyte in a direction perpendicular to the electrode. The hydrodynamics of the problem are presented clearly and the important idea of variation of the potential of the ion-selective electrode along a radial coordinate is introduced, but the authors did not attempt to analyze their results by means of a quantitative transport theory.

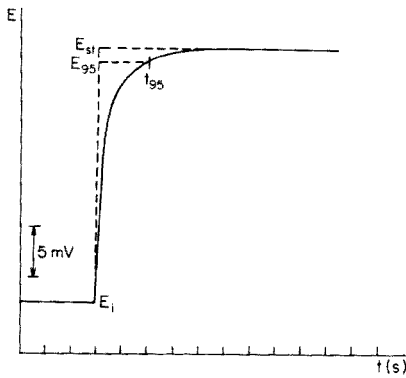


Fig. 8. Potential-time profile of calcium ion-selective electrode after a sudden impressed change in  $\text{Ca}^{2+}$  activity. No interfering ions present [222].

The contributions referred to so far in this section have dealt with fixed-site electrodes. In comparison with those, liquid-membrane electrodes show considerably larger response times [222]. The response time of neutral carrier electrodes has been analyzed theoretically by Morf et al. [227]. In their theoretical treatment, the effects of interfering ions and the charging of the double layer at the interface membrane-outer electrolyte solution (cf. [152]) were neglected. The transport of ion  $J^+$  in the adherent electrolyte layer occurs across the Nernst layer of thickness  $\delta$ , while inside the membrane a simple linear diffusion of the complex  $C_{JV}$  takes place. The interfacial equilibrium is given by eqn. (21) which, for the sake of simplicity ( $C_{JV} = C_X$ ) can be written as

$$C_{JV}(p) = K c'_J \quad (46)$$

where  $c'_J$  is the concentration of  $J^+$  in electrolyte (1) close to the phase boundary. For the flux of  $J^+$  in electrolyte (1) close to the phase boundary

$$J' = D' \frac{c_{J,2} - c'_J}{\delta} \quad (47)$$

where  $c_{J,2}$  is the final concentration of  $J^+$  in solution (1). A continuity relationship is valid between the fluxes in solution (1) and in the membrane at the phase boundary

$$J' = J(p) \quad (48)$$

If it is assumed that the effective diffusion-layer thickness  $(\pi Dt)^{1/2}$  (cf. [144]) is considerably smaller than the thickness of the membrane ( $d$ ), transport within the membrane will be described by the partial differential equation for linear diffusion in a semi-infinite space from Fick's second law. The resulting flux equation is

$$J' = DK \frac{c'_J - c_{J,1}}{(\pi Dt)^{1/2}} \quad (49)$$

where  $D$  is the mean coefficient of the complex  $JV^+$  together with the accompanying anion  $X$  in the membrane. If the time constant  $\tau$  is defined as

$$\tau = \frac{DK^2\delta^2}{\pi D'^2} \quad (50)$$

then by combining eqns. (47), (48) and (49) we obtain

$$c'_J - c_{J,1} = [c_{J,1} - c_{J,2}] \left( 1 - \frac{1}{(t/\tau)^{\frac{1}{2}} + 1} \right) \quad (51)$$

and, finally, for a dilute solution

$$c'_J/c_{J,2} = \exp [F(E(t) - E_{st})/RT] = 1 - \left( 1 - \frac{c_{J,1}}{c_{J,2}} \right) \frac{1}{(t/\tau)^{\frac{1}{2}} + 1} \quad (52)$$

Figure 9 shows the characteristic behaviour of the electrode if the concentration in the test solution is decreased or increased, as predicted by eqn. (52). Thus, in practical work, it is advisable to store the electrode in a solution of a lower concentration than that of the test solution; this has been already noted [222, 230] as an experimental finding. Obviously the effective response time will be shorter if the time constant  $\tau$  is smaller. Therefore the membrane solvent should be of low polarity, the ion carrier should be present at a moderate concentration, and the Nernst layer thickness should be small, which can be achieved by means of stirring [227]. Figure 10 shows a comparison of the transient behaviour of a valinomycin electrode with a plastic matrix and polar and non-polar solvents [227]. Theory and experiment

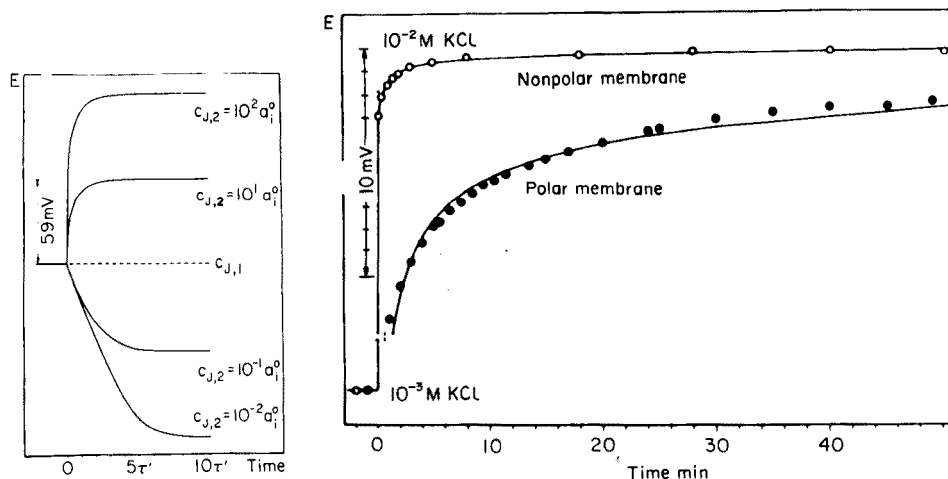


Fig. 9. Theoretical  $E-t$  profiles for a neutral ion-carrier electrode calculated from eqn. (52) [227].

Fig. 10. Time profiles of a  $K^+$ -selective valinomycin electrode based on a PVC matrix. The initial solution contained  $10^{-3}$  M KCl and the final solution  $10^{-2}$  M KCl. The polar membrane solvent was *o*-nitrophenyloctyl ether while the non-polar membrane contained dipentyl phthalate [227].



have also been compared for a silicone—rubber valinomycin electrode [223].

An experimental study of response times of PVC matrix membrane electrodes has been published [226].

*(v) Temperature coefficient [231–234]*

The temperature coefficients of ion-selective electrodes have been discussed in some detail [8, 233]. This quantity can be divided into several terms: the temperature coefficient of the “standard” potential of the electrode, the temperature coefficient of the activity term and, finally,  $(R/z_i F) \ln a_i$ . The last-named term is the correction which is usually performed by the temperature compensator of a pH meter. The second term can, at least in some cases, be derived from the tabulated values of ion activities (see Calibration, p. 18). The temperature coefficient of the standard potential of the electrode consists of terms referring to the inner reference electrode and to the membrane potential. The latter term depends on the temperature coefficient of the selectivity coefficient [8]. The experimental determination of the temperature coefficient of the standard potential is carried out with an isothermal cell or by a non-isothermal method (“thermal cell”) where the reference electrode dipping into the external solution is kept at 25°C [233]. This latter method was also used by Lindner et al. [232].

A detailed study of the solid-state chloride-selective electrode in the temperature range 0°–95°C was made by Baucke [231, 231a], who criticized [231a] the procedure described in ref. 378 of Part I.

A method for compensation of temperature variation of the sample measured with an ion-selective electrode has been described [234].

*(vi) Direct potentiometry [126, 134, 142, 235–241]*

The important problem of the detection limit in direct potentiometry [126], which was touched on earlier (p. 4), has been discussed by Parthasarathy et al. [240]. An indirect determination of a component of a sample by addition of an excess of an agent to which the electrode responds has been described [238]. Several papers deal with adaptation of conventional pH meters for measurement of other ion activities [239, 241] and with conversion of signals from ion-selective electrodes to a linear concentration scale [235, 237]. A nomogram for the standard addition method has been reported [236].

*(vii) Potentiometric titrations [242–248]*

The errors in the Gran method (Part I, p. 361) have been discussed [243, 244, 247] as well as the intrinsic end-point errors in precipitation and compleximetric titrations with ion-selective electrodes [246]. The precision of the potentiometric null-point determination in the titration of NaF with a solution of  $\text{Th}(\text{NO}_3)_4$  has been reported [242]. Null-point potentiometry (Part I, p. 362) has been discussed by Buffle et al. [245]. A differential potentiometric titration with two ion-selective electrodes with different selectivities (e.g., the  $\text{Ag}_2\text{S}$ — $\text{AgI}$  pair) has been described [248].

(viii) *Automatic procedures* [66, 82, 93, 110, 111, 128, 249–267]

Ion-monitoring with ion-selective electrodes has been reviewed several times [66, 82, 93, 110, 111, 131, 251, 253].

The principles of automated direct potentiometry have been discussed [262], and the method has been applied to the simultaneous determination of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  [264] and to water hardness estimations [263]. Another example of this technique [250] is an on-line computer-controlled potentiometric analysis system, based on standard addition to the unknown solution in a cell containing an ion-selective electrode and a reference electrode. The cell e.m.f. values acquired by a computer-optimized sampling technique and the standard addition data are fitted to the Nernst equation by means of the nonlinear least-squares technique. A related automated gradient addition technique [252] was used for sulphide monitoring with  $\text{Hg}^{2+}$  addition. Simultaneous computer-controlled monitoring with up to five different ion-selective electrodes in a flowing system has been described [266]. The monitoring of particulate atmospheric nitrate can be done in a flow-through system with a nitrate ion-selective electrode and a fluoride electrode as reference [181].

Automated potentiometric titrations [249, 254–257] are a subject of much interest. The principal components of an on-line minicomputer process titrator for sea-water analysis with ion-selective electrodes [249] are shown in Fig. 11. Input voltage signals from the ion-selective electrodes are transferred via an analogue scanner to a digital voltmeter where they are digitalized before being transferred to the minicomputer via a digital scanner. As the digital computer cannot read a signal more than 15 times per second, rapidly changing signals must be transferred to the computer via an A/D converter. The results are obtained on either of the two terminals or graphically on the X–Y plotter. Another automatic system [255] has been described for titrations with ion-selective electrodes as detectors and a cathode-ray display of the titration curve, Gran plot, second derivative and error function. The equivalence point was obtained by least-square regression analysis. An example of a titration of bromide with  $\text{Ag}^+$  ions is shown in Fig. 12. An ion-selective electrode system for continuous monitoring of cyanide is based on the computerized Gran plot technique [254]. The conditions for correct functioning of Gran plots have been established by use of a digital computer [256].

Ion-selective electrodes can be used as chromatographic detectors [259a, 261]. An example of detecting  $\text{NO}_2^-$  and  $\text{NO}_3^-$  with a nitrate-selective electrode after an ion-exchange liquid chromatographic separation is shown in Fig. 13 [261].

An AutoAnalyzer system for kinetic enzyme determinations [258] is shown in Fig. 14. The system consists of an automatic sampler, a proportioning pump, a water bath capable of temperature control to  $\pm 0.1^\circ\text{C}$ , a flow-through electrode assembly and a high-impedance recording voltmeter. The samples are aspirated into a stream of air-segmented substrate solution flowing at

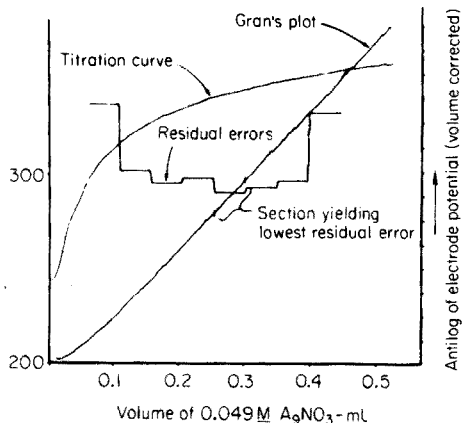
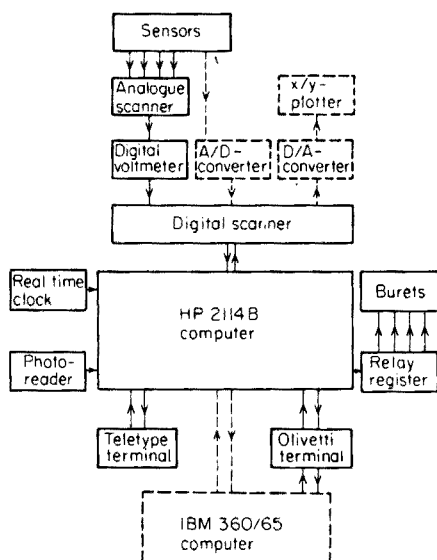


Fig. 11. Computerized data-collecting and processing system in use at the Department of Analytical Chemistry, University of Gothenburg [249].

Fig. 12. Titration of  $35.5 \mu\text{g Cl}^-$  with  $\text{Ag}^+$  in  $0.1 \text{ M KNO}_3$  [255].

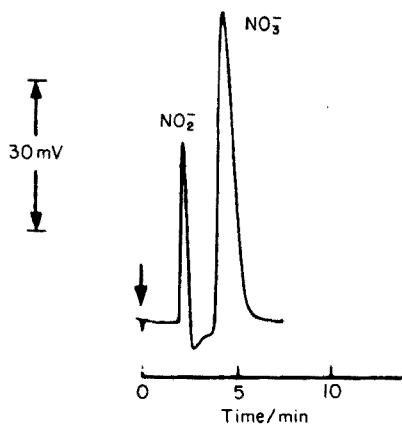


Fig. 13. Chromatographic separation of a  $1\text{-}\mu\text{l}$  sample containing  $0.1 \text{ M NO}_3^-$  and  $0.1 \text{ M NO}_2^-$  with a  $\text{NO}_3^-$ -selective electrode (Orion Model 92-07). Eluent  $0.01 \text{ M KH}_2\text{PO}_4$ ,  $0.01 \text{ M Na}_2\text{SO}_4$  [261].

constant rate, so that the change in concentration of the indicator ion produced (or consumed) is proportional to the activity of the enzyme.

A small analog computer has been used in continuous measurement of intracellular ion activities with ion-selective micro-electrodes [250a].

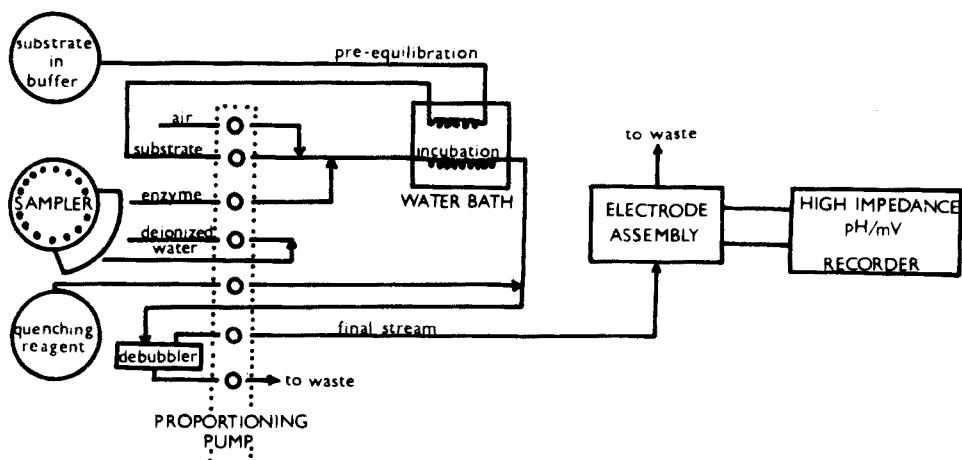


Fig. 14. Schematic diagram of a continuous flow apparatus. The solid lines represent flexible tubings and/or borosilicate tubes [258].

For biochemical assays in space vehicles (pH,  $\text{CO}_2$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ , total Ca and ionized Ca in blood), the Space-Stat analyzer was designed in Orion Research [128]. The same company produces a Stat analyzer for  $\text{Na}^+$  and  $\text{K}^+$  in whole blood and an Ionized Calcium Analyzer. The STAT-ION (Technicon) determines simultaneously  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  in body fluids [259]. Automatic direct potentiometry of  $\text{Na}^+$  and  $\text{K}^+$  in blood serum with the SMAC system has been described [260, 265].

(ix) *Response in non-aqueous media* [267–275]

The use of ion-selective electrodes in non-aqueous media is subject to grave limitations including dissolution of membrane material by complexation with the solvent, attack on the membrane matrix or on the seal between the membrane and the electrode body, etc. It is obvious that measurements with liquid-membrane electrodes are almost impossible.

The lanthanum trifluoride electrode gives a reproducible but rather slow response in non-aqueous media [268]. It has been used for a reaction study in water-propylene carbonate mixture [274] and as a reference electrode in an acetonitrile-water mixture [273]. Measurements with silver halide electrodes in various non-aqueous solvents have been attempted [267, 269, 271, 272]. Ion-selective electrodes based on precipitates embedded in a silicone rubber matrix function only in mixtures with a high content of water [270].

For measurements in fused alkali metal nitrates, a liquid membrane electrode with ion-exchangers such as tetraalkylphosphonium nitrate [272a] is suitable. A student experiment with ion-selective electrodes in fused salts has been reported [275].

*(x) Response in biological fluids [107, 276–280b]*

The general features, including the potentialities and limitations, of ion activity measurements with selective electrodes in biological media [276, 279] including *in vivo* analysis [280] have been outlined.

When the ions are bound in complexes with components of the medium to only a small degree (e.g. alkali metal ions or chloride), comparison of the data acquired with ion-selective electrodes with those obtained by other methods shows the validity of the electrode technique [277, 280a].

Reference standards for the determination of potassium and calcium ion activities in blood serum have been listed [278].

*(xi) Ion-selective electrodes as reference electrodes [181, 268, 281, 282]*

Ion-selective electrodes can also be used as reference electrodes, particularly in cells without a liquid junction [281]. The fluoride electrode is suitable for this purpose [181, 268]. An ion-selective electrode has even been used in voltammetric measurements [282].

## C. FIXED-SITE ION-SELECTIVE ELECTRODES

The theoretical foundations of the response of fixed-site electrodes were discussed in Part I; more recent papers have given a deeper insight only into the behaviour of the electrodes based on heavy metal chalcogenides (see p. 5). There has been no substantial progress in the design and technology of the main types of this group of electrodes. Thus, the present section will deal mainly with applications of solid-state electrodes; earlier reviews are available [283–285].

*(i) Silver halide-selective electrodes [286–440]*

The photosensitivity of silver halide electrodes, which is an unwelcome property of homogeneous silver halide electrodes in particular, was investigated by Donners and de Wooy's [308] and by Veselý [434]. Halide-selective electrodes have been used as detectors for halide and cyanide ions after combustion of oils and chromatographic separation [354]. A general study of the potentiometric determination of halide ions has been published [291]. The halide electrodes have been used for estimation of halides in alkaloids [343] and for a study of complexes of benzene-1,2-diamine with nickel(II) halides [309].

*Chloride-selective electrodes.* Sulphide ions interfere with the determination of chlorides [388]. The chloride determination in phosphate rock is affected by the presence of  $\text{Br}^-$ ,  $\text{I}^-$  and  $\text{S}^{2-}$  which poison the membrane surface [310]. Factors influencing the sensitivity of the AgCl electrode have been reported [396]. The preparation and properties of a homogeneous AgCl membrane have been described [287]. A suitable chloride-selective electrode can be prepared even in a student laboratory course [372]. A chloride-selective electrode containing  $\text{ZrO}_2$  in silicone rubber has been

proposed [425]. The applications of chloride-selective electrodes are listed in Table 3. It should be noted that the determination of chloride in sweat is a basic diagnostic method for cystic fibrosis.

The chloride-selective electrode has been used in the micro-determination of hydroxyl groups in polymers. Under the action of phosgene, the OH group is converted to the OCOCl group. By reaction with *m*-chloroaniline, chlorine was separated from this group as  $\text{ClC}_6\text{H}_4\text{NH}_2 \cdot \text{HCl}$  which was then titrated with silver nitrate to the potentiometric end-point [409].

Sulphur dioxide can be determined by passing through a chloromercurate—

TABLE 3

## Applications of chloride-selective electrodes

Use	Reference
Study of Cd and Zn chloride complexes	296
Study of magnesium complexes	420
Microdetermination, of Cl in organic compounds	323, 403
—, of amino groups	324
Chloride, in serum	289, 313, 326, 345, 364
—, in fruit juice	290
—, in waters	292, 373, 384, 390, 392, 428
—, in sweat	295, 298, 319, 321, 389, 422
—, in Cu plating baths	303
—, in phosphate rocks	311, 393
—, in whole blood	313, 374
—, in soils and soil extracts	314, 327, 334, 362, 363, 365, 391, 412, 417, 427
—, in skin surface	318
—, in silicate rocks	328, 330
—, in milk	329, 421
—, in corn syrup	341
—, in meat products	344
—, in a mixture of water with alcohols	348, 360, 385
—, after gas chromatographic separation	355
—, in chloramphenicol ointment	359
—, in urine	364
—, in sugar industry	376
—, in surface coatings	382
—, continuous monitoring of	383, 384, 399
—, in pulping liquors	395
—, in beer	404
—, in yttrium compounds	413
—, in $\text{Al}(\text{OH})_3$	419
—, in brewing water	429
—, in pesticides	433
Study of dissolution rate of KCl tablets	426

EDTA solution, two  $\text{SO}_3^{2-}$  replacing four chloride ions in the tetrachloro-mercurate. The chloride released is then determined by the standard addition method [361].

Cyclization of methyl-bis-( $\beta$ -chloroethyl)amine hydrochloride [353] and the formation of aluminium chloride diisopropylate [414] can be followed with chloride electrodes.

The chlorinated solvent in the decaffeinated coffee samples can be detected with a chloride electrode [378].

*Bromide-selective electrodes.* Various applications of these electrodes are shown in Table 4. The electrode can serve for direct potentiometry of  $\text{SCN}^-$  [357]. The cure rate of epichlorohydrin-bisphenol A epoxy resins can be estimated by reaction of the substance suspended in *p*-dioxane with HBr and potentiometric titration of excess of halide with  $\text{Hg}(\text{ClO}_4)_2$  and the bromide electrode [410, 411]. The oscillating Zhabotinsky reaction has been followed with this electrode [358]. Stability constants of silver bromide complexes in water and water-acetone mixtures have been determined [301, 302]. The basic properties of the electrode have been described [315].

*Iodide-selective electrodes.* The properties of the iodide-selective electrode depend strongly on the pressure and on the procedure of preparing the AgI precipitate, because either a  $\beta$ -hexagonal or a  $\gamma$ -cubic modification may be formed [434]. The former shows a better performance in the ion-selective electrode, but unfortunately, is gradually converted to the  $\gamma$ -modification.

Electrodes based on a mixture of AgI and  $\text{Ag}_2\text{S}$  show an even higher conductivity than  $\text{Ag}_2\text{S}$  alone. The proportion of the ternary compound present,  $\text{Ag}_3\text{SI}$  (see ref. 562 of Part I) increases with higher applied pressure [434]. The upper concentration limit for iodide determination is considered to be established by silver iodide complex formation [397]. Scanning electron microscopy of the crystal membrane surface showed that the deterioration of the behaviour of the electrode after protracted exposure to 1 M iodide is due to pore formation [418].

Various applications of iodide-selective electrodes are listed in Table 5. The electrodes also show a response to  $\text{Hg}^{2+}$  ions [333, 400a, 438] and to

TABLE 4

## Applications of the bromide-selective electrodes

Use	Reference
Bromide, in soils and plant tissues	286
—, in waters	298a
—, in plasma	304, 402
—, in wine	317
—, in soft drinks	431
Microdetermination of Br in organic compounds	323, 403

TABLE 5

Properties and applications of iodide-selective electrodes

Use	Reference
General papers	307, 342, 350, 352, 375, 380, 401, 405, 416, 424, 434, 436, 438
Iodide, in milk	294
—, in urine	381
—, in water	440
Halides in halogenated pharmaceuticals	306
$I^-$ , $I_2$ , $I_3^-$ equilibrium study	368
Iodine in selenium	439

$Au^{3+}$  ions [438]. The iodide electrode can be used for determination of oxidants reacting with iodide (total content of oxidants in air [430],  $IO_3^-$  [400],  $IO_4^-$  [335],  $SO_3^{2-}$  [338], palladium ions in catalysts [406]). The iodide electrode has been used as indicator electrode in titrations with silver(I) solutions for the determination of formaldehyde (after reduction of  $I_2$ ) [337] and of tetraphenylborate [432]. It has also been used in the determination of thiourea [316], of iodate after reduction with hydrazine [325], and of Bi(III) by titration with pyrrolidine dithiocarbamate [296]. It indicates the end-point of the titration of potassium polyvinylsulfate with tetradecyldimethylbenzylammonium chloride in the presence of iodide [339]. It can also be used in the kinetic microdetermination of Cr(VI) [349]. Since molybdenum and tungsten ions catalyze the reaction between hydrogen peroxide and iodine, a catalytic determination of these ions can be done by monitoring the iodide formed [288, 347]. A similar method is possible for vanadium(IV) determination [346]. The iodide permeability across phosphatidyl model membranes was measured by the iodide electrode [407]. This electrode also shows a response to diammine tetrakis(isothiocyanato)chromate(III) [379].

The preparation and analytical evaluation of a heterogeneous membrane based on AgSCN for a thiocyanate-selective electrode has been described [337, cf. 423].

*Cyanide-selective electrodes.* As has been discussed in Part I, the iodide electrode shows a response to cyanide ions; the response originates from dissolution of the AgI membrane with a resulting increase of iodide ions in the vicinity of the membrane. The applications of this electrode are listed in Table 6. A flow-through electrode for cyanide determination has been designed [94]. In some media it is advantageous to separate cyanide by distillation before determination with a cyanide electrode [398]. Formaldehyde, thioglycolic acid, hydroxylamine, pyridine and pyrazolone interfere with the cyanide determination [386]. The cyanide electrode can be used as an indicator electrode for titrimetric determination of pentacyanonitrosyl ferrate [415].



TABLE 6

## Applications of the cyanide-selective electrodes

Use	Reference
General papers	305, 340, 369, 438
Cyanides, monitoring in respiration and photosynthesis	297
—, in waters	298a, 300, 320, 332, 387, 408
—, in industrial wastes	300
—, in biological material	300
—, in air	300
—, in the presence of chelating agents	331, 356
—, in electroplating baths	351, 366, 367
—, in tobacco smoke	435

An assay of  $\beta$ -glucosidase can be based on the decomposition of amygdaline by the enzyme and the measurement of the cyanide formed with the electrode [370].

Rhodanase catalyzes the reaction  $S_2O_3^{2-} + CN^- \rightarrow SCN^- + SO_3^{2-}$ . The decrease in cyanide concentration is monitored with the cyanide electrode and the reaction rate constant is a measure of rhodanase activity [322, 336, 371].

Determinations of cyanide with a cyanide electrode based on AgI and with a cyanide gas-sensing electrode have been compared [128]. In the gas-sensing version the inner sensor is based on a  $Ag^+$ -sensing electrode ( $Ag_2S$  electrode) in a  $Ag(CN)_2^-$  solution. The increase in the sensitivity of the cyanide determination with this type of electrode has been reported by Fleet and Storp [312]. Cyanide in the p.p.b. range can be determined with an  $Ag_2S$  electrode [299].

(ii) *Silver sulfide-selective electrodes [441–511]*

The methods of preparation, the basic properties and the response to  $S^{2-}$ ,  $Hg^{2+}$  and  $CN^-$  of  $Ag_2S$  electrodes have been discussed by Veselý et al. [506] who also reviewed interesting, though unsuccessful, early attempts to obtain a sulfide electrode. Several papers have been concerned with pressed pellet-type sulfide electrodes [458, 468, 478, 491, 492, 511]. Electrodes based on silver selenide and telluride [457, 458], and on  $Ag_2S$  precipitates in a silicone rubber matrix [495] have been reported. A  $Ag_2S$  Selectrode has been prepared [494]. The skeptical view of argentimetric applications of ion-selective electrodes [470] seems rather misplaced. Applications of the sulfide-selective electrode are listed in Table 7.

An  $Ag_2S$  indicator electrode is satisfactory for titrations with Ag(I) of the products of samples pyrolyzed in a stream of ammonia [507], and for indirect determinations of phosphate and arsenate [504] and multivalent cations [471, 472]. Sulfide can be determined in mixtures containing

TABLE 7

## Applications of sulfide-selective electrodes

Use	Reference
S <sup>2-</sup> , in soils	444, 459
—, in waters	447, 448, 474, 482, 489, 502, 510
—, in river sediments	453
—, after conversion of polysulfides and sulfites from pulping liquors	449, 456, 486, 487, 503
—, in lime	473
—, in silicates	476
—, in pig iron	490
—, in beer	501
H <sub>2</sub> S, in air	452
—, in tobacco smoke	475
Ag <sup>+</sup> in urine	461
—, in waters	298a, 496
—, in fixing baths	508
Study of AgCl solubility in various solvents	445
<sup>35</sup> S in sulfate solutions	446
Determination of solubility products of silver arsenate and arsenite and sulfide	450
Study of H <sub>2</sub> S and methylmercaptan from sulphur-containing amino acids	455
Argentimetric determination	
thioacetamide	451, 484, 485
sulfide	454, 481
<i>p</i> -urazine	463, 466a
halides	466, 497, 509
thiourea	466a, 485
trace sulfur in petroleum	467, 499
mercaptopyridines	479
phenylthiourea and <i>N,N</i> -diphenylthiourea	483
NH <sub>4</sub> diethyldithiophosphate	493
azide	497
thiols	488, 498
thiocyanate	509
Titration of S <sup>2-</sup> , by sodium plumbite	477
—, by lead nitrate	500

polysulfides after their conversion to the thiosulfate [462]. Titrations with triethylenetetramine or tetraethylenepentamine are possible when silver nitrate is used as indicator with an Ag<sub>2</sub>S electrode [460]. Mercaptans [465] and thiophenic compounds [464] can be identified by gas-chromatographic separation and conversion to H<sub>2</sub>S which is then sensed with the Ag<sub>2</sub>S electrode; see also [469].

An automated determination of sulfur-containing proteins [441, 442] is based on measurement of the free silver(I) activity with the electrode, after

silver-mercaptide formation with the sulfur groups in the proteins. This method can be used in clinical analysis of total protein changes and of albumin-globulin ratios in serum. Monitoring of the antibody-antigen precipitin reaction can be based on this method [443]. The immunoglobulin fraction of goat antiserum to human serum albumin precipitates the antigen before analysis of the residual antibody in the supernatant liquid. The analysis with the electrode is done either after the precipitin has been dissolved in dilute alkali or by determining the residual protein in the supernatant liquid.

The  $\text{Ag}_2\text{S}$  electrode also responds to cysteine [505], and has been used for the study of *o*-acetylserine sulphydrylase [480].

(iii) *Divalent-metal chalcogenide electrodes [512–569b]*

The theory of the divalent-metal chalcogenide electrode was outlined on p. 5, and in Part I, p. 367.

*Copper-selective electrodes.* Several papers have been devoted to preparation of electrodes based on  $\text{Cu}_2\text{S}$  [536, 538, 554],  $\text{Cu}_{2-x}\text{S}$  precipitates [549, 550, 551, 564],  $\text{CuS}$  [513a, 555] and  $\text{Cu}_{2-x}\text{Se}$  [512, 513, 569b]. Flow-through electrodes have been designed [518, 563]. The unwelcome effect of chloride [522] was re-examined. At submicromolar concentrations, the copper electrode can change the copper concentration of the analyzed solution, because oxygen attacks the surface of the electrode [517]. Oxidizing agents corrode the electrode surface and undefined potentials are formed in the cracks [540]. Various applications of the copper electrode are shown in Table 8.

TABLE 8

Applications of copper-selective electrodes

Use	Reference
Study of Cu(II) complexes with EDTA and DTPA	514
Titration to a Cu-EDTA indicator, of Zr(IV), Fe(III) and Th(IV) with EDTA	515
—, of Sc(III) and Th(IV)	560
—, of $\text{Cu}^{2+}$ with EDTA	520, 565
—, of 8-hydroxyquinoline with $\text{Cu}^{2+}$	523, 524
—, of citrate with $\text{Cu}^{2+}$	523
Study of Cu(II) complexes with uramildiacetic acid	526
Study of Cu(II) complexes with glycine, EGTA and EDTA	529
Study of Cu(I) complexes in acetonitrile	531
Study of Cu(II) complexes of EDTA and NTA	547
Study of Cu(II) complexes with phenanthroline, bipyridine, iminodiacetate, glycine, ammonia and acetate	547
Compleximetric titrations with copper i.s.e.	548, 566
Study of Cu(II) complexes with NTA	552
Copper determination in waters	558

*Lead-selective electrode.* The properties of the electrode based on a PbS—Ag<sub>2</sub>S mixture have been re-examined [528]. Several versions of the lead electrode (PbTe, PbSe, PbS + Ag<sub>2</sub>S) were tried in Pb<sup>2+</sup> buffers [542] and a polythene-based PbS precipitate electrode has been reported [544]. Applications of the lead-selective electrode are listed in Table 9. A sulfate-selective electrode can be prepared from a mixture of Ag<sub>2</sub>S, PbS, PbSO<sub>4</sub> and Cu<sub>2</sub>S [546, 553].

*Cadmium-selective electrode.* Electrodes based on CdS in a polyethylene matrix [545], on a CdS—Ag<sub>2</sub>S mixture in a silicone rubber matrix [535], on CdS [569a], on a CdS—Ag<sub>2</sub>S sintered membrane [528] and on a CdS—Ag<sub>2</sub>S—Cu<sub>2</sub>S sintered membrane [537] have been reported. The cadmium electrode is suitable for Cd<sup>2+</sup> titration [519, 561], for the determination of stability constants of cadmium—amino acid complexes [532, 567], for Zn<sup>2+</sup> titration with EDTA [562], for Ca<sup>2+</sup> determination in waters [298a], and for H<sub>2</sub>S determination in petroleum fractions [553a].

A zinc chalcogenide electrode [569a] and a mercury-selective electrode (based on HgS or HgSe in an epoxide matrix) [568] have been proposed.

(iv) *The lanthanum trifluoride electrode [570—773]*

The lanthanum trifluoride electrode is, at present, the most important ion-selective electrode, as can be seen from the number of published papers. Its general properties and analytical applications have often been reviewed [572b, 600, 640, 641, 655, 683a, 736a, 743, 757]; other reviews discuss the use of this sensor in biology and medicine [647, 732].

TABLE 9

Applications of lead-selective electrodes

Use	Reference
SO <sub>4</sub> <sup>2-</sup> titration, of organic base sulfates	516
—, together with S <sup>2-</sup> after oxidation	525
—, in water and soil extracts (in 70% ethanol)	527
—, of trace sulfur, in petroleum after oxidation	533
—, of trace sulfur in coal after oxidation	534
—, in food colours	539
—, in waters	543
—, in the presence of PO <sub>4</sub> <sup>3-</sup>	556
—, dioxane addition	557
Pb <sup>2+</sup> titration, with EDTA	521
Ba <sup>2+</sup> , Sr <sup>2+</sup> titration	530, 559
Pb <sup>2+</sup> determination in mixtures	541
Pb <sup>2+</sup> in waters	298a
SO <sub>2</sub> determination in flue gases	569

The similarity of the lanthanum trifluoride electrode to the glass electrode has been re-emphasized [752b] (cf. Part I, p. 370), a diffusion potential appearing in the interior of the membrane in both cases. A study based on potentiometry, x-ray powder analysis, i.r. spectroscopy and tritium radiometry led to the conclusion that a competitive adsorption of hydroxyl and fluoride ions takes place in the hydrophilic film on the  $\text{LaF}_3$  crystal face and influences the response of the electrode [753]. The role of adsorption of fluoride and of dissolution of the membrane has been discussed [396, 592]. The response mechanism of the electrode was studied by means of  $^{18}\text{F}$  transport [735]. Europium doping of the  $\text{LaF}_3$  single crystal results in an increase in its conductivity [742, 752a].

The preparation of an  $\text{LaF}_3$  electrode by pressing and sintering [579, 644], and of an electrode based on a fluoride exchange resin [598] have been reported. A microelectrode for  $2\ \mu\text{l}$  of sample was designed [615]. The fluoride electrode is satisfactory as a reference electrode in mixed solvents [736].

Buffers superior to TISAB (Part I, p. 371) have been proposed [703]. In the first version the buffer consists of 1 M NaCl, 1 M neutral sodium citrate and 0.06 M 1,2-diaminocyclohexanetetraacetic acid (DCTA) at pH 6, and is diluted in a 2:1 buffer-sample ratio. The second version is based on 1.25 M NaCl, 1.36 M sodium citrate and 0.06 M DCTA at pH 6.5, and the dilution ratio is 1:10. Its main advantage is the chelation of  $\text{Al}^{3+}$ . A modified TISAB solution (with DCTA) is satisfactory [669a, 722]. A buffer composed of perchloric acid, citric acid and triethanolamine was proposed for the fluoride determination in phosphate minerals [311]. The addition of 10% tiron was also recommended [741]. For  $\text{Al}^{3+}$  masking, see also [771].

For titrimetric determination of fluoride,  $\text{La}^{3+}$  is considered best at concentrations higher than 1 mM  $\text{F}^-$ , and  $\text{Th}^{4+}$  in the concentration range 0.2–1 mM  $\text{F}^-$  [623]. Linear regression was applied to potentiometric titrations of millimolar solutions of fluoride with  $\text{La}^{3+}$  [621] (see also [723]). A statistical evaluation [587] of the colorimetric, titration and fluorimetric methods and of direct potentiometry with the fluoride electrode led to the conclusion that direct potentiometry is most advantageous for fluoride concentrations between 25 and 250  $\text{mg l}^{-1}$ ; see also [602, 643, 664, 760]. The varying solubilities of  $\text{LaF}_3$  have been discussed in relation to applications [625].

The fluoride electrode can be used as an indicator electrode for Fe(III)–EDTA titrations after addition of one drop of  $10^{-3}$  M NaF to the solution [717]. Traces of fluoride can be determined after extraction with triphenyl antimony(V) dichloride in  $\text{CCl}_4$  in the presence of CDTA and a phosphate buffer [599]; for a similar study, see [573]. A coulometric titration of  $\text{La}^{3+}$  is possible with fluoride generated from the  $\text{LaF}_3$  membrane [679]. The fluoride electrode is suitable as a chromatographic detector [671].

Differential [686] and null-point [687] potentiometry with the fluoride-selective electrode have been reported. The determination of Si, Al, Fe, Ca

and Mg by addition of a sample to 0.1 M fluoride solution and measurement of the decrease in fluoride activity has been suggested [693].

The response of the fluoride electrode in the presence of monofluorophosphate [580] and of fluoronitrobenzene [772] has been described.

The applications of the fluoride electrode to physicochemical problems are listed in Table 10. The numerous analytical applications are shown in Table 11.

A micro and semimicrodetermination of arsenate can be based on precipitation of  $\text{AsO}_4^{3-}$  with  $\text{La}^{3+}$  and subsequent titration of the excess of  $\text{La}^{3+}$  with a fluoride solution using the fluoride electrode as indicator [724]. A method of determining  $\text{F}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  without separation was worked out [725].

(v) *Other systems [774–807]*

A variety of solid-state ion-selective electrodes is based on miscellaneous precipitates embedded in plastic matrices. They include a cesium electrode based on Cs-12-molybdophosphate [776] and a Tl(I) electrode with Tl(I) molybdo- or tungstophosphate [775] both in epoxy matrix, and electrodes for these two ions based on tungstoarsenates in Araldite [791]. A  $\text{HPO}_4^-$ -sensitive pellet membrane [803] consists of the monohydrogen phosphate salt of a silver–thiourea complex polymerized with glutaraldehyde and  $\text{Ag}_2\text{S}$ . A phosphate electrode has been based on  $\text{BiPO}_4$  in a PVC membrane [804]. In the same group of electrodes belongs the  $\text{K}_2\text{ZnFe}(\text{CN})_6$  electrode for

TABLE 10

Applications of the fluoride-selective electrode to physico-chemical problems

Use	Reference
Ionization constant of hydrogen fluoride	572a, 577, 607, 702
Stability constants of fluoride complexes of U(VI) and U(IV)	572a
Stability constants of fluoride complexes of Th(IV)	577, 670, 695
Stability constants of fluoride complexes of Ta(V)	578
Stability constants of fluoride complexes of alkaline earth metals	585, 595, 616
Stability constants of divalent first row transition metal fluoride complexes	586
Stability constants of $\text{BF}_n(\text{OH})_{4-n}$	633, 692a
Mixed stability constants	637
Stability constants of fluoride complexes of Nb(V)	676
Stability constants of fluoride complexes of Al(III)	572
Gibbs energy of transfer of NaF from water to hydrogen peroxide	606
Acidity function and fluoride activity function in anhydrous HF and $\text{H}_2\text{O}$ –HF mixtures	690
Hydrolysis of $\text{ZrF}_4$	696
Kinetics of substitution of $\text{F}^-$ by methyloxalate in fluorobenchroreotate derivatives	738

TABLE 11

## Analytical applications of the fluoride ion-selective electrode

Use	Reference
F <sup>-</sup> , in waters	298a, 579a, 587, 590, 596, 610, 618, 627, 632, 663, 668, 691, 693a, 699a, 712, 714, 719, 721, 731, 754, 755, 756, 758, 759, 760, 762, 766, 768
—, in phosphate rocks	310, 393, 731
—, in selenium	439
—, in tooth enamel	570, 571, 583, 591, 594, 626, 642, 649, 677
—, in plants	574, 627, 652, 658, 659, 660, 661, 747, 749a, 752
—, in radiolysis products of CFCl <sub>3</sub> , CF <sub>2</sub> Cl <sub>2</sub> , and CF <sub>3</sub> Cl	574a
—, in inhibition of the Hill reaction in bean chloroplasts	574b
—, in glass	575, 697, 699, 731, 759
—, in air	580a, 651, 680, 699, 747a
—, in plaque and tooth deposits	581, 733
—, in saliva	581a, 582, 582b, 589, 726, 727
—, in bacterial suspensions	582a
—, in vitro study of affinity to salivary components	582b
—, in welding fluxes	584
—, in biological samples	588, 667, 672, 770
—, in pharmaceuticals	593, 631, 639, 664, 683, 691
—, in geological materials	602, 608, 654, 704, 707
—, from fluorinated organophosphate cholinesterase inhibitors	603
—, in urine	604, 619, 627, 653, 694, 749, 763, 764, 765
—, after isoflurane and methoxyflurane anaesthesia	605, 612, 629
—, in wine	609, 610, 692
—, in milk after gas chromatographic separation	611
—, in serum	612, 630, 634, 663, 744, 750a
—, in sparingly soluble phosphates	613
—, in phosphate processing	614, 673
—, in pickling baths	617, 622
—, in feces	620
—, in burnt-out nuclear fuel processing	624
—, in soils	608, 627, 669, 678, 751a
—, in bones	627, 705, 713, 715, 773
—, in fertilizers	627
—, in plating baths	628, 751
—, in cosmetic agents	632
—, in phosphoric acid	635, 734
—, in CaSO <sub>4</sub>	635
—, in inorganic compounds	636
—, in organic compounds	636, 638, 650, 711, 728, 745
—, in nerve gas	639
—, in stack emissions	643, 688, 708
—, in oxide materials	645, 646

TABLE 11 (continued)

Use	Reference
—, in slags in steel	656
—, continuous monitoring	657
—, in silicate rocks	662
—, in milk	665
—, after dissolution of SiO <sub>2</sub>	666
—, in HF production	674
—, in wood preservatives	675
—, in tooth-pastes	681, 685, 716
—, in cane sugar	682
—, in Pu containing oxides	684
—, in feeds	689, 748a
—, in aluminium processing	700, 737, 748
—, in mouth rinses	582, 701
—, in beer	706
—, in pure Zr	709, 710
—, in teeth	715
—, in household products	718
—, in boron-containing materials	720
—, in organometallic compounds	728, 745
—, in uranium compounds	729
—, in ores	730
—, in gases	739
—, in rice	740
—, in coal	746
—, in body fluids	750
—, in petroleum	767
—, in clays	769
Al <sup>3+</sup> , titration in an EtOH—H <sub>2</sub> O mixture by NaF	576
—, in paper	648
—, in anodizing electrolyte	698
Th—U and U—Zr alloys, F <sup>-</sup> -titrimetric determination of UO <sub>2</sub> <sup>2+</sup> and Th <sup>4+</sup>	597

alkali metal ions [777]. An electrode selective for alkaline earths and alkali metals can be made with barium dextran sulfate in silicone rubber [805]. A CuI electrode responds to copper ions [793]. The silver—diethyldithiocarbamate electrode shows a response to nitrate ions, perhaps because of trace amounts of nitrate absorbed in the material [792]. Chromate electrodes can be made from BaCrO<sub>4</sub> [790] and PbCrO<sub>4</sub> [780]. A sulfate electrode based on a BaSO<sub>4</sub>—cellophane membrane has been described [782]. PbI<sub>2</sub> was used for another sulfate electrode [781]. An electrode containing an AgI—TlI mixture responds to Tl(I) ions [779a] while electrodes based on Cu<sub>2</sub>HgI<sub>4</sub> [807] and Ag<sub>2</sub>HgI<sub>4</sub> [778a] respond to all components of the precipitate. A solid-membrane electrode for HCO<sub>3</sub><sup>-</sup> has been reported [779].

Halide electrodes based on mercury halides in a HgS matrix [789, 794, 795] show some promise. A chloride-selective electrode has been prepared

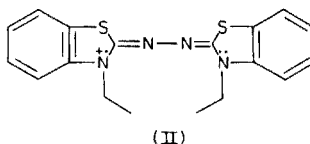
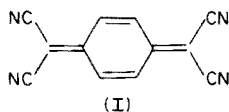


from a pellet membrane consisting of a mixture of triphenylantimony(V) dichloride, carbon and paraffin [774a].

Finally, in this section, electrodes will be described which show a definite electronic conduction and respond to oxidation–reduction systems in the solution; they are therefore on the periphery of the field of ion-selective electrodes.

A chalcogenide glass electrode (28% Ge, 60% Se, 12% Sb) doped with Fe (2% maximum) shows a Nernstian response to  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  and some response to nitrate ions [774, 786]. A titration of  $\text{SO}_4^{2-}$  by  $\text{Ba}^{2+}$  was described with this indicator electrode [784] which responded to  $\text{Fe}^{3+}$  ions bound in the sulfate complex. The method was applied to natural water analysis [785]. An electrode with a rotating disc membrane responds to  $\text{NO}_2$ . Another chalcogenide electrode containing  $\text{Cu}_6\text{As}_4\text{S}_9$  is sensitive to  $\text{Cu}^{2+}$  ions [788] and was used for determination of  $\text{Cu}^{2+}$  in sea water in concentrations down to 1 p.p.b. Cu [787].

Another group of electrodes is based on organic radical-ion salts [796–799, 801, 802, 806]. One of these is the ion radical derived from 7,7,8,8-tetracyanoquinodimethane(I) [796, 801, 802] which forms sparingly soluble



salts with various cations. An electrode with a membrane containing such a salt responds to the particular cation as a cationic electrode of the second kind (as shown already in [806]). A perchlorate electrode can be based on the perchlorate salt of the *N*-ethylbenzothiazole-2,2'-azine radical cation [798].

Other electrodes of this type contain cyanoethylene metal polymers and other organic semiconductors [800].

A silicone rubber membrane electrode with embedded hemine responding to  $\text{Fe}^{3+}$  has been described [778].

#### D. LIQUID-MEMBRANE ELECTRODES

The liquid-membrane ion-selective electrodes are, mechanistically speaking, divided into ionized ion-exchanger and neutral ion-carrier systems. This basic classification will be preserved in the present review while further grouping will be ordered according to the ions.

The scope of practical application of liquid-membrane electrodes has increased considerably since the introduction of plastic film systems, which have contributed greatly to enhanced reliability and which have made it possible to prepare these sensors even in a simply equipped laboratory.

The ionized ion exchangers should show a sufficient degree of hydrophobicity. This can be achieved by long-chain alkyl groups (in the dialkylphosphate ion of the calcium and related electrodes or in tetraalkylammonium

ions of a number of anion-selective electrodes) or with aromatic or pseudo-aromatic groups (in the substituted tetraphenylborate of the potassium and other cation-selective electrodes or in 1,10-phenanthroline complexes of heavy metals encountered in the Orion nitrate and some other anion-selective electrodes).

(i) *Calcium and related ion-selective electrodes [174, 194, 808–920]*

*General properties.* The selectivity for  $\text{Ca}^{2+}$  has been studied with respect to alkali metal cations and  $\text{NH}_4^+$  [809, 810], together with the response of the electrode in acidic solutions [811] and in the presence of surfactants [872], humic acid, salicylate, phthalate, resorcinol or phenol [887] and organic bases and urea [820]. The dependence of the selectivity coefficient on the concentration of various cations has been determined [851]. The calcium-selective electrode is suitable for accurate activity coefficient measurements [818, 910], and for  $\text{Ca}^{2+}$ -activity determinations at high pH values [917]. Various solvent mediators of the phthalate and phosphonate type were evaluated for PVC matrix-based electrodes with Ca-bis(dialkyl)-phosphate as ion-exchanger [829]; the best properties were shown by di-n-octylphenyl phosphonate. Analogous results were obtained in an investigation of ion exchangers and plasticizers for coated-wire calcium-selective electrodes [822]. In a similar study [839], the n-alcohols ( $\text{C}_5$ – $\text{C}_{10}$ ), isomers of octanol and trialkyl phosphates were used as membrane solvents. Improved selectivity for  $\text{Ca}^{2+}$  appeared with longer alkyl chains on the phosphates. Various calcium electrodes were tested in potentiometric titrations of  $\text{Ca}^{2+}$  [854]. The exchange of  $\text{Ca}^{2+}$  in the PVC matrix electrode has been studied with  $^{45}\text{Ca}$  [812]. The properties of the PVC matrix membrane electrode [843, 919] and of a coated-wire electrode [821] for  $\text{Ca}^{2+}$  have been described. A diethylhexylphosphoric acid solution in a tributylphosphate–theonyltrifluoroacetone mixture (3:1) has been proposed as a plasticizer for a PVC membrane electrode [877]. Toluene can also serve as the membrane solvent for a calcium electrode [842].

A  $\text{Ca}^{2+}$  Selectrode with a plastic membrane and octylphenylphosphonate as plasticizer has been reported [194]; the exchanger used — di-(n-octyl-phenyl) phosphoric acid — showed improved selectivity for  $\text{Ca}^{2+}$ . The suggestion that protolytic impurities in the exchanger affected the selectivity was disproved by Jagner and Østergaard-Jensen [859]. Calcium micro-electrodes suitable for intracellular measurements have been constructed [813, 826]. The preparation of di-n-octylphenylphosphonate [828, 844] and of mono- and di-n-decylphosphoric acids [844] as membrane components has been reported.

*Applications.* The calcium(II) electrode is by far the most important sensor for determination of ionized calcium in serum and whole blood. Table 12 gives a detailed survey on this application. Closely related to such applications are studies of calcium–serum albumin interactions [857, 898, 899, 901] with a calcium-selective electrode. Other applications of this sensor are

TABLE 12

Determination of serum and blood calcium with the calcium-selective electrode (cf. Part I, Table XVII)

Use	Reference
Serum ionized calcium, general and methodological papers	808, 836, 837, 847, 867, 868, 869, 870, 871, 890, 891, 893, 897, 905, 906, 911, 914, 915
—, in haemorrhagic shock	814
—, of parturient cows	816
—, of newborn infants	819, 830, 892
—, in metabolic disorders	834
—, after centrifugation	838
—, in hypocalcaemia	840
—, in relation to exchange transfusion	841, 849, 889, 892
—, of fracture patients	848
—, of rats	850
—, maternal—fetal relationship	855
—, effect of secretion	856
—, in urticaria	860
—, in hyperparathyroidism	861, 873, 882, 888
—, response to infusion of acid—citrate—dextrose solution in dogs	864
—, during treatment by haemodialysis	865, 912
—, during cardiac surgery	879
—, during administration of thyrocalcitonin to monkeys	894
—, during administration of thyrocalcitonin to rats	895
—, effect of food ingestion	908
—, effect of hydrochlorodiazide	913
—, during pregnancy	916
Whole blood ionized calcium	817, 836, 846, 900, 902, 903, 907

listed in Table 13. The limitations of the application of this electrode to sea-water analysis have been pointed out [859]. The transport of  $\text{Ca}^{2+}$  in mitochondria can be studied with this electrode [845].

*Divalent cation electrode* (cf. Part I, p. 382). With this electrode trivalent and tetravalent ions can also be determined [823]. A version of this electrode is suitable for determinations of alkaline earth metal ions in diluted HCl [878]. Polyamines interfere in the determination of  $\text{Mg}^{2+}$  at physiological pH [863]. Table 14 shows the various applications of the divalent cation electrode.

(ii) *Nitrate-selective electrode* [173, 261, 921–979]

The original Orion nitrate electrode is based on a tris(substituted 1,10-phenanthroline)Ni(II) complex as the cation-exchanger (cf. ref. 562 of Part I) while in the Beckman and other Orion electrodes tetraalkylammonium

TABLE 13

Applications of calcium-selective electrodes in inorganic chemistry, environmental studies and technology

Use	Reference
Solubility of $\text{CaSO}_4$	876, 918
—, of Ca molybdate	883
Dissolution rate of gypsum and anhydrite	815
Stability constants of $\text{CaATP}^{2-}$ and $\text{Ca}_2\text{ATP}$	881
—, of $\text{CaADP}^-$ and $\text{Ca}_2\text{ADP}^+$	833
$\text{Ca}^{2+}$ adsorption by $\beta\text{-MnO}_2$	896
Ca in waters	852, 858, 859, 862, 885
Ca in soils	831, 832, 866, 874
Ca in apple juice	827
Ca in beer	886

TABLE 14

Applications of the divalent cation electrode

Use	Reference
Stability constants of Mg-carbonate species	884
Stability constants of $\text{Mg}^{2+}$ and $\text{Mn}^{2+}$ complexes with ATP	880
Stability constants of $\text{MgADP}^-$	833
$\text{Mg}^{2+}$ —bovine albumin binding	835
$\text{Mg}^{2+}$ —nucleic acids binding	904
Water hardness determination	824, 853, 875, 909, 920
Mg in soils	825

cations are used [7]. The Corning nitrate electrode is based on tridecylhexadecylammonium nitrate dissolved in *n*-octyl-*o*-nitrophenylether [978]. Other versions of the nitrate-selective electrode contain as ion-exchangers dimethylhexyldecylbenzylammonium nitrate in decanol, cetyltrimethylammonium nitrate or tetraoctylammonium nitrate in octanol [938, 939], tetradecylammonium nitrate in dibutylphosphate [941, 942, 955], other tetraalkylammonium [936, 965] and phosphonium [969] nitrates and polymeric ion-exchanging systems [924]. A nitron-based nitrate electrode has also been proposed [940, 974].

PVC-membrane [932] and carbon-paste [173] nitrate electrodes are possible. An electrode based on a porous wick saturated with the ion-exchanger without any internal solution has been suggested [943]. A gas-sensing electrode for  $\text{NO}_2$  can be used in soil extract analysis [973].

Various applications of the nitrate-selective electrodes are listed in Table 15. Nitrate determination in surface and ground waters with these electrodes has been found advantageous in comparison with the phenol method [971],

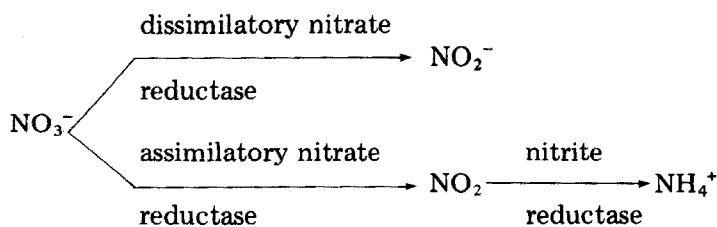
TABLE 15

## Applications of the nitrate-selective electrode

Use	Reference
Nitrate, in plants	921, 923, 927, 930, 947, 959, 970, 972
—, in soils	921, 922, 930, 931, 957, 959, 962, 963, 968, 970, 973, 977a
—, in calton petioles	925
—, in pickling baths	926
—, in waters	928, 952, 953, 954, 957, 958, 959, 961, 964, 971, 975, 976
—, in effluents	929, 962
—, in air	934
—, in presence of $\text{NO}_2^-$	937
—, titration by nitron	944
—, in baby food	950, 956
—, in plutonium oxide solutions	951
—, in presence of $\text{ClO}_3^-$	956
—, in bacteria cultures	962
—, in fertilizers	962
—, in food	977
—, in nitrification solutions	979
Nitrates and nitrites, by means of oxidation by $\text{KMnO}_4$	960
Nitrates and nitrites, after chromatographic separation	260a
<i>N</i> -oxides	933, 935, 948, 949, 960

whereas other authors [967] state that the brucine colorimetric method is simpler and more sensitive at low concentrations.

In cultures of *Escherichia coli*, nitrate is reduced by action of two reductase enzymes



The nitrate reduction has been studied with the nitrate and the nonactin ammonium electrodes [945, 946].

(iii) *Potassium-selective electrodes based on ionized ion-exchangers* [280, 980–1054]

In this type of potassium electrode (cf. Part I, p. 384) the ionized ion-exchanger, potassium tetra(*p*-chlorophenyl) borate [984], is dissolved in *n*-octyl-*p*-nitrophenylether [983]. The electrode shows a selectivity for

potassium compared to sodium which is much smaller than that of the valinomycin electrode (Part I, p. 395) but is sufficient for many biological applications. In the tiny microelectrodes used, e.g., in intracellular applications (Part I, p. 384 and 396), this kind of electrode is superior to the valinomycin electrode because of the much higher conductivity of the ion exchanger [1008a].

Attempts have been made to use a tetraphenylborate electrode for potassium determinations [981, 993, 994, 999, 1000] but this ion exchanger is inferior to the chlorinated species [1051], which also shows a better performance than the tetra(*p*-phenoxyphenyl) borate [984]. The electrode based on the last-mentioned substance shows a considerable response to hydronium ions [1051]. The PVC-film version of the potassium electrode [983, 990] has been used for potassium determinations in blood serum [982, 1021]. However, the most important application of these electrodes is in connection with intracellular and extracellular potassium monitoring in individual cells and, with regard to the extracellular space, particularly in whole excitable tissues. The extracellular space is small so that considerable accumulation effects during neuron activity can be expected [995].

The principal device, the ion-selective microelectrode, designed by Walker [1045, 1047] was shown in Part I, p. 396. In excitable tissues the electrical field between the indicator and the reference electrode influences the resulting e.m.f. values. To minimize this effect a double-barrelled assembly was introduced to electrophysiology by Coombs et al. [989]. An ion-selective version of this system [1044] is shown in Fig. 15. As the tiny tip of the microelectrode can be easily damaged in contractile tissues, a more robust side-pore microelectrode was designed [1044] (Fig. 15). An example of extracellular  $K^+$  measurement in the spinal cord of a cat under external stimulation is shown in Fig. 16. The *in vivo* measurements with potassium microelectrodes have been reviewed [280]. The applications of this electrode are listed in Table 16. For a general paper, see also [1038].

In the framework of extracellular potassium studies, the potassium efflux can be achieved by an iontophoretic method of potassium injection [1017, 1019]. Measurements of the response time of the ion-selective microelectrode were based on this method; the response time did not exceed several milliseconds.

#### *(iv) Other ionized ion-exchanger systems [1055–1162]*

The experience of recent years has shown that there is a great variety of amphipathic ions (containing both hydrophobic and hydrophilic groups) which can function as ion-exchanging ions in liquid membranes, and that almost any ion which is soluble in water will be sensed to a greater or lesser extent by at least one of the liquid membrane electrodes. These facts have led to a considerable growth of publications in this field, though very few of these electrodes have been used in solving real analytical problems.

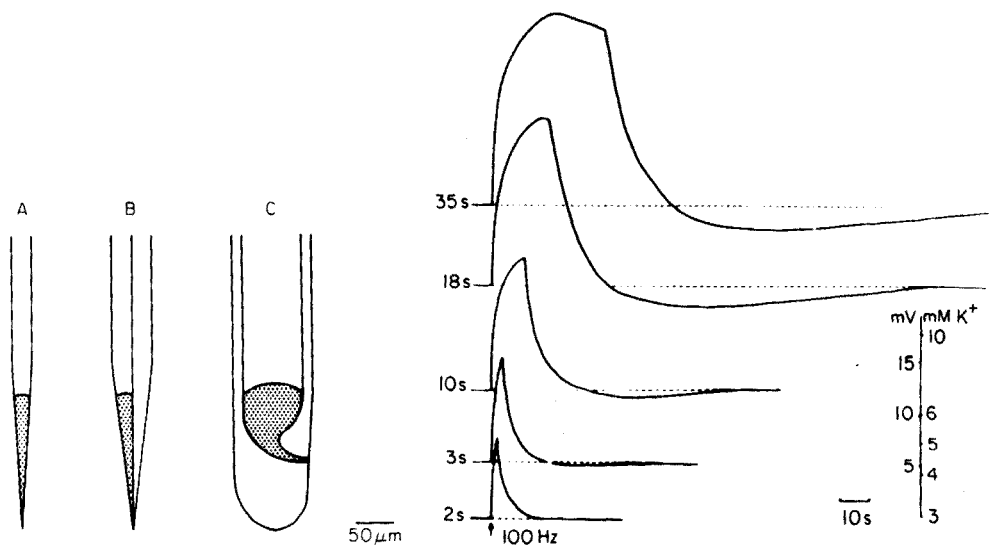


Fig. 15. A single-barrelled (A), double-barrelled (B) and side-pore microelectrode [1044].

Fig. 16. Monitoring of extracellular potassium in the spinal cord of a cat under external stimulation of *nervus tibialis posterior* during time periods indicated on each curve [1039].

Electrodes with tetraphenylborate or its derivatives respond to a number of inorganic and organic cations [154] (cf. p. 8). The acetylcholine electrode (see ref. 37 of Part I), which has the same ion-exchanging ion and membrane solvent as the potassium electrode [1059] (cf. p. 8), has been used to assay the inhibitory influence of organic pesticides on cholinesterase [1059] and to estimate cholinesterase activity in blood [1061]. Trace (p.p.b.) quantities of cesium in simulated radioactive waste can be determined with a liquid membrane electrode based on cesium tetraphenylborate [1062]. An ammonium electrode based on the same ion-exchanger has been used for titrations [1102a]. An ion-selective electrode responding to vitamins B<sub>1</sub> and B<sub>6</sub> contains the tetraphenylborate salts of these substances [1108].

Among the electrodes based on 1,10-phenanthroline complexes, the perchlorate ion-selective electrode (Part I, p. 385) can be used to measure the thermal decomposition of perchloric acid [1096]. Vicinal glycols can be determined after their reaction with periodate by measurements with a perchlorate electrode which also responds to periodate [1078]. A coated-wire perchlorate electrode has been reported [191]. The interference of voluminous less hydrated anions with the response of the perchlorate electrode has been discussed [1138].

The tetrafluoroborate electrode (Part I, p. 385) has been used for the analysis of borosilicate glass [1117], of boron in silicon [1122] and of aluminium oxide—boron carbide mixtures [1159].

TABLE 16

## Applications of potassium-selective microelectrode

Use	Reference
Intracellular K <sup>+</sup> , in <i>Aplysia</i> neurons	986
—, —, effect of acetylcholine	1014
—, —, active ion-transport	1032
—, —, in <i>Helix pomatia</i> neurons	1016, 1018
—, —, effect of acetylcholine	1027
—, —, in sheep Purkinje fibres	1046
—, —, effect of CO <sub>2</sub> in neurons	1048
—, —, in frog heart	1049, 1050
—, —, in single skeletal muscle fibres	997
—, —, in membranes of <i>Escherichia coli</i>	985
—, —, in frog lens	1029
Extracellular K <sup>+</sup> , in mammalian brain cortex, during experimental seizures	998, 1001
—, —, effect of pyrrolidine derivatives	991
—, —, under peripheral stimulation	992
—, —, effect of diphenylhydantoin	996
—, —, under spreading depression	1020, 1031, 1034
—, —, during anodic depolarization	1023, 1054
—, —, during epileptogenesis	1024
—, —, effect of cholinometric drugs	1033
—, —, unrestrained animals	1007, 1008
—, —, in mammalian spinal cord, effect of nembutal and picrotoxin	987
—, —, under peripheral stimulation	1009, 1010, 1011, 1013, 1017, 1025, 1037, 1039, 1040, 1041, 1042, 1043
—, —, in cat lateral geniculate nucleus	1022, 1035
—, —, in cat striate cortex	1036
—, —, in luminal fluid of turtle thyroid follicles	988a
—, —, in immature cortex	1026, 1030
—, —, in avian hyperstriatum	1028
—, —, in muscle venous blood	998
—, —, in heart muscle	1006
—, —, in frog sartorius muscle	1012
K <sup>+</sup> , in proximal renal tubules	1002, 1003, 1004, 1005
K <sup>+</sup> , in renal distal tubules	1052, 1053
K <sup>+</sup> , in small intestine epithelium	1015
K <sup>+</sup> , in outer capsule of frog muscle spindle	980

The response of the Orion nitrate electrode to phthalate isomers made possible the determination of these species after ion-exchange liquid-chromatographic separation [261]. The Orion nitrate and perchlorate electrodes can be used to determine halogen and alkylsubstituted benzoates, halogen-substituted phenylacetates and anions of phenylsubstituted fatty acids [1101]. An iodide electrode is based on a 1,10-phenanthroline chelate



[1111]. The ferroin ion functions as an ion-exchanger in electrodes for chromate [1153] and alkylbenzenesulfonates [1152].

An electrode with a dialkylphosphate salt of  $\text{UO}_2^+$  responds to the uranyl ion [1126].

Of the electrodes containing tetraalkylammonium salts in the membrane, the chloride liquid-membrane electrode has found most applications (see Table 17). The Corning version is based on tri-*n*-octylpropylammonium chloride [1162].

An ion-selective electrode supposedly selective for  $\text{HCO}_3^-$  ion [1161] was shown to respond to  $\text{CO}_3^{2-}$  ions [1097, 1099]. A later version [1097] is based on Aliquat 336S (methyltricaprylammonium ion, cf. Part I, p. 382) in trifluoroacetyl-*p*-butylbenzene fixed in a Millipore cellulose acetate membrane. This was used for serum carbon dioxide determination [1098].

Aliquat 336S (for a general study, see [1089]) has also been used for perchlorate [1154], chloride, bromide and perchlorate [1103], iodomercurate and chloromercurate [1072], chlorocuprate [1074] and chloroferrate [1071] electrodes. The last mentioned electrode was applied to Fe(III) determination in rock silicates [1073].

Other tetraalkylammonium ions form the basis of a chloride electrode (with trioctylammonium or tetradecylammonium chloride [1228, cf. 938]); an electrode for chloride, bromide, nitrate and iodide [938]; a bromide electrode with decylammonium ion and other ion-exchangers [1118], and with cetyltrimethylammonium bromide in aliphatic alcohols [1123]; an electrode for bromide, iodide, nitrate and perchlorate [965]; an iodide electrode with tetradecylammonium iodide in chlorobenzene [1094, cf. 1124, 1142], a thiocyanate electrode with tetradecylammonium or cetyltrimethylammonium thiocyanate [1093] or with *N*-cetylpyridinium or octadecyldimethylbenzylammonium thiocyanate in nitrobenzene [1145]; an electrode sensitive to thiocyanate, perchlorate and chloride with octadecyldimethylbenzylammonium ion [1143, 1144]; a perchlorate electrode with tetrabutylammonium or tetrapropylammonium perchlorate

TABLE 17

Applications of chloride liquid-membrane electrode

Use	Reference
Intracellular $\text{Cl}^-$ , in <i>Aplysia</i> neurons	986, 1068
—, in single muscle fibres of giant barnacle	997
—, effect of acetylcholine	1014
—, active transport	1032
—, in frog heart muscle	1050
Extracellular $\text{Cl}^-$ , in brain cortex under peripheral stimulation	1017
—, in luminal fluid of turtle thyroid follicles	988a
Salt in cheese	1137

[1056, cf. 1092, 1132, 1158]; a chlorate electrode with tridodecylhexadecylammonium chlorate in *n*-octyl-*o*-nitrophenylether [1100]; a sulfate electrode with trioctylammonium or trilaurylammonium ion [1127]; an electrode sensitive to Eriochrome black T [1136] and to 8-quinolinol-5-sulfonate [1146] both based on tetradecyldimethylbenzylammonium ion; of biphthalate, naphthalenesulfonate, salicylate, thiocyanate and perchlorate electrodes [1105].

Several electrodes with tetra-substituted phosphonium ions have also been proposed. Electrodes based on tetraphenylphosphonium or tetraoctylphosphonium ions respond to nitrate, chloride, bromide, iodide, thiocyanide, sulfate and phosphate ions [1147, 1148]. A perrhenate electrode is based on tetradecylphosphonium perrhenate dissolved in dibutylphthalate [1155]; another version has been reported [1091].

In a tetrachloroaurate(III) electrode, tetraphenylarsonium ion is used [1070]; an electrode with bis(4-ethyl-3,5-dipropyl-1-pyrazolyl)methane also responds to this ion [1090]. A perchlorate electrode with a membrane containing tetrabistriphenylphosphinesilver(I) in nitrobenzene is supposed to show improved selectivity properties [1160]. Electrodes based on triphenyltin or quaternary ammonium phosphates respond to phosphate [1133].

Several electrodes have been designed for determination of ionic surfactants [184, 1063–1066, 1076, 1084, 1086, 1088, 1131, 1134, 1139, 1140a]. They contain in their membranes either a long alkyl chain cation [1140a, 1076] or anion [1063–1066, 1076, 1088, 1139] or both [184, 1084, 1134, 1086]. The electrode based on decylsulfate [1064] was used in a study of the binding of anionic surfactants to bovine serum albumin [1066, 1139].

Various electrodes have been based on organic dye complexes dissolved in the membrane. The methylene blue dibenzoatodioxouranate is used for a  $\text{UO}_2^+$  electrode [1079]. Some electrodes sensitive to anions are based on Brilliant green [1081, 1083, 1085, 1135], Crystal violet [1104, 1106, 1107, 1109, 1110, 1113, 1114] and other basic dye salts [1080].

Heavy metal dithizonates [1057, 1075, 1077, 1119, 1120, 1121, 1156, 1157], dithiophosphates [1130, 1150], a diethyldithiocarbamate [1149] and other complexes [1058, 1082, 1151] have also been proposed as ion-exchangers for liquid membrane electrodes. Electrodes of the ionized ion-exchangers type for  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  [1067, 1129], picrate [1055],  $\text{Cu}^{2+}$  [1069], methylephedrine and ephedrine [1087], various drugs [1115], Se(IV) [1125],  $\text{ZnCl}_4^{2-}$  and  $\text{PdCl}_4^{2-}$  [1140b],  $\text{Hg}^{2+}$  [1102], heavy metals and thiocyanate [1140], antiseptics and artificial sweeteners [1141] have also been described.

In an immunoelectrode [1112], the antibody is attached to a thin layer of a hydrophobic polymer which is deposited on a metallic conductor. The surface charge of the polymer–solution interface depends on the free charge of the antibody. In the presence of an antigen this charge is varied together with a change in the electrical potential difference between the

metal and the solution. As an antibody model Concanavalin A was attached to a coated wire electrode while certain polysaccharides served as antigen models.

(v) *Electrodes with neutral ion-carriers [1163–1234]*

The properties of neutral ion carriers have been reviewed in several papers and books [1176–1178, 1187–1189, 1205, 1222] and further reviews have been devoted to ion-selective electrodes based on these systems [38, 1221]. Transport properties in the presence of these neutral carriers have been studied with respect to the selectivity features of the transport phenomena [1201, 1234]. The response characteristics of electrodes based on ion-exchangers and ion carriers have been compared [1200].

Numerous potassium electrodes have been based on neutral macrocyclic carriers: an electrode designed with a porous cellulose acetate film soaked with a dimethylphthalate solution of valinomycin or gramicidin [1184]; PVC membrane-based valinomycin electrodes [1194, 1203, 1219, 1220]; an electrode with valinomycin dissolved in a mixture of Nujol, diphenylether and lecithine (1:1:6) [1173]; a valinomycin Selectrode [180]; electrodes with valinomycin fixed in a silicone rubber matrix [1210, 1211]; and a coated-wire valinomycin electrode [1175]. Surfactants of the alkylethanol-amine type are supposed to interfere with the functioning of the valinomycin electrode [1181]. The valinomycin electrode has been used in potassium titrations with a sodium tetraphenylborate solution [1183]. Applications of the valinomycin electrode are listed in Table 18.

Ammonium electrodes have been based on nonactin dissolved in butyl-sebacate in a porous cellulose acetate film [1184], in a mixture of Nujol, 2-phenyloxodiphenylether (or bromodiphenylether) and lecithine [1173],

TABLE 18

Applications of the valinomycin potassium electrode

Use	Reference
K <sup>+</sup> , in blood serum	260, 265, 869, 1198
—, in waters	264, 1170, 1175
—, in soils	1171
—, in plant cells	1185, 1231, 1233
—, transport across membrane of <i>Escherichia coli</i>	1193
—, efflux from human red cells	1199
—, in urine	1206
—, in feldspar	1213
—, uptake by cells	1218
—, in pharmaceuticals	1226
—, in plant extracts	1233
Formation constant of the associate of ADP <sup>3-</sup> with K <sup>+</sup>	833

or in a silicone rubber matrix [1180]. The selectivity of the macrotetrolide electrode towards organic oxonium ions has been determined [1230]. The nonactin electrode can be used for the automatic determination of ammonia in boiler feed-waters [1195–1197]. Its function is equivalent to that of the ammonia-sensing probe which cannot be used in systems with volatile amines [1197]. Arginine can be determined by decomposition to ornithine and urea with arginase; the urea is then converted by urease to carbon dioxide and ammonium ions, which are measured with a nonactin electrode [1202].

With regard to synthetic carriers, ion-selective electrodes based on crown polyethers (dicyclohexyl-18-crown-6, dibenzo-18-crown-6, benzo-15-crown-5, dibenzo-30-crown-10) dissolved in nitrobenzene have been investigated by Rechnitz and Eyal [1214]. The selectivity coefficients are approximately equal to the ratio of stability constants determined in a tetrahydrofuran–water mixture. Using PVC film membranes, Ryba et al. [1215] found that dimethyldicyclohexyl-18-crown-6 ( $K_{K,Na}^{Pot} = 1.0 \cdot 10^{-2}$ ) and dipropyldicyclohexyl-18-crown-6 ( $K_{K,Na}^{Pot} = 1.8 \cdot 10^{-2}$ ) in dipentylphthalate are most suitable for potassium determinations, the latter showing an almost instantaneous response. Excellent properties are also exhibited by dimethyldibenzo-30-crown-10 [1216]. These results were confirmed by the electrode behaviour of 11 synthesized crown polyethers [1207, 1208]. Serum potassium has been determined with the dimethyldibenzo-30-crown-10 electrode [1227] and a miniature version of this electrode has been described [1217]. The characteristics of the electrode based on dimethyldibenzo-30-crown-10 have been described as unsatisfactory [1220] but the experimental procedure used seems to be open to criticism [1217]. Plastic film electrodes based on dibenzo-18-crown-6 have been prepared from various plastic materials, PVC showing superior properties [1194].

A barium-selective electrode containing a neutral carrier (nonylphenoxy-poly(ethyleneoxy)ethanol) proposed by Levins [1191, 1192] opened a new field of ion-selective electrodes based on acyclic carriers. The best plasticizer for the membrane of this electrode is said to be di-2-nitrophenylether [1182]. A strontium version of this electrode has been reported [1172].

On the basis of theoretical considerations, which have been reviewed [see, e.g. 1224], Simon and co-workers [1163, 1164, 1168, 1169] synthesized a variety of acyclic neutral carriers which show remarkable selectivity towards lithium, sodium or alkaline earth metal ions. Those substances had to fulfil the following requirements which are, in fact, met almost in full by natural species of the valinomycin type [1163, 1212].

(a) The multidentate ligand must provide a stable cavity formed by polar coordinating groups. The cation in question fits tightly into that cavity. The apolar groups form a lipophilic shell around the whole structure.

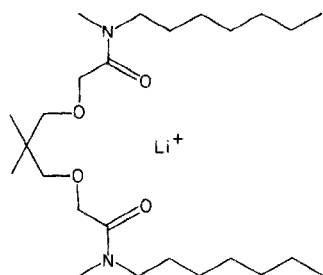
(b) For alkali and alkaline earth metals, coordination by oxygen atoms is preferred; nitrogen atoms cause undesirable protonation effects.

(c) The coordinating centres should be arranged in such a way as to form five membered rings including the central ion (Pfeiffer's rule [1209]).

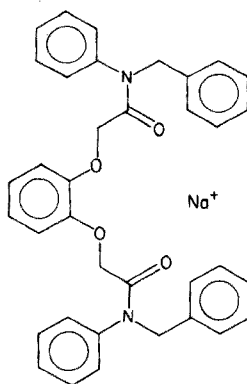
(d) When divalent ions should be preferred to monovalent species of the same size, the ligand layer around the central ion should be thinner.

(e) Increase in the dipole moments of the polar groups enhances the stability of the complexes and the preference for divalent rather than monovalent cations.

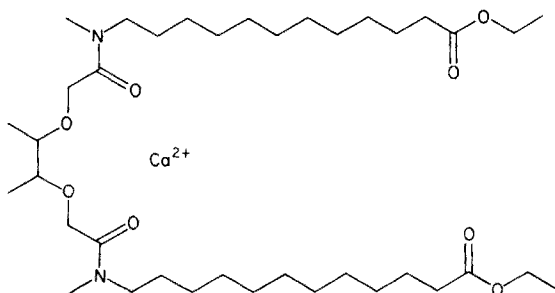
Altogether, 154 substances of the dioxaoctane dicarboxylic acid diamide type were prepared [1163, 1164, 1168]; among these, the best selectivity in electrodes for  $\text{Li}^+$  [1179],  $\text{Na}^+$  [1167],  $\text{Ca}^{2+}$  [1165, 1166] and  $\text{Ba}^{2+}$  was shown by the species III, IV, V and VI [1163, 1223, 1225]. Carbon-13 n.m.r. relaxation time measurements showed that the ester carbonyls participate only in 1:1 metal-ligand complexes [1174]. The stability constants of the alkali metal and alkaline earth metal complexes were determined [1186].



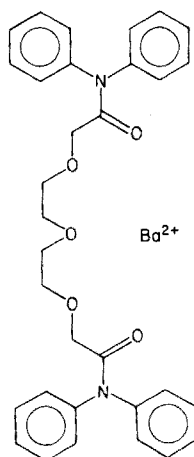
III



IV



V



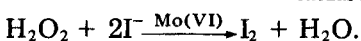
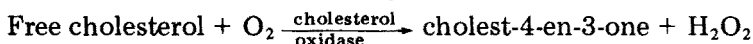
VI

A lithium microelectrode constructed from the lithium carrier III (9.7%), tris (2-ethylhexyl) phosphate (85.5%) and sodium tetraphenylborate (5.5%), has been used for studies of lithium accumulation by snail neurons [1229]. A calcium microelectrode based on the species V has also been designed [1204]. Serum calcium can be determined by an electrode based on the same carrier [1173a].

Thoma et al. [1228] synthesized a chiral ion-carrier showing enantiomer-selective behaviour toward  $\alpha$ -phenylethylammonium ions [1228] cf. [1190].

## E. ENZYME ELECTRODES

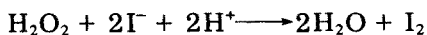
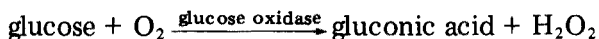
Enzymatic reactions are characterized by their specificity and, in many cases, by a single reaction path leading to a definite product. The utilization of these reactions for electroanalytical purposes, i.e. for conversion of a solution component to a species that will be sensed by an electrode, can be performed, basically, in two ways. In the first approach, the electroactive species is produced in homogeneous solution, and the product is determined by an electrode. In the present review, several such procedures have been described on p. 25 and p. 32. One of two quite recent examples is the determination of L-arginine and L-lysine by means of the carbonate-selective electrode [1235]. L-Arginine or L-lysine carboxylase is used to split carbon dioxide from the amino acid molecule, and  $\text{CO}_2$  is then determined with the electrode; the whole process is carried out in an Auto-Analyzer system (p. 25). For serum cholesterol determinations, three reactions are utilized:



The decrease in iodide concentration is sensed by an iodide-selective electrode in an automated analysis system [1236].

In the second approach, the genuine sensor is covered with a gel layer containing the enzyme. The sensors are either amperometric or potentiometric [1237]. The potentiometric sensors are usually ion-selective electrodes including the glass electrode. In Part I enzyme electrodes of the latter type were described on pages 366 and 374.

The importance of enzyme electrodes is witnessed by numerous review articles [74, 107, 280b, 1238–1243]. The urea electrode (Part I, p. 374) has been improved by using an ammonium electrode based on nonactin embedded in a silicone rubber matrix [1180]. This enzyme electrode can be used for determination of urea in blood [1244]. An L-phenylalanine enzyme electrode has been designed on the same basis [1245]. A glucose enzyme electrode has been based on the reactions



with the iodide-selective electrode as sensor [1246]. An improved  $\beta$ -glucose oxidase enzyme electrode for amygdaline (cf. refs. 361, 550, 550a of Part I) has also been reported [1247].

In general, however, applications of ion-selective electrodes of the types included in the present review have recently lost ground to systems based on glass electrodes, e.g. the ammonia gas-sensing electrode (p. 17, but see [1197]) for the urea electrode.

## F. CONCLUSIONS

The tremendous growth of material published on ion-selective electrodes shows the vitality of this novel field of chemical analysis, and marks, together with anodic stripping voltammetry and differential pulse polarography, a revival of electrochemical analytical methods. The reader of this and analogous reviews cannot perhaps avoid an impression that although many new sensors and methods have been described, practical applications have been possible only in a limited number of cases. Further, he may often be at a loss to decide which of several versions of an electrode should be used in a particular case. Here, the work of Moody and Thomas in comparing various systems is rewarding.

Concerning the perspectives of the theory of this field, one could expect (and, in fact, also recommend), a wider introduction of the concepts and methods which are already well established in electrochemical kinetics.

In the near future, the family of solid-state ion-selective electrodes will most probably not undergo profound changes in the systems themselves, whereas basically new applications, particularly in the biomedical field, are in progress. The evolution of liquid membrane electrodes may be of greater interest. While studies of new ionized ion-exchangers may still expand, a more hopeful direction is the investigation of systems which interact specifically with a particular ion in the membrane phase. In addition to the work on acyclic ion carriers which has already started successfully, various other systems will undoubtedly be found, perhaps modelling biological species showing analogous characteristics. As an example, the strongly modified cyclic polyethers showing "host-guest" properties [1248] may be mentioned. Of great value are those sensors which respond selectively to biologically important substances like amino acids and can even distinguish optical isomers. This development is expected to result in a revival of enzyme electrodes based on ion-selective electrodes other than glass electrodes. The strongest impetus to progress here will probably come from biology while biomedical applications must remain in the centre of interest, for some present devices (e.g. the potassium microelectrode and the ionized calcium electrode) already play a rôle second to none.

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condensates on ion-selective electrodes. I am grateful to colleagues all over the world who send reprints and reports in the field of ion-selective electrodes, and hope that they will continue to do so in future.

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