PRECIPITATE-BASED ION-SELECTIVE ELECTRODES

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ABSTRACT

A critical and wide-ranging review of the whole field of precipitate-based ion-selective electrodes is presented. The current theories of the mechanism of the electrode response are discussed and related to the experimental data. The most important analytical and physicochemical applications of the electrode are summarized, and, in particular, some examples of the use of electrodes to study complex formation are treated in detail.

INTRODUCTION

When Kolthoff[79] first proposed fused silver chloride and silver bromide discs for the detection of chloride and bromide in 1937, and later, in 1961, when we[122] pointed out the possibility of highly selective direct measurement of iodide ion, using silver iodide precipitate incorporated in paraffin wax, it could not have been foreseen how great a development had been initiated. In contrast to the lack of success in the fifties in the search for ion-selective electrodes, in the sixties many such electrodes, based on precipitates, were developed (*Table 1*) and many studies of their most important parameters were carried out.

Parallel with the discovery of other types of electrodes not based on precipitates, great efforts have been put into clarifying the mechanism of the electrode response of the precipitate-based type, and in finding new lines of development for novel ion-selective electrodes. Unfortunately, in this respect we are still very much in the early stages and so it is understandable that there has been practically no increase in the range of selective electrodes (with respect to the ionic species) available since the middle of the sixties.

In this paper the conclusions and data are drawn partly from the literature and partly from our findings for the precipitate-based electrodes. Opinions given in the literature are contradictory in some cases and we propose to add our own comments on some of them later. Furthermore, on the basis of up-to-date results we will offer our opinion about further developments.

We use the nomenclature 'precipitate-based electrodes' instead of solid-state electrodes because there are other types of solid-state ion-selective electrodes such as ion-exchange electrodes. In all solvents the properties of the precipitate-based electrodes depend on the solubility of the active component of the electrode in the appropriate solvent, whereas the properties of other types of solid-state electrode will depend on other parameters.

Table 1. Precipitate-based ion-selective electrodes

Sensitive to ion	Solid state	Active material	Matrix	Selectivity (Comments)	Workers	References
Ca^{2+}	Heterogeneous	Ca-oxalate and other Ca-salts	Paraffin + non-ionic detergent on gauze	'Fairly acceptable'	Tandeloo and Krips (1957)	167, 168
Ba^{2+}, SO_4^{2-}	Heterogeneous	$BaSO_4$ $BaCrO_4$	Paraffin without gauze	Not perfectly selective to either anions or cations. (Slow to attain equilibrium)	Fischer and Babcock (1958) Fischer and Yates (1960)	46 47
K^+	Heterogeneous	K-tetraphenylborate	Polystyrene + gauze	Not selective	Tandeloo and Kripps (1959)	169
Ca^{2+}	Heterogeneous	Ca-stearate	Paraffin as above	Stronger response to Ca^{2+} than oxalate. No response to K^+	Tandeloo and van der Voort (1960)	170
Ca^{2+}	Heterogeneous	Ca-oxalate	Paraffin + detergent	Non-specific, porous ('Exhibit memory')	Cloos and Fripiat (1960)	28
I^-	Heterogeneous	AgI	Paraffin	KCl does not interfere ($\pm 5mV$ reproducibility)	Pungor and Hollós-Rokosinyi (1961)	122
Mg^{2+}, Sr^{2+}	Multilayer	Ca-stearate Mg-stearate	—	—	Gregor, Glatz and Schonhorn (1963)	55
I^-	Heterogeneous	AgI	Silicone rubber	10^{-1} M KCl does not interfere	Pungor, Tóth and Havas (1966)	130
SO_4^{2-}	Heterogeneous	$BaSO_4$	Silicone rubber	Phosphate interferes	Pungor, Tóth and Havas (1964)	119, 120, 121
Ag^+, X^-; PO_4^{3-}; Al^{3+}; Ni^{2+}; Bi^{3+}, PO_4^{3-}	Heterogeneous	AgX, $MnPO_4$, Al-oxine, Nickel-DMG, $BiPO_4$	Silicone rubber	High selectivity (the electrodes for PO_4^{3-}, Al^{3+}, Ni^{2+}, Bi^{3+} are not selective)	Pungor, Havas and Tóth (1965)	126, 131
Co^{2+}	Heterogeneous	$Co_3(PO_4)_2$	Collodion, paraffin	Levelled by KCl, Li_2SO_4 (porous membrane)	Morazzani, Pelletier and Baffier (1965)	105
F^-	Homogeneous	Rare earth fluorides	—	(Single crystal)	Frant and Ross (1966)	49
H^+, OH^- Na^+		TiO_2, Fe_2O_3, SnO_2, ZrO_2	Polyethylene Polypropylene			

PRECIPITATE-BASED ION-SELECTIVE ELECTRODES

Ion	Type	Precipitate	Support / matrix	Remarks	Reference	Ref.
Al^{3+} / SiF_6^{2-}, K^+ / Both ions / Both ions	Heterogeneous	Al_2O_3 / K_2SiF_6 / $Ag_4Fe(CN)_6$ / $PbWO_4$	Paraffin / Agar or paper / Agar / Paraffin	(Titrations only studied)	Geyer and Syring (1966)	53
Ca^{2+}	Heterogeneous	Ca-oxalate	Paraffin + non-ionic detergent + gauze	Not completely permselective; not specific. (Gauze necessary for conduction. No difference between pure paraffin and paraffin + Ca-oxalate)	Shatkay (1967)	12, 155
F^-	Homogeneous	LaF_3	—	(For microchemical analysis)	Durst and Taylor (1967)	40, 41
SO_4^{2-} / PO_4^{3-}	Heterogeneous	$BaSO_4$ ppt / $BiPO_4$	Silicone rubber	—	Rechnitz, Lin and Zamochnick (1967)	138
Ag^+, S^{2-}	Homogeneous	Ag_2S / $BaSO_4$ / Ni-DMG	Silicone rubber	Respond to total free cations	Light and Schwartz (1968)	92
Divalent ions	Heterogeneous	$Co_3(PO_4)_2$ / $Ni_3(PO_4)_2$ / $CuHPO_4$ / $MnHPO_4$ / $MnCO_3$	Paraffin / Silicone rubber	(Conditioning very important crystalline form; hydration and anion not important)	Buchanan and Seago (1968)	23
F^-	Heterogeneous	CaF_2 / ThF_4 / LaF_3	Silicone rubber	Selective response to F^- Not reproducible	McDonald and Tóth (1968)	103
Ag^+, S^{2-}	Heterogeneous	Ag_2S	Silicone rubber	Selective response to F^- Unaffected by Cl^-, Br^-, I^-	Pungor, Schmidt and Tóth (1968)	125
Cl^- / Br^- / I^- / F^-	Homogeneous	$AgCl$ / $AgBr$ / AgF / LaF_3	—	Sm, Pr, Eu, Ho doped single crystal	Vesely and Jindra (1968)	177
NO_3^-	Heterogeneous	$Ni(NO_3)_2$	$PhOH + HCHO + NH_3$	Responsive to univalent anions and H^+; unresponsive to multivalent anions and cations	Dobbelstein and Diehl (1969)	36

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Table 1 (continued)

Sensitive to ion	Solid state	Active material	Matrix	Selectivity (Comments)	Workers	References
PO_4^{3-}	Heterogeneous	Inorganic phosphate salts	Silicone rubber	—	Guilbault and Brignac (1969)	58
I^-, Br^-, Cl^-	Heterogeneous	AgI AgBr, AgCl	Polyethylene	—	Mascini and Liberti (1969)	100
Cd^{2+}	Homogeneous	$CdS + Ag_2S$	—	—	Brand, Militello and Rechnitz (1969)	14
F^-	Homogeneous	—	—	Eu^{III} doped single crystal	Williams (1969)	180
Cu^{2+}	Heterogeneous	Cu_2S	Silicone rubber	—	Hirata and Date (1970)	63
Cu^{2+}	Homogeneous	Cu_2S	—	Ceramic membrane	Hirata, Higashiyama and Date (1970)	65
S^{2-}	Heterogeneous	Ag_2S	Polyethylene	—	Mascini and Liberti (1970)	101
Cu^{2+} Cd^{2+} Pb^{2+}	Homogeneous	$Ag_2S + MeS$	—	(Patent)	Frant and Ross (1970)	51
F^-	Homogeneous	Pb^{2+}, Bi^{3+}, Y^{3+}, Sc^{3+} or Lanthanide F^-	—	Non-polarized ion-selective electrode (Semiconductor membrane and a Pb and/or Bi metal contact) (patent)	Farren and Staunton (Perkin–Elmer) (1970)	45
ClO_4^-	Heterogeneous	Aliquot 336	Epoxy treated glass frit	—	Tateda, Fritz and Itani (1970)	165
K^+	Heterogeneous	K-salt biological material	—	Little interference from other common cations (Beckman Model 39622)	Krull, Mask and Cosgrove (1970)	83
NH_4^+	Heterogeneous	NH_4-salt biological material	—	Little interference from other common cations (Beckman Model 39626)	Cosgrove, Mask and Krull (1970)	32
F^-	Homogeneous	LaF_3	—	Sm, Pr, Eu, Ho, Nd doped LaF_3 single crystal	Vesely (1971)	175

Pb^{2+}	Homogeneous	PbS	—	Ceramic membrane	Hirata and Higashiyama (1971)	67
Pb^{2+}	Heterogeneous	PbS	Silicone rubber	—	Hirata and Date (1971)	64
Cu^{2+}	Heterogeneous	$CuS + Ag_2S$	Polyethylene	—	Mascini and Liberti (1971)	102
S^{2-}, Halides, Hg^{2+}, Ag^+, Cu^{2+}, Pb^{2+}, Cd^{2+}	Homogeneous	Ag_2S, Ag-halides, HgS, Ag_2S, CuS, PbS, CdS	—	Ppt. on the surface of a graphite rod (Selectrode—the universal ion-selective solid-state electrode)	Ruzicka and Lamm (1971)	145, 146
Cu^{2+}, Ag^+, NH_4^+, e	Homogeneous	TCNQ salts	—	—	Sharp and Johansson (1971)	154
CN^-	Homogeneous	CuS	—	—	Gordievskii et al. (1971)	163
CN^-	Homogeneous	V_2O_5	(β-glucosidase in acrylamide gel)	—	Rechnitz and Llenado (1971)	139
CN^-	Homogeneous	Ag	—	—	Gordievskii et al. (1971)	164
Cu^{2+}, Pb^{2+}	Homogeneous	Cu_2S, PbS, Ag_2S, Cu_2S	Ceramic membrane with sintered metal sulphides	—	Hirata and Higashiyama (1971)	66
CN^-	Homogeneous	$AgI + Ag_2S$	Methyl methacrylate	(Patent)	Fleet and Storp (1971)	48
Cl^-	Heterogeneous	AgCl	—	—	Neff, Sambucetti and Carlos (1971)	107
Cs^+	Heterogeneous	Cs 12-molybdo-phosphate	Silicone rubber	—	Coetzee and Basson (1971)	29
Cu^{2+}, Hg^{2+}	Homogeneous	$Cu_{1.8}Se$	—	(Single crystal)	Vesely (1971)	176
Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}	Homogeneous	Ag_2S + MeS	—	On the surface of a silver wire	Anfält and Jagner (1971)	4

Table 1 (continued)

Sensitive to ion	Solid state	Active material	Matrix	Selectivity (Comments)	Workers	References
Cu^{2+} Ag^+ S^{2-}	Homogeneous	—	—	Selectivity, sensitivity, influence of pH, response time are discussed	Adametzova and Gregr (1971)(Crytur model)	1
CN^- Ca^{2+}	Homogeneous	$CaF_2 + LaF_3$	—	Mg^{2+}, Sr^{2+}, Pb^{2+}, Ba^{2+}, Na^+, K^+ ions interfere	Farren (1971) (Perkin–Elmer)	44
Ca^{2+}	Heterogeneous	Ca-didecylphosphate in dioctylphosphonate	5% PVC in cyclohexanone	Na, Mg, Ni, Ba, Sr, Pb, Zn interfere. Coated wire electrode	Cattrall and Freiser (1971)	27
Cu^{2+}	Heterogeneous	$Cu_{2-x}S$	Silicone rubber	Very high selectivity for the copper	Pungor, Tóth and Pick (1972)	132

The precipitate electrodes can be prepared in three ways: from single crystals; from pressed crystals, and from crystals embedded in a suitable material. The first two kinds of electrodes form the group of homogeneous electrodes, while the third type gives the heterogeneous electrodes. However, no basic difference exists between these two types of electrodes (except for some effects, which have not yet been explained). There are of course, differences between the mechanical properties of the electrodes, their lifetime and so forth, but from the electrochemical point of view they should be treated together.

With regard to the construction of the electrodes, the electrode membranes, either homogeneous or heterogeneous, are sealed onto the end of glass or plastic tubes, or screwed on with the help of an inert material which does not swell or cause a short circuit between the two sides of the membrane layer.

THEORETICAL SECTION

Mechanism of the electrode response

The correlations and ideas derived from glass and the so-called ion-exchange electrodes greatly helped in the theoretical description of the precipitate-based electrodes. From these guidelines the electrode behaviour may be interpreted in two ways. The first is based on ion transport through the membrane, derived for ion-exchange electrodes. The second is related to the theory given for the mechanism of the glass electrode, in which it is proposed that different ions take part in the ion-transport phenomenon than in the surface equilibria.

At the beginning of our research we tried to interpret the membrane phenomena by ion-transport[122]. However, later on, experimental results were obtained which were contradictory. No electrochemical difference was found experimentally between electrodes made as a sandwich (silver or platinum plates between two membrane layers assuring electrical contact only through the metal) and normal electrodes[118].

Our opinion about the surface ion-exchange reaction was strengthened by radioactive measurements of the exchange rate of the iodide ions on the silver iodide precipitate-based electrodes[118]. The rate of the exchange reaction was fast and was dependent on the surface charge of the precipitate embedded in the electrode membrane. Of course the charge transport through the crystal and its mechanism are also very important in the interpretation of the behaviour of the electrodes. In this context we would like to mention the paper of Durst and Ross[42], describing the application of an LaF_3 electrode doped with Eu for the coulometric generation of F^-, with an efficiency of 99.2 per cent. Sher and co-workers[156] showed that the LaF_3 electrode has a conductivity of 10^{-7} $ohm^{-1} cm^{-1}$ which can be explained by the following reaction:

$$LaF_3 + vacancy \rightarrow LaF_2^+ + F^-$$
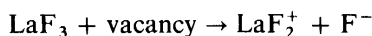
Silver halides and silver sulphide are also ionic conductors (silver sulphide is partly an electric conductor). By analogy with LaF_3, Ross[142] has stated

that the theory of solid-state electrodes is simple because no ions other than those composing the crystal go through the membrane, and the potential is a result of the ion transport through the membrane. This statement shows that he has not taken into consideration the ion-exchange theory described in the literature[24, 118]. Brand and Rechnitz[15], using impedance measurements, have provided further evidence for the surface-exchange theory. However, their detailed discussion seems to be scarcely justified by the small amount of experimental data. In their work they classify four types of electrodes, according to electrical analogies to the response mechanism. The first group, to which the LaF_3 electrode belongs, have, in the analogy, two frequency-dependent impedances in series, one of which is accounted for by the $La(OH)_3$ film on the surface of the electrode, while the other is due to the LaF_3 itself. Brand and Rechnitz assume that there is no difference between the fluoride transport in the two layers. They put the silver chloride electrode into the second group, where there is no surface film on the silver chloride. According to them, in both groups the halide is transported through the membrane and ion-exchange equilibria are established on the surfaces. In the third group, consisting of Br^-, I^-, S^{2-}, Pb^{2+} and Cd^{2+} electrodes and in the fourth group, the copper electrode, ion transport through the membrane has not been proved, and in an electric field charge accumulates on the surface. The authors are of the opinion that measurement of the electrode impedance is a good way of evaluating the rate of the ion-exchange reaction on the surface.

A new contribution has recently been made by Hirata and co-workers[64, 66, 67] to the study of the electrical conductivity of the membrane phase. They found that electrically conducting sintered PbS has no response to Pb^{2+}. In spite of this the electrode functions if the sintered phase contains a large amount of Ag_2S in addition to PbS. In this case ion transport through the membrane and the exchange reaction on the surfaces are affected by different ions. It is interesting to mention that they found a Pb^{2+} response if the PbS was incorporated into silicone rubber. This phenomenon so far, however, cannot be explained.

The importance of surface ion-exchange reactions in the response mechanism has been underlined by our experiments carried out studying the adsorption of various anions on the surfaces of AgI precipitates[117, 124, 149]. From these experiments, it was concluded that halide and pseudo-halide ions, after losing their coordinated water, were adsorbed on the surface of the silver iodide, while other ions such as PO_4^{3-} and SO_4^{2-} are adsorbed without loss of the coordinated water. Furthermore, the investigation showed that the anions forming slightly soluble silver salts are exchanged in a very fast reaction by other anions which form less soluble salts with silver.

Since the development of the precipitate-based ion-selective electrodes it has been stated unambiguously that electric conductivity is a necessary condition for the electrode response in addition to the surface-exchange equilibria. The conductivity can be assured by crystal defects or doping of single crystals as suggested by Frant and Ross[49] who used Eu for doping LaF_3. The last method needs further investigation as emphasized by the work of Vesely[175], who found that there is no unambiguous correlation in

the case of the LaF$_3$ electrode between the doping and the electrochemical behaviour. His finding is in accordance with the opinion of Lingane[94] who believes that doping is unnecessary.

From our research[98] we have concluded that there is a correlation between the number of crystal defects and the standard potential of the electrode. *Table 2* shows the difference between the standard potentials of electrodes of the second kind and the corresponding ion-selective electrodes, the active component of which has been exposed to light for different time intervals.

Table 2. Effect of exposure time on the differences between the potentials of membrane electrodes and electrodes of the second kind

Membrane electrode	Exposure time (min)	ΔE (mV)
AgCl	5	80
	10	72
	20	60
AgBr	5	157
	10	139
	20	131
	30	73
AgI	10	177
	20	151
	30	104

As the slopes remained constant the calibration curves of the electrodes were shifted parallel to each other. In a simple case when the membrane precipitate consists of univalent ions, there is a correlation between the shift of the standard potential and the number of crystal defects. This correlation is as follows:

$$\Delta E = \frac{RT}{F} \ln (a_{\text{X}})_{\text{c}} \times \left(\frac{K_{\text{s}}}{K_{\text{c}}}\right)^{\frac{1}{2}}$$

where K_{s} is the solubility product of the precipitate, K_{c} is the equilibrium constant for the formation of the defect in the crystal, and $(a_{\text{X}})_{\text{c}}$ is the activity of the component X in the crystal and varies between 1 and K_{c}.

The electrode function, however, is not influenced by the standard potential. This was proved not only by us but also by Loshkarev and Yudina[95], who found this for the sulphide electrodes.

The migration of the crystal defects can be described by the Nernst–Plank equation. Buck[24] has applied this equation for the derivation of an expression for the lower detection limit of ion-selective electrodes and reached basically the same conclusion which we reached using the theory of Donnan potentials established on the surfaces[131].

$$E = \frac{RT}{F} \ln \left[\frac{C_{\text{Ag}^+}(-\text{L}) + [C^2_{\text{Ag}^+}(-\text{L}) + 4K_{\text{sp}}(\gamma_\pm)^{-2}]^{\frac{1}{2}}}{C_{\text{Ag}^+}(\text{L}) + [C^2_{\text{Ag}^+}(\text{L}) + 4K_{\text{sp}}(\gamma_\pm)^{-2}]^{\frac{1}{2}}} \right] \frac{\gamma_{\text{Ag}^+}(-\text{L})}{\gamma_{\text{Ag}^+}(\text{L})}$$

where (L) and ($-$L) denote the two sides of the membrane and K_{sp} is the solubility product.

For the calculation of the lower detection limit Covington[33] gave a simpler equation, which also takes into account the solubility of silver halides in halide solutions.

Naturally this lower detection limit varies from electrode to electrode and with the medium used for measurements. Furthermore, the limit shifts to lower concentrations with higher ionic strength. Shifts of several decades can be achieved by alteration of some parameters—as will be discussed later on.

In solutions containing more than one potential-determining ion, the membrane potential of the precipitate-based electrodes can be described on the basis of the ion-exchange equilibrium by the following equation[118], which is analogous with the Nikolsky equation

$$E = E_0 + \frac{RT}{F} \ln a_i \sum_k K_{ik} \frac{a_k}{a_i}$$

where K_{ik} is the selectivity constant of the electrode. (We have derived an equation for the calculation of K_{ik}, which is given later.) Accordingly the selectivity constant may be determined unequivocally from the solubility products of the precipitates built into the membrane and also those formed during the exchange reaction.

Buck[24] has modified this concept and stated that it is valid only for such immiscible precipitates as silver chloride and silver iodide, and he has proposed a more complex expression used for mixed crystals such as mixed $La(OH)_3$ and LaF_3, for which the selectivity constant is:

$$K_{OH,F} = \frac{u_{OH}}{u_F} \times \frac{\gamma_{OH}}{\gamma_F}$$

where u is the mobility of the ion in the crystal, and γ is the activity coefficient in the crystal.

For the practical determination of the selectivity constant the method used by Eisenman[43] for glass electrodes was first employed. This calculation is based on the potential difference measured with the electrode in solutions containing only the reversible ion, and then in solutions containing only the interfering ion, both solutions containing the same counter-ions with activity 0.1 M. The equation for the calculation is

$$\Delta E = \frac{RT}{F} \ln K$$

This method has a fundamental error. It ignores the fact that the concentration of the potential-determining ion, when in a pure solution of the interfering ion, is determined solely by the dissolution of the precipitate. So the measuring conditions do not relate to the required conditions and are not well defined: these defects in the measuring conditions are admirably exemplified by the poor experimental results[136].

Table 3. Selectivity constants of halide ion-selective electrodes for some anions.
K_{ik}^* denotes values measured by direct method; K_{ik}^{**} denotes values measured by indirect method

Ion	Chloride-selective electrode			Bromide-selective electrode			Iodide-selective electrode		
	K_{ik} calc.	K_{ik}^* meas.	K_{ik}^{**} meas.	K_{ik} calc.	K_{ik}^* meas.	K_{ik}^{**} meas.	K_{ik} calc.	K_{ik}^* meas.	K_{ik}^{**} meas.
Cl^-	1	1		2.0×10^{-3}	1.8×10^{-3}	6.0×10^{-3}	9.6×10^{-7}		3.7×10^{-7}
Br^-				1	1		2.0×10^{-4}	2.1×10^{-4}	1.8×10^{-4}
SCN^-				1.5×10^0	0.2×10^0		3.0×10^{-4}		2.4×10^{-4}
OH^-							1.0×10^{-8}		0.9×10^{-8}
CrO_4^{2-}	5.2×10^{-5}		4.5×10^{-5}	2.5×10^{-7}		1.1×10^{-7}	5.0×10^{-11}		6.6×10^{-11}
CO_3^{2-}	6.3×10^{-5}		4.6×10^{-5}	3.1×10^{-7}		1.0×10^{-7}			
PO_4^{3-}	1.3×10^{-4}		0.5×10^{-4}	6.3×10^{-7}		3.1×10^{-7}	1.2×10^{-10}		0.2×10^{-10}
AsO_4^{3-}	3.3×10^{-4}		2.0×10^{-4}	1.6×10^{-6}		1.2×10^{-6}	3.2×10^{-10}		2.6×10^{-10}
$Fe(CN)_6^{4-}$							2.4×10^{-6}		3.5×10^{-6}
I^-							1	1	

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Therefore we have worked out methods[128], on a theoretical basis, for the determination of the selectivity constant. In this calculation the activities at the coprecipitation point have been used. The expression for the selectivity constant is as follows:

$$K_{ik} = \frac{S_{ji}^{1/a}}{S_{jk}^{1/n}} = \frac{(a_i)_s^{b/a}}{(a_k)_s^{m/n}}$$

and the activities at the coprecipitation point are substituted in the calculations. In the formula, S_{ji} and S_{jk} are the solubility products of precipitates, $(I_j)_a (I_i)_b$, and $(I_j)_n (I_k)_m$, while $(a_i)_s$ and $(a_k)_s$ are the activities of the principal ion and the interfering ion at the coprecipitation point. The determination of the selectivity constants can be carried out either by direct or indirect methods. Some results obtained by such methods are collected in *Tables 3, 4* and *5*.

Table 4. The selectivity constants of the sulphide-selective electrode for some anions

Interfering anion (X^-)	$pK_{S,X}$ Measured	Calculated*
I^-	7.8	7.85-8.60
Br^-	11.6	11.51-12.09
Cl^-	14.2	14.10-14.50
OH^-	16.2	16.00-16.73
SCN^-	12.1	11.86-12.13
SO_4^{2-}	21.2	22.00
PO_4^{3-}	16.1	14.75-18.45
CN^-	3.20	3.30-5.96
$S_2O_3^{2-}$	10.70	10.47-11.42

* The values were calculated using the highest and lowest solubility constant data of Ag_2S found in the literature.

In these tables the calculated and measured selectivity constants are compared and they are in good agreement. Furthermore, it can also be seen that the selectivity of some electrodes to many ions is so good that there are practically no interferences to the electrode response.

Naturally, the electrode potential is a result of the difference in the electrochemical potentials of solvated and desolvated ions, which are bonded in

Table 5. The selectivity constants of the sulphide-selective electrode for some cations

Interfering cation (Y^+)	$pK_{Ag,Y}$ Measured	Calculated*
Tl^+	24.2	24.48-29.25
Cu^{2+}	13.7	10.91-13.30
Pb^{2+}	21.8	20.93-21.80
Cd^{2+}	22.4	20.46-22.30
Ni^{2+}	23.3	21.70-28.90
Zn^{2+}	27.9	22.27-26.80
Fe^{2+}	31.5	26.82-31.20
Mn^{2+}	36.2	33.24-38.80
La^{3+}	40.3	44.17

* The values were calculated using the highest and lowest solubility constant data of Ag_2S found in the literature.

the crystal lattice. In this respect the research of Morf and Simon[106] is very valuable; they proposed a rather simple method for the calculation of the hydration enthalpy of the cations. A similar method for anions would be welcome for the theoretical interpretation of anion-selective electrodes.

Many authors have investigated the effect of complexes on the precipitate-based electrodes. The studies have been carried out in two directions. The first was to clarify the nature of the electrode response in solutions containing complexes of the appropriate ion. Secondly, it was fascinating to study the behaviour of the electrodes in solutions of ions which dissolve the precipitate as a complex.

A further complication in the measurement of ions which form complexes is that they may react with the solvent, for example basic anions, such as cyanide, will form acids. Using sulphide and cyanide anion-selective electrodes it was clearly demonstrated that they measure only free anions[125, 148, 173].
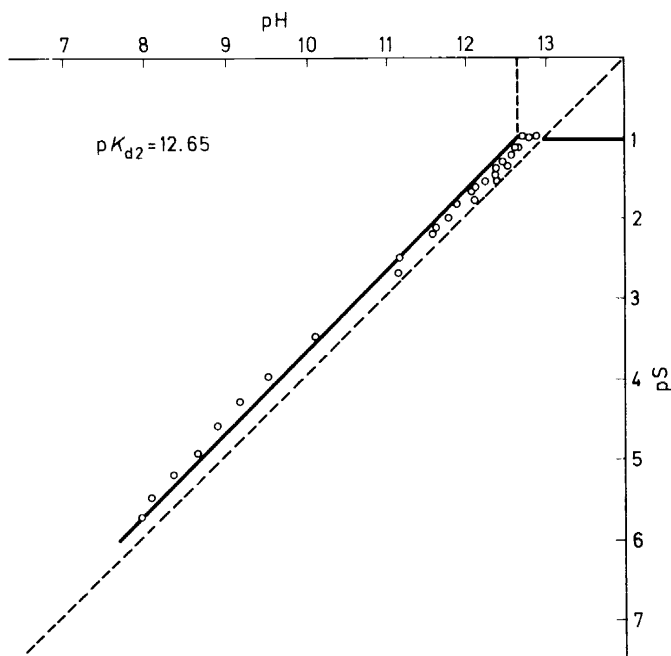

Figure 1. Relation between pH and the sulphide concentration measured with a sulphide-selective electrode in Na_2S solutions

For sulphide the results, shown in *Figure 1*, give good agreement between the theoretical and experimental values. We measured, at 25°C at an ionic strength of 0.1 M, a value of $pK_2 = 12.65$ compared to the literature value $pK_2 = 12.92$. Hseu and Rechnitz[69] using the Orion sulphide electrode

measured the actual sulphide concentration at various pHs. On the basis of their experimental results, they calculated a value for pK_2 which agreed with one other determination ($pK_2 = 14.92$) made more than forty years ago[20, 21, 78]. Since the difference between the pK value of Hseu and Rechnitz and that found by us is quite large, and because we have repeated such measurements and calculations with different systems with unexceptionable results, we concluded that their results must remain open to doubt.

In the case of cyanide we determined the stability constant and found a value of 9.20 which is in agreement with the literature value[173].

Various authors investigated the association and dissociation problems of fluoride. Shrinivasan and Rechnitz[157] and later on, Vanderborgh[174] published results for the stability constant of hydrogen fluoride using a fluoride ion electrode, which agree well with literature data published previously. For example, Broene and de Vries[19] using a glass electrode found $pK = 3.173$ at $25°C$ and Vanderborgh using an Orion fluoride electrode found a pK value of 3.189 at $25°C$.

If any ion present in the solution is a complexing agent, then it may react with the membrane. A good example of this is cyanide ion and silver halide membrane electrodes. Due to the formation of complex silver cyanide, the cyanide ion liberates halide on the surface of the electrode, which diffuses in the opposite direction to the cyanide ion reaching the surface from the bulk of the solution. From this the actual cyanide concentration at the surface may be assumed to be virtually zero, except at very high cyanide concentrations. This was the basis for our deduction of the dependence of the potential on the cyanide activity.

$$E = E_0 + \frac{RT}{F} \ln (a_x + K a_{CN}^2)$$

where a_x is the activity of halide liberated and present at the surface of the electrode; this will equal $\frac{1}{2} a_{CN}$ in the absence of the appropriate halide in the solution. K is the dissolution constant, for which we[173] have found experimental values of between 1 and 0.1. The electrode behaviour, indicated by the equation, is illustrated in *Figure 2*.

Concerning the details of the mechanism, it is doubtful whether the reaction

$$AgX + 2CN^- \rightleftharpoons Ag(CN)_2^- + X^-$$
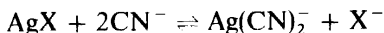
alone determines the electrode response. Fleet and Storp[48], who investigated the iodide-based cyanide electrode, propose that the simple precipitation-exchange reaction also plays a role:

$$AgX + CN^- = AgCN + X^-$$
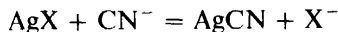
Silver halides can be completely dissolved in a cyanide solution when the cyanide present is equivalent to that of the halide. However, if complex formation needs a large excess of complexing agent, the electrode also responds to that kind of complexing ion. This is the situation when an iodide electrode is used for the determination of $S_2O_3^{2-}$. In this case the K value lies between 10^{-2} and 10^{-3}. The same is also true when measuring cyanide with a sulphide electrode.
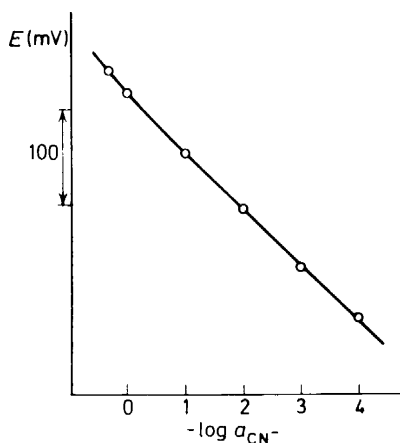
118

Figure 2. Calibration curve for the determination of cyanide; —, calculated curve; ◯, measured point.

Whatever basic halide electrode is used for the determination of cyanide the electrode responds with the same efficiency to the cyanide as to the anion composing the electrode. The selectivity constant for other ions remains the same as it would be in the presence of the anion corresponding to the appropriate electrode. This was one of the fundamental experiments on the basis of which we deduced the potential equation mentioned previously. This is demonstrated in *Table 6*, where an iodide-based electrode was used and selectivity constants for various ions in the presence of both cyanide and iodide ions in the solution were determined. It is worth noting that the complexing agent destroys the electrode, and so the lifetime of electrodes is limited.

If the anion investigated forms complexes with metal ions, then the electrode potential allows us to observe the complex formation and to get information about the stability data. Szabó[162] has been able to demonstrate, by using an iodide-selective electrode, the formation of the I_3^- complex. This was also shown by Liberti and Mascini[88]. There are now many results of complex formation studies in the literature obtained from work with ion-selective electrodes. It is generally found that complexes of low stability

Table 6. Potentiometric selectivity of iodide membrane electrodes

Ion	Selectivity constants in the presence of	
	CN^-	I^-
Cl^-	10^{-5}–10^{-6}	10^{-6}
Br^-	10^{-3}–10^{-4}	10^{-4}
I^-	1	—
CN^-	—	1
NH_4^+	10^{-5}–10^{-6}	10^{-6}
SO_4^{2-}	10^{-5}–10^{-6}	10^{-6}

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produce no interference with the electrode response. For example Rechnitz[136, 137] has shown that metal ions forming complexes of low stability with halides do not influence the calibration curve of halides. In the presence of stable complexes the free ligand activity or that of complex-forming cations can be measured. In our laboratory[173] we have investigated cyanide complexes and found that one can distinguish, in the case of silver the two complexes, $Ag(CN)_2^-$ and $Ag(CN)_3^{2-}$; for copper the $Cu(CN)_4^{3-}$ ion, and for mercury and nickel the $Hg(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$ ions. No cyanide complexes of Cd and Zn could be observed. Fleet and Storp[48] explained this finding by saying that the hydroxide complexes were formed preferentially to the cyanide complexes.

We should also like to mention a very detailed study of the copper(II) complexes of ethane-1-hydroxy-1,1-diphosphoric acid, which was made with a copper electrode by Wada and Fernando[178]. They compared their results with those obtained by spectrophotometry and by potentiometry using a glass electrode. This study underlined the advantages of the copper electrode for such purposes.

Kinetic studies of the formation of FeF^{2+} and AlF^{2+} complexes have been performed by Shrinivasan and Rechnitz[158]. They were able to distinguish the kinetic steps of AlF^{2+} complex formation in the presence of aqueous and hydroxo-aluminium complexes.

A further example of a study of metal–fluoride complex formation is provided by Bond and Hefter[13] who calculated the formation constants of lead fluoride complexes using a fluoride electrode.

Very important results concerning the lower detection limit of electrodes have been obtained by the investigation of complexes. Our investigations with cyanide lend weight to the fact that the lower detection limit shifts further down in the presence of complexes. At the same time Mesmer[104] has demonstrated similar phenomena with beryllium complexes, with which the lowest detectable fluoride concentration in 1 M sodium chloride solution was 7×10^{-8} M.

Aziz and Lyle[5] successfully investigated fluoro-complexes of the metals gadolinium, europium, scandium, iron, magnesium, and calcium: the β values are all lower than 10^6 l mol^{-1} and this was found to be the limit of the method. Their investigation therefore excluded a study of the thorium complexes. In spite of this, Baumann[10] reports that she investigated the zirconium, thorium and lanthanum fluoro-complexes in solutions of ionic strength of 0.5 to 2 M. Among the various complexes, she was able to distinguish the ZrF^{3+} and ZrF_2^{2+} complexes for zirconium, the ThF^{3+} and ThF_2^{2+} complexes for thorium and the LaF^{2+} complex in the case of lanthanum.

One problem encountered in this work is that lanthanum fluoride influences the fluoride measurement by the dissolution of its surface, which releases fluoride ions into the solution. In this respect the polycrystalline electrodes have a further disadvantage by having a higher dissolution rate than the single crystals.

Baumann also reports that the Nernstian response of the fluoride electrode extends down to 5×10^{-9} M in the presence of thorium and zirconium, 8×10^{-7} M in the presence of lanthanum and 3×10^{-7} M in the presence

of perchloric acid. At the same time, however, in pure fluoride solutions the response is linear down to only 8×10^{-5} M.

Buffers

Unfortunately, among the ion-selective electrodes, we only have buffers of high capacity for pH electrodes. Because of this lack of suitable buffers for other ions, the calibration of electrodes responsive to these other ions is difficult. Moreover, junction potentials are a further problem which has been discussed in a paper by Bates and Alfenaar[7]. However, following the need for further scales of ionic activity, some practical methods have been devised for their construction. For concentrations greater than 10^{-3} M the calibration can be carried out directly with solutions of the appropriate ion, the ionic strength being maintained by electrolytes for whose components the selectivity constants are lower than 10^{-8}.

Another calibration method which is available uses the complexes or precipitates which are in equilibrium with the appropriate ion. It should be mentioned that such systems generally have low-buffer capacities. To this group belong those buffers suggested by Havas and his co-workers[61]; they have used saturated solutions of silver halides for calibration points. The disadvantage of this method is the great susceptibility to change of the solubility of the silver halides by any one of a number of parameters.

There are many papers published in the literature on the application of the fluoride electrode. Because the fluoride ion takes part in an acid-base equilibrium and is also a good complexing agent for various metal ions, it is necessary to ensure reproducible conditions for the fluoride measurements. Frant and Ross[50] suggested the TISAB buffer (Total Ionic Strength Adjusting Buffer). This has a pH of 5.0 and an ionic strength of 1.75 M: it consists of 1.0 M sodium chloride, 0.25 M acetic acid, 0.75 M sodium acetate and 0.001 M sodium citrate. In this medium fluoride determination can be carried out down to 10^{-6} M fluoride ion activity without interference.

The behaviour of the electrodes in non-aqueous solvents

A systematic study of the behaviour of the precipitate-based electrodes has been carried out by Kazarjan and Pungor[74, 75]. The silver halide electrodes were used in alcohols, ketones and other solvents such as dimethylformamide. In this investigation aqueous and aqueous/non-aqueous solvent mixtures in different ratios were used. The solubility product of the silver halides and the selectivity constants of the electrodes were measured in the different solvent mixtures. The calculated and measured selectivity constants are compared in *Tables 7* and *8*.

It may be seen from the tables that the theoretical values agree with the measured values and thus one may conclude that the ion-exchange concept is also valid in these systems.

In these experiments we found that it was necessary to first condition the electrode in the appropriate solvent mixtures as the membrane is heterogeneous; during the soaking we observed a swelling effect.

As expected the theory for the lower detection limit of the electrodes derived for aqueous solvents is also valid for other media. So, for example,

Table 7. Selectivity constants of an iodide-selective electrode to bromide in mixtures of distilled water and an alcohol

Solvent	Ratio of solvent (v/v %)	Mole fraction of solvent	pK Theor.	pK Calc.	pK ΔpK
CH_3OH	10:90	0.047	3.64	3.78	− 0.14
	40:60	0.228	3.48	3.60	− 0.12
	60:40	0.400	3.34	3.38	− 0.04
	90:10	0.802	3.02	3.02	− 0.00
	100: 0	1.00	2.93	—	—
C_2H_5OH	10:90	3.20	3.62	3.70	− 0.08
	40:60	16.20	3.50	3.55	− 0.05
	60:40	29.80	3.34	3.30	− 0.04
	90:10	67.70	3.00	2.76	+ 0.24
	100: 0	100.00	—	—	—
n-C_3H-OH	10:90	2.60	3.70	3.74	− 0.04
	20:80	5.60	3.58	3.54	+ 0.04
	30:70	9.20	3.58	3.46	+ 0.12
	40:60	13.70	3.58	3.42	+ 0.16
iso-C_3H-OH	10:90	2.60	3.74	3.78	− 0.04
	20:80	5.60	3.64	3.60	+ 0.04
	30:70	9.20	3.56	3.49	+ 0.07
	40:60	13.70	3.50	3.16	+ 0.34

in 90 per cent ethanol, the lower detection limit of the iodide electrode lies at about 10^{-9} M, this decrease being produced by a difference of approximately 1.5 units between the solubility product exponent in this medium and in water.

For measurements with the fluoride electrode, Lingane[94] reported that in alcoholic solvents the lower detection limit of the fluoride electrode shifts downward by nearly one decade.

Another study in non-aqueous solvents, using the lead electrode, consisting of lead sulphide plus silver sulphide, has been carried out by Rechnitz and Kenny[134]. They used this electrode with success in methanol, dioxane, acetonitrile and dimethylsulphoxide.

Table 8. Selectivity constants of an iodide-selective electrode to bromide in non-aqueous solvents

In mixtures of distilled water and acetone			In mixtures of distilled water and dimethylformamide		
Ratio of acetone to H_2O (v/v %)	pK Theor.	pK Experimental	Ratio of DMF to H_2O (v/v %)	pK Theor.	pK Experimental
10:90	3.82	3.75	10:90	3.74	3.75
20:80	3.68	3.60	40:60	3.26	3.20
30:70	3.62	3.56	60:40	2.64	2.60
40:60	3.56	3.55			

Transient phenomena of the electrode

The transient phenomena of the precipitate electrodes are very important from both theoretical and practical points of view, but primarily because of the information afforded concerning continuous measurement techniques[129]. Despite this importance, there has been little research in this field. This may be explained partly by the intrinsic measurement difficulties and partly by the complexity of the interpretation of the results.

The immersion and injection techniques for producing transient phenomena are equally useful. In our review paper summarizing the state of the art, we concluded that, for the halide electrodes, the literature data were not always useful because the results were sometimes influenced by the response lag of the measuring systems. Our results[172] and those of Rechnitz[137] have indicated that the response time is, for halide electrodes, less than one second.

Our most important conclusions, reached with our heterogeneous electrodes, are as follows:

(i) The response time can be described by one exponential equation.

(ii) The response time is only slightly dependent on the thickness of the membrane layer.

(iii) The response time decreases if the solution contains non-interfering ions in large excess.

(iv) The response time of the iodide-based cyanide electrode in cyanide solutions is the same as in iodide solutions. This strongly suggests that the potential-determining processes are identical for the two responses.

Using a sulphide electrode, rather than a halide electrode, Light[92] found a response time of about one millisecond.

PRACTICAL SECTION

Measuring techniques

The measuring techniques applied to the precipitate-based electrodes are the same as those used for every other kind of electrode.

The measurements may be carried out either in cells with liquid–liquid junctions or without liquid–liquid junctions. In the latter case we must choose a reference electrode which is reversible to one of the components in the system—one which does not interfere with the ion-selective electrode. At the same time this component may also be used to maintain the constancy of the ionic strength. We have used in this way, as a reference electrode, the ion-exchange based perchlorate electrode[123]. Such an experimental system is especially suitable for the investigation of complex equilibria, the ionic strength being maintained by perchlorate.

Cells with liquid–liquid junctions have to be constructed in such a way that the electrolyte in the salt bridge does not interfere with the measuring electrode.

If both the measuring and reference electrodes have high internal resistances, then the leads connecting them to the measuring instrument should be shielded and both instrument inputs should have high impedances, rather than just one as with a normal pH meter. To meet these requirements,

Brand and Rechnitz[17] have designed a device with two, very high impedance, matched and symmetrical inputs using operational amplifiers.

Measurement with ion-selective electrodes can be carried out in several different ways. The activity of the ion can be estimated directly, as when using a glass electrode for pH determination, or alternatively the standard addition technique[8, 16 22, 39, 97], which is also a direct method, can be used. In many cases this latter technique gives better results than the simple direct-measuring procedure. A further elaboration is the so-called multi-addition technique. This technique has the advantage, compared to the simple calibration procedure, that it is not necessary to know anything other than that the electrode response is linear with the logarithm of the ionic activity in the measurement range. This multiple standard addition technique gives very accurate results, particularly when combined with a computer.

Precipitate-based electrodes can be used as indicator electrodes in potentiometric titrations. One method where they may be particularly used to advantage is null-point potentiometry. Durst[37] has devised an arrangement using this technique for the measurement of nanogramme quantities in volumes of 50 µl.

Errors

The errors arising from the direct application of membrane electrodes have recently been studied. Krull[82] studied generally the influence of errors of the selectivity constant on the analytical results and his findings are also valid for the precipitate-based electrodes, if the measurement of the selectivity constant is incorrect.

In direct potentiometry an error of 1 mV leads to an error of nearly 4 per cent in the determined concentration. Moreover, this error increases if the measurement is carried out in a non-Nernstian part of the calibration curve.

If precipitate-based electrodes are used for end-point indication in a titration, the precision of the determination is higher than in direct measurement. Schultz[150] has suggested that in ideal conditions the titration curve should be symmetrical about the end-point. However, these ideal conditions are only assured if, among other things, the system to be titrated does not contain ions for which the selectivity constant is appreciable ($< 10^{-8}$). Schultz has written the equation of the titration curve when the titrand contains interfering ions, as follows:

$$\frac{n(E - E_0)}{0.059} = -\log\left(c_i + \sum k_j \frac{c_j V_0}{V_0 + V_t}\right)$$

If the interfering ion is in the titrant:

$$\frac{n(E - E_0)}{0.059} = -\log\left(c_i + \sum k_z \frac{c_z V_t}{V_0 + V_t}\right)$$

and if both the titrand and titrant contain interfering ions, the expression becomes

$$\frac{n(E - E_0)}{0.059} = -\log\left(c_i + \sum k_j \frac{c_j V_0}{V_0 + V_t} + \sum k_z \frac{c_z V_t}{V_0 + V_t}\right)$$

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Carr[26] discusses the question of errors in detail and points out that the end-point error of a precipitation titration is only negligible if interfering ions are absent. Schultz[151] studied the same question for chelatometric titrations and found that the titration error increases as a function of the selectivity constant.

The difficulties increase if the composition of the titration product is uncertain, as was found, for example, by Lingane[93] when using metal–fluoride complexes in determinations.

Anfält and Jagner[2] studied various titration methods using ion-selective electrodes from the point of view of the errors, and concluded that the most precise data were achieved by use of the Gran[54] method, corrected by Ingman and Still[70]. Liberti and Mascini[87] have published a paper describing an application of the Gran method.

A further measuring error arises if the electrode becomes polarized, as has been pointed out by Buck[25]. Hence, because of the high resistance of precipitate-based electrodes, the input impedance of the measuring device must be high, normally not less than 10^{12} ohms.

SOME ANALYTICAL APPLICATIONS OF PRECIPITATE-BASED ION-SELECTIVE ELECTRODES

Some of the more recent analytical applications of precipitate-based electrodes are collected in *Table 9*. We should like to briefly discuss some of these applications.

One type of application is in the determination of very low concentrations. As examples we can mention the determination of cyanide in sewage, some results of which are presented in *Table 10*, and of cyanide in leaves, as shown in *Table 11*. In this estimation of cyanide in leaves, a particular advantage is that the usual preliminary distillation step is unnecessary. A further application is shown in *Table 12*, which contains results of chloride determinations in potassium hydroxide; such determinations are of especial importance in semiconductor technology. In this method the sample is initially passed over a cation-exchange resin, and the eluted chloride measured with the electrode.

Another type of application is in the titration of such compounds that react to produce components to which the electrode is reversible, as for example in the determination of thiourea[114]. Thiourea is only slightly hydrolysed in aqueous solution, as may be demonstrated by potentiometric measurements using a sulphide-selective electrode. The approximate concentration of sulphide ion, as calculated by the Nernst equation, in alkaline 10^{-1} M thiourea solution is extremely small—about 10^{-15} M. On titration of the solution with silver nitrate in the presence of 0.1 N sodium hydroxide, the following reaction takes place:
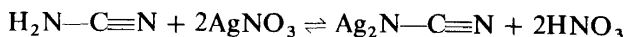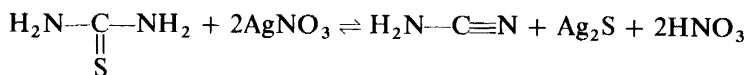
$$H_2N\text{---}\underset{\underset{S}{\|}}{C}\text{---}NH_2 + 2AgNO_3 \rightleftharpoons H_2N\text{---}C\equiv N + Ag_2S + 2HNO_3$$

$$H_2N\text{---}C\equiv N + 2AgNO_3 \rightleftharpoons Ag_2N\text{---}C\equiv N + 2HNO_3$$

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Table 9. Some recent applications of precipitate-based electrodes

Component or ion	Method	Electrode	Measuring range	Titrant	Error	Interfering ions	Non-interfering ions	Sample	Media	Comments	References
Ag^+	Direct	Ag^+	$pAg = 0-17$	—	—	Hg^{2+}	$S_2O_3^{2-}$ SO_4^{2-}	—	—	Response time and temperature dependence data	92
Halides	Indirect	Ag^+	$0.1-10$ μeq.	$AgNO_3$	0.35%	—	—	Inorganic materials	80% acetic acid	After burning, half-automatic	81
Hg^{2+}	Indirect	Ag^+	$0.1-40$ ppm	Dithiooxamide	$\approx 0.3\%$	Co^{2+} Ag^+	Zn^{2+} Cd^{2+} Pb^{2+} Fe^{3+}	—	Buffer	—	73
CN^- Cl^-	Indirect	Ag^+	mmol	$AgNO_3$	0.4%	—	—	—	—	Consecutive potentiometric titration	31
Cl^-	Direct	Cl^-	$pCl = 1-5$	—	± 0.05 pCl	—	—	Urine, blood serum	—	In the presence of proteins	112
Cl^-	Indirect	Cl^-	$pCl = 1-3$	$AgNO_3$	$<1\%$	—	—	—	—	—	
Cl^-	Indirect	Cl^-	$pCl = 1-3$	$AgNO_3$	2.1%	Br^-, I^-	—	Plants	Acidic	Direct Cl^- determination can not be used	85
Cl^-	Direct	Cl^-	$pCl = 1-4$	—	± 0.05 pCl	Br^-, I^-, S^{2-}	—	Pharmaceuticals	—	Calculated activity coefficient	113
	Indirect	Cl^-	$pCl = 1-3$	$AgNO_3$	1%						
Amygdalin	Direct	CN^-	$pAm = 3-5$	—	—	Cu^{2+} Cd^{2+} Hg^{2+}	—	—	Buffer $pH = 10-11$	Immobilized β-glucosidase on the CN^- electrode surface, lifetime 200 h	139
Cyano-cobalamin (vitamin B_{12}) CN^-	Direct	CN^-	$pB_{12} > 6$	—	± 0.04 pCN	—	—	Pharmaceuticals	Alkaline $pH > 7$	CN^- was liberated by reducing agents and light	35
CN^-	Direct	CN^-	$pCN \approx 5$	—	—	—	—	Fruits, brandy	60% alcohol $pH > 11$	—	59
	Indirect	CN^-	$pCN \approx 4$	$AgNO_3$	—						
CN^-	Direct	CN^-	$pCN = 1-6$	—	5%	Hg^{2+} Cu^{2+} Ni^{2+}	—	Waste water	$pH > 11$	—	173

Substance determined	Ion	Technique	Range	Reagent	Precision	Interferences	Diverse ions	Sample	Conditions	Remarks	Ref.
CN⁻	CN⁻	Indirect	pCN > 4	AgNO₃	1%		Br⁻, I⁻			—	11
CN⁻	CN⁻	Direct	>1 ppm		2%			Plant extractions		—	166
CN⁻	CN⁻	Indirect		Ni-salt		K_3PO_4, KSCN, NaCl, Na_2SO_4 at 4×10^{-2} M solns			NaOH or NH₃ solns	At the end-point is $[Ni(CN)_4]^{2-}$	166
CN⁻	CN⁻	Direct	pCN = 5				S²⁻, Cl⁻	Air, drinking water, ind. waste, biol. media		In the presence S²⁻ or Cl⁻ HCN must be isolated	30
CN⁻	CN⁻	Direct	pCN = 2-6							—	127
	Cl⁻	Direct	pCl = 1-5			$Hg^{2+}, Cu^{2+}, Ni^{2+}$		Waste water		—	
Cl⁻	Cl⁻	Indirect	pCl = 1-3	AgNO₃						—	
I-131	I⁻	Direct	pI = 1-6							—	18
Hg²⁺	I⁻	Indirect	$pHg^{2+} < 6$	NaI	±0.4%			Milk		Hg complexing ligands can be masked with metals	111
Pharma-ceuticals	Cl⁻	Direct	pCl = 1-4		0.01-0.04 pX			Basic materials of pharmaceuticals		Organically bonded halogens can be measured after burning, half-automatically	34
	I⁻	Indirect	pI = 1-3	AgNO₃						—	
Halides	Cl⁻, Br⁻	Direct	pX = 1-6				S²⁻	p.a. KOH		Direct determination of halides (a) partial oxidation (b) ion-exchange Study of "p-sel"	62
Halides	I⁻	Indirect		AgNO₃			S²⁻			—	
Halides	X⁻	Direct	pX = 1-6		±0.05-0.15 pX				pH = 5	—	96
NaBPh₄	Halides	Indirect	0.2 mM	AgNO₃	0.38-0.49%					Back titrn. excess NaBPh₄	159
K⁺	Ag⁺ or halides	Indirect	4-20 mg	AgNO₃						—	

Table 9 (continued)

Component or ion	Method	Electrode	Measuring range	Titrant	Error	Interfering ions	Non-interfering ions	Sample	Media	Comments	References
Me^{2+}	Indirect	Cu^{2+}	pMe = 3-5	TEPA, EGTA, 1,10-phenanthroline	—	Cl^-, pE, Na^+	—	—	pH = 3-11	Zn, Cd, Ni, Pb, Ca. Mg indirect determination with copper-chelate indicator	144
Cu^{2+}	Indirect	Cu^{2+}	pCu = 2-5	EDTA, TEPA, 5,6-dimethyl-1,10-phenanthroline	—	—	—	Non-aqueous methanol acetone acetonitrile	—	—	133
Me^{4+} Me^{3+} Me^{2+}	Indirect	Cu^{2+}	5-7 µM Me	EDTA	<1%	—	—	—	pH = 5 Na-acetate buffer pH = 10 0.1 M NaOH	Zr, Th, La, Sm, Fe, Ca, Hg indirect determination with Cu-EDTA indicator	9
NTA	Indirect	Cu^{2+}	pCu = 3-4.3	NTA	—	—	PO_4^{3-}, SO_4^{2-} $R-SO_3^-$ $Na_5P_3O_{10}$	Water detergents	pH = 9.6 0.1 M NH_3-NH_4NO_3 buffer	—	135
Al^{3+}	Indirect	Cu^{2+}	pAl = 2.5-3.5	DCTA	—	Mg^{2+} Ca^{2+}	Na, NH_4^+	—	pH = 5.5	Indirect potentiometric titration	160
Ca^{2+} + Mg^{2+}	Indirect	Cu^{2+}	0.03-0.41 µM Me	EDTA	—	—	—	Water	pH = 9.2 borate buffer pH = 10.0 phenolate buffer	Water analysis Cu-EDTA indicator method	99
Cs^+	Indirect	Cs^+	6.5-72.4 mg Cs^+	$H_3PMo_{12}O_{40}$	—	Li^+	Na^+	$NaBPh_4$, $CsNO_3$, $LiNO_3$	Aqueous	The end-points were determined from Gran plots	29
F^-	Linear null-point potentiometry	F^-	0.038-19 ng ml^{-1}	—	1%	—	—	Water	—	Water analysis	37
F^-	Indirect	F^-	pF = 5-6	$La(NO_3)_3$	—	—	—	—	6% alcohol	The solubility products of LaF_3, EuF_3 have been measured	94
F^-	Direct	F^-	pF = 3-5	—	—	—	—	—	Acidic at various	pK_{HF} has been determined	174

Method	Ion	Range		Interference	Error		Sample	Buffer / medium	Remarks	Ref.
Direct	F^{-}	pF $<$ 6	—	Proteins	$\pm$10%	—	Biological samples	—	—	171
Direct	F^{-}	$>$0.1 ppm	—	—	—	—	—	—	Reproducibility 0.05 ppm	90
Direct	F^{-}	1 mg ml^{-1}	—	—	1%	—	Natural water	Distilled water	F^{-} determination after ion-exchanging processes	91
Indirect	F^{-}	—	0.005 M Th(NO$_3$)$_4$	—	4%	—	—	Water–alcohol	—	
Direct	F^{-}	pF $<$ 6.3 in 1 M NaCl	—	—	1.7%	—	NaCl	TISAB	Sewages	179
Indirect	F^{-}	pF = 1–6	—	—	2.3%	—	Natural water	—	In micro-samples	38
Direct	F^{-} (micro)	pF = 2–5.3	—	Fe^{2+}, Fe^{3+}	—	—	Biological samples	—	After distillation	76
Direct	F^{-}	2 ppm	—	—	—	—	—	—	—	
Standard addition	F^{-}	0.0734 mM kg^{-1}	—	Stable F^{-} complexes	$>$0.2%	—	Sea water	—	Half-automatic titration, end-point is calculated by computer	3
Direct	F^{-}	2–6%	—	Al^{3+}, Fe^{3+}, Ca^{2+}	0.05–0.1%	—	Oxides, fluorspar, opal glass	TISAB	Fast method	115
Direct	F^{-}	—	—	F^{-}	0.1–1%	—	Phosphate rock, apatite	pH = 6.5 NH$_4$OAC buffer	—	116
Direct	F^{-}	1–10 ngF^{-} l^{-1}	—	B	—	—	Organic fluorine	HOAC + NaCl + Na-citrate + NaOH pH = 5.5	In burnt sample	68
Indirect	F^{-}	0.1 ppm	—	—	—	—	Polluted air	Na-monocitrate NaOH buffer	Automatic control, the air being filtered through a suitable medium	89
Potentiometric std.	F^{-}	10–2000 ppm	—	—	5.7% 9.3%	—	In vegetation	—	Acid exts. from pulverized plant tissue	71
Direct	F^{-}	0.01–1.0 ppm	—	Cyanamide H$_3$PO$_4$, silicic acid, H$_2$CO$_3$	—	Co, Mg, Fe, Al, Cr, Ti	In fertilizers and plant	—	F was distr. (calibration for silicofluoride)	182

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Table 9 (continued)

Component or ion	Method	Electrode	Measuring range	Titrant	Error	Interfering ions	Non-interfering ions	Sample	Media	Comments	References
F^-	Indirect	F^-	—	$Th(NO_3)_4$	—	—	Cryolite AlF_3	—	H_2SO_4	After distillation	140
F^-	Direct	F^-	$pF = 6-11$ $pF = 5$ or $0.19\ ppm$	—	2%	—	—	—	Aqueous in the presence of complexing ions, TISAB	Interpretation of the results using a computer	52
F^-	Direct	F^-	$1.84\ mg$	—	-6.81%	—	—	In the presence of complexing ions detn. F^- in opal glass	$pH = 5.3$	—	6
Al^{3+}	Direct	F^-	$pAl = 4-6$	—	$0.6-2.5\%$	Be, Fe $PO_4 > 0.2$ $\mu M\ ml^{-1}$	Mg^{2+}, Cu^{2+} Pb^{2+}	—	$pH = 3.8$ $\mu = 0.3$	Micro and semimicro determination	72
HF	Direct	F^-	$0.41-7.72\%$ CaF_2	—	$0.01-0.19\%$	—	H_2SO_4, $BaSO_4$ SO_2, $CuSO_4$	Waste $CaSO_4$ and gases	—	—	84
CN^-	Direct	CN^-	$0.1\ mgCN^-\ l^{-1}$	—	—	—	—	Waste water	—	—	109
F^-		F^-						River water	TISAB		110
F^-	Direct	F^-	$0.05-1\ mg$ $F^-\ l^{-1}$	—	—	—	—	Biological samples	TISAB	—	
Cl^-		Cl^-						Biological samples	TISAB		
Pb^{2+}	Direct	Pb^{2+}	$pPb = 2-6$	—	—	Ni^{2+} Mn^{2+} Zn^{2+}	—		Water alcohol dimethyl sulfoxide	In blood unsuccessful	134
Pb^{2+}	Indirect Direct	Pb^{2+} Pb^{2+}	$pPb = 3$ $pPb = 1-5$	EDTA	—	Ag^+, Tl^+, NH_4^+	—	—	—	Selectivity determined	86
PO_4^{3-}	Indirect	Pb^{2+}	K_2SO_4 K_2CrO_4 $0.5-1.5\ mg$	$Pb(ClO_4)_2$	$1-2\%$	Cl^-, F^-, CrO_4^{2-}	SO_4^{2-}, NO_3^-	—	Buffer $pH = 8.25-8.75$	—	152
$C_2O_4^{2-}$	Indirect	Pb^{2+}	$1-25\ mg$ $C_2O_4^{2-}$	$Pb(ClO_4)_2$	0.06%	Complexing and ppt-ing species	Ac^-, formate propionate, phthalate	—	$40\% p$-dioxane $pH = 3.5-10.5$	—	153
SO_4^{2-}	Indirect	Pb^{2+}	$pPb < 4.3$	$Pb(ClO_4)_2$	$\pm 1\%$	Ag^+, Cu^{2+} Hg^{2+}, PO_4^{3-}	—	—	$50 v/v\%$ dioxane–water	—	143

Determinand	Method	Measured ion	Concn range	Titrant	Precision	Reagent added	Interferences	Conditions	Medium / pH	Remarks	Ref.
S^{2-}	Direct	S^{2-}	pS = 0–20	—	—	—	—	—	Alkaline pH $\geq$ 13	Response time and temperature dependence data	92
S^{2-}	Indirect	S^{2-}	—	$AgNO_3$	—	Hg^{2+}	$S_2O_3^{2-}$, SO_4^{2-}, I^-, Br^-, F^-, CN^-	—	—	—	108
S^{2-}	Indirect	S^{2-}	pS < 4	$Na_2Pb(OH)_4$	—	—	Cl^-, Br^-, I^-, SCN^-, SO_3^{2-}	—	—	—	161
Inorganic S^{2-}	Indirect	S^{2-}	—	$AgNO_3$	—	—	—	Alkaline pulping liquor	1 M NH_4OH	Direct method was also studied	—
Organic S^{2-}	Back titration	S^{2-}	—	$AgNO_3$	—	—	—	—	—	—	—
S^{2-}	Indirect	S^{2-}	5 ppm	$AgNO_3$	<1 ppm	$S_2O_3^{2-}$	CO_3^{2-}, SO_3^{2-}	In proteins except lysozyme	Aqueous soln.	—	57
SS group	Indirect	S^2	—	$AgNO_3$	7%	—	—	—	—	—	60
Thiols	Indirect	S^{2-}	—	$AgNO_3$	1%	Hg^{2+}	—	—	—	—	56
Halides	Indirect	S^{2-}	0.04–1.5 µeq.	$AgNO_3$	±0.1 pS^{2-}	—	—	—	75% acetic acid	Automatic	80
NH_4-diethyl dithiophosphate	Direct	S^{2-}	—	—	—	$Na_2S_2O_3$	—	Flotation mill solns	—	Metallurgical industry; selectivity is discussed	141
Thiourea	Direct	S^{2-}	pS = 1–6	—	—	—	Redox-couples	—	—	—	114
Thiourea	Indirect	S^{2-}	pS = 1–3	$AgNO_3$	—	—	—	—	Alkaline	Investigation and identification of the product by elementary analysis and i.r.	—
Na_2S	Indirect	S^{2-}	pS = 0–17	$AgNO_3$	—	—	—	In the presence of different anions and cations	—	Measured and calculated selectivity constants show good agreement	147
H_2S	—	S^{2-}	—	—	—	—	—	—	Alkaline	Selective gas-chromatographic detector (potentiometric output)	148
HCl	—	Cl^-	10^{-10} M Me_2S_2	—	—	—	—	—	—	—	77

In the first step, one sulphur splits off to form silver sulphide and at the same time cyanamide is formed. The resulting cyanamide reacts with a further two molecules of silver nitrate and a silver cyanamide precipitate is formed.

Table 10. Determination of cyanide in sewage

Sample	Dilution	Cyanide content of sewage (ppm) Direct method*
1	1:1	13.1
	1:5	14.6
	1:10	13.1
	---	24.7
2	1:1	23.4

* The values are calculated back to the undiluted solution.

The products of the titration were separated by filtration and were analysed gravimetrically and also for their elemental composition. In addition their infrared spectra were taken. For comparison the spectra of pure cyanamide and thiourea were also recorded. These experiments proved the proposed reaction path. The titration allows an accurate determination of thiourea and a fully detailed method has been worked out with the help of our co-worker Mrs Kucsera. The reaction, which takes place rapidly as the titration proceeds, is followed conveniently by a sulphide ion-selective electrode in 10^{-1}–10^{-3} M thiourea solutions.

Table 11. Determination of cyanide in various materials by direct potentiometric measurement with the pCN electrode

Type of material	Designation or variety	Cyanide content (ppm)	Type of material	Designation or variety	Cyanide content (ppm)
Bitter almond		280	Peach leaves	Alexander	39
Spicy almond	Bt 13 55	92		Sunbeam	63
	Bt 13 62	95		May Flower	72
	Bt 13 65	98		Mariska	74
	Bt 13 66	86		Champion	76
Sweet almond	Bt 70	22		Elberta	91
	Bt 1	31		Ford	120
	Bt 11	54			
Sudan grasses*	1. A	298	Sudan grasses	5. A	130
	B	86		B	49
	C	89		C	16
	2. A	27		6. A	71
	B	14		B	45
	C	2		C	36
	3. A	312		7. A	123
	B	70		B	62
	C	12		C	34
	4. A	17		8. A	175
	B	27		B	70
	C	2		C	1

* Sudan grasses are altered by the fertilization practices (sample numbers) and successive developmental stages (capital letters) of the plants in the respective sample.

Table 12. Direct determination of chloride in KOH using a chloride membrane electrode

[Cl⁻], (M)		Cl⁻ content (%)	Error (%)
Calc.	Found		
1.00×10^{-4}	1.02×10^{-4}	7.24×10^{-3}	2
1.00×10^{-4}	1.04×10^{-4}	7.38×10^{-3}	4
1.00×10^{-4}	1.05×10^{-4}	7.45×10^{-3}	5

Another case where ion-selective electrodes may be used indirectly for the determination of compounds to which there is no direct response, is in combustion analysis. In organic microanalysis, combustion is frequently employed and ion-selective electrodes may be conveniently used to determine halides in the combustion products. Some results are collected in *Table 13.*

Table 13. Potentiometric determination of pharmaceuticals using a chloride ion-selective electrode

Compound	Sample taken (mg)	Halide content (%)		Δ(%)
		Calc.	Found	
2,6-Dinitro-chlorobenzene	18.105	17.21	17.43	+1.2
	24.084	17.21	17.42	+1.2
	21.074	17.21	17.67	+2.6
	24.018	17.21	17.71	+2.9
	20.757	17.21	17.42	+1.2
Chlorpromazine HCl	20.203	19.96	20.44	+2.4
	20.787	19·96	20·03	+0.3
	17.290	19.96	19.98	+0.1
	19.950	19.96	19.99	+0.1
	17.782	19.96	20.03	+0.3

SOME OTHER APPLICATIONS OF ION-SELECTIVE ELECTRODES

As well as the above analytical applications, ion-selective electrodes can be used in the field of physical chemistry for investigating equilibria and kinetics of various reactions. In this article we have referred to many papers where the electrodes have been used for determining acid-base dissociation constants and formation constants of complexes. Another interesting new application, which is furnished by the short response time of the electrodes, is the study of oscillating reactions. Woodson and Liebhafsky[181] used the iodide electrode in a study of the ClO_3^-/H_2O_2 reaction and Körös *et al.* (personal communication) are using our bromide electrode for investigating such reactions as that between BrO_3^- and malonic acid.

CONCLUSION

In the last decade the field of ion-selective electrodes has undergone an astonishingly rapid development with many new sensors being developed

and applied in a wide range of analytical and physicochemical research. But can we predict future developments in this branch of chemistry? In our opinion the number of precipitate-based electrodes will be limited, but in the application of these electrodes to the monitoring of chemical processes there will be a rapid expansion. However, future major developments cannot be expected unless we can discover the exact relations between the properties of the precipitates used for the electrodes and their electrochemical behaviour.

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