

Analysis with Ion-Selective Electrodes

J. Veselý D. Weiss K. Štulík

ANALYSIS
WITH ION-SELECTIVE
ELECTRODES



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AUTHORS' PREFACE

Ion-selective electrodes have become one of the most useful tools for rapid analysis or on-line monitoring in contemporary analytical chemistry. As such, they have already been treated in a number of reviews and monographs although no book has been devoted to analytical aspects.* The collection of lectures, *Ion-Selective Electrodes*, edited by R. A. Durst and published by the National Bureau of Standards, Washington 1969, is a classic in the field but is already outdated. The book by J. Koryta, *Ion-Selective Electrodes*, Cambridge University Press 1975, is directed primarily to the physico-chemical aspects of membrane potentials, but also gives a brief survey of analytical applications. Two other books, namely, that by G. J. Moody and J. D. R. Thomas, *Selective Ion-Sensitive Electrodes*, Merrow, Watford 1971, and that by K. Camman, *Das Arbeiten mit ion selektiven Elektroden*, Springer Verlag, Berlin 1973, (2nd Ed., 1977) deal to a greater or lesser degree with various aspects of the topic. Recently, more books have appeared, e.g. N. Lakshminarayanaiah, *Membrane Electrodes*, Academic Press, New York 1976, and P. L. Bailey, *Analysis with Ion-Selective Electrodes*, Heyden, London 1976, and many reviews dealing with various aspects of the field.

The present book attempts a general up-to-date review of the field and places the greatest emphasis upon analytical use of the electrodes; consequently, apparatus and measuring techniques are treated in detail, while the theoretical part gives a survey of the results obtained, without detailed derivation of the pertinent equations. Important analytical applications are discussed in detail and groups of similar determinations are tabulated. No detailed treatment of pH-measurement is given, as this field has been covered by good monographs and reviews.

We are indebted to all the authors, publishers and manufacturers who gave us permission to use their material in the book. Further we would like to thank Dr. M. Štulíková for helpful comments on the text during translation of the Czech manuscript, and Mr. J. Šunka for help in the preparation of the figures.

* Since preparation of this book, a volume devoted to applications in organic analysis has appeared in this series (see Baiulescu and Coşofreţ in list of titles available).

TABLE OF CONTENTS

Authors' Preface	5
Chapter 1 Introduction and Theory	13
1.1 Ion-selective electrode potential	13
1.1.1 Theoretical membrane potentials	16
1.1.1.1 Membranes with fixed ion-exchange sites	18
1.1.1.2 Liquid membranes with dissolved ion-exchangers	20
1.1.1.3 Liquid membranes with electroneutral ion-carriers	22
1.1.2 Potentials of working ion-selective electrodes	23
1.2 Importance of selectivity coefficients and their determination	28
1.3 Calibration of ion-selective electrodes	33
1.4 Electrodes with additional membranes	35
1.4.1 Gas-sensing electrodes	35
1.4.2 Enzyme electrodes	37
1.4.3 Electrodes differentiating organic substances with different structures	38
1.5 Analytical application of ion-selective electrodes	38
References	39
Chapter 2 Instrumentation	43
2.1 Ion-selective electrode construction	43
2.1.1 Introduction	43
2.1.2 Electrodes with an internal reference solution and internal reference electrode	44
2.1.3 Electrodes with solid internal contacts (solid-state and liquid-state electrodes)	46
2.1.4 Solid membrane electrodes	48
2.1.5 Liquid ion-selective electrodes (LISE's)	50
2.1.6 Gas-sensing and enzyme electrodes	54
2.1.7 Microelectrodes	56
2.1.8 Combined electrodes	59
2.2 Reference electrodes	59
2.2.1 Silver chloride electrode	60
2.2.2 Calomel electrode	64
2.2.3 Thallium amalgam-thalious chloride ("thalamide") electrode	66
2.2.4 Other reference electrodes	67
2.3 Liquid junction	68
2.3.1 Introduction	68
2.3.2 Types of liquid junction	69
2.3.3 Minimization of errors due to the liquid junction potential	71
2.3.4 Calculation of liquid junction potentials	73

2.3.5 Suspension effect	75
2.4 Measuring instruments	76
2.4.1 Activity meters	76
2.4.2 Automatic titration	77
2.4.3 The pX-stat	78
2.4.4 Automation of direct potentiometric determinations	78
2.4.5 Electrostatic noise and shielding	78
2.5 Effect of temperature	79
References	83
Chapter 3 Experimental Techniques	89
3.1 Preparation of the sample for the measurement	89
3.1.1 Sample decomposition	89
3.1.2 Preparation of the sample solution for the measurement	92
3.2 Discontinuous measurements	93
3.2.1 Calibration curves and simulated standards	96
3.2.2 Determination of overall concentration by addition techniques	98
3.2.2.1 Known-addition and known-subtraction methods	100
3.2.2.2 The analyte-addition and subtraction methods	102
3.2.2.3 Double-addition methods	104
3.2.2.4 Multiple addition and subtraction methods	105
3.2.3 Potentiometric titrations	105
3.2.4 Graphical and numerical evaluation methods	110
3.2.5 Modified techniques	114
3.3 Continuous and automated measurement	115
3.4 Ion-selective electrode measurements in biochemistry, biology and medicine	119
References	122
Chapter 4 Applications of Ion-Selective Electrodes	125
4.1 Determination of fluorine compounds	125
4.1.1 Determination of fluorides	125
4.1.1.1 Fluoride-selective electrode	125
4.1.1.2 Properties of fluoride-selective electrodes	126
4.1.1.3 Selectivity of the determination	130
4.1.1.4 Titration determination	133
4.1.1.5 Determination of fluoride in waters, inorganic solutions, the atmosphere and gaseous mixtures	133
4.1.1.6 Determination of fluoride in mineral raw materials	135
4.1.2 Determination of fluorine in organic substances	135
4.2 Determination of chlorine compounds	138
4.2.1 Determination of chloride	138
4.2.1.1 Chloride electrodes	138
4.2.1.2 Selectivity	141
4.2.1.3 Titration of chloride	142
4.2.1.4 Determination of chloride in inorganic materials	143
4.2.1.5 Determination of chloride in organic materials	144
4.2.2 Determination of perchlorate	144
4.3 Determination of bromine compounds	146
4.3.1 Determination of bromide	146

4.3.1.1	Bromide-selective electrode	146
4.3.1.2	Titration of bromide	147
4.3.1.3	Determination of bromide in natural materials	147
4.4	Determination of iodine compounds	148
4.4.1	Determination of iodide	148
4.4.1.1	Iodide-selective electrodes	148
4.4.1.2	Determination of iodide in various materials	151
4.5	Determination of cyano compounds	152
4.5.1	Determination of cyanide	152
4.5.2	Determination of thiocyanate	156
4.6	Determination of sulphur compounds	157
4.6.1	Determination of sulphide	157
4.6.2	Determination of sulphate	160
4.6.3	Determination of sulphur dioxide	162
4.7	Determination of nitrogen compounds	163
4.7.1	Determination of ammonia	163
4.7.2	Determination of urea, amino-acids and other nitrogen-containing substances, by using enzymatic reactions	165
4.7.3	Determination of nitrite and nitrogen oxides	166
4.7.4	Determination of nitrate	166
4.8	Determination of phosphorus compounds	171
4.8.1	Determination of phosphate	171
4.9	Determination of carbon compounds	172
4.9.1	Determination of carbon dioxide and carbonate	172
4.10	Determination of boron	173
4.11	Determination of alkali metals	174
4.11.1	Determination of lithium	174
4.11.2	Determination of sodium	174
4.11.2.1	Sodium-selective electrodes	174
4.11.2.2	Determination of sodium in inorganic and organic materials	176
4.11.3	Determination of potassium	177
4.12	Determination of magnesium and of water hardness	182
4.12.1	Determination of magnesium	183
4.12.2	Determination of water hardness	184
4.13	Determination of calcium	184
4.13.1	Electrodes	185
4.13.2	Properties of calcium-selective electrodes	187
4.13.3	Determination of calcium	188
4.13.3.1	Titration	188
4.13.3.2	Direct potentiometry	190
4.14	Determination of silver	192
4.15	Determination of mercury	193
4.16	Determination of copper	194
4.17	Determination of lead	197
4.18	Determination of cadmium	198
4.19	Determination of various inorganic materials	199
4.20	Determination of various organic compounds	203

References	205
Appendix	228
<i>Table A</i> The values of the factor $(RT \ln 10)/F$ for univalent and bivalent ions at various temperatures	228
<i>Table B</i> Individual activity coefficients of ions in water	229
<i>Table C</i> Standard reference values of ionic activity in solutions of sodium chloride, potassium chloride, potassium fluoride and calcium chloride at 25 °C	230
<i>Table D</i> Conversion factors between ppm and mole/l	230
<i>Table E</i> Determination of concentration by the known-addition method	231
<i>Table F</i> Determination of concentration by the known-subtraction method	233
<i>Table G</i> Determination of concentration by the analyte-addition method	235
<i>Table H</i> Determination of concentration by the analyte-subtraction method	236
<i>Table I</i> Concentration by double known-addition	238
<i>Table J</i> Concentration by single known-addition with slope determined by dilution	239
<i>Table K</i> List of abbreviations	240
Index	241

LIST OF IMPORTANT SYMBOLS

a	activity	U	particle mobility
c, C	concentration	V	solution volume
D	diffusion coefficient	z	electric charge on a particle
E	electrode potential	α	side-reaction coefficient; degree of dissociation
E^0	standard potential	γ	activity coefficient
$E^{0'}$	normal potential	λ	equivalent conductivity
F	Faraday constant	Λ	equivalent conductivity at a given concentration
h	hydration number	μ	stoichiometric coefficient; chemical potential
I	ionic strength	μ^0	standard chemical potential
J	material flux	$\tilde{\mu}$	electrochemical potential
k	distribution coefficient	ϕ	internal electrical potential
k_{11}^{Pot}	selectivity coefficient	$\Delta\phi$	potential difference
K	equilibrium constant	$\Delta\phi_D$	Donnan potential
K_s	solubility product	$\Delta\phi_L$	liquid-junction potential
m	molality	$\Delta\phi_M$	membrane potential
R	universal gas constant	Φ	osmotic coefficient
S	slope of the dependence of E vs. $\log a$		
t	transport number		
T	absolute temperature		

Chapter 1

INTRODUCTION AND THEORY

The oldest and still by far the best ion-selective electrode (ISE) is the glass electrode for pH measurements, which was discovered at the beginning of the present century [1, 2], and became a standard laboratory tool in the late thirties. Attempts to prepare glass electrodes selective for other ions appeared rather early [3, 4] and at present there are commercially available glass electrodes selective for several cations, chiefly the alkali metals and silver (see e.g. [5]). Some early experiments with solid-membrane ISE's were largely unsuccessful (see e.g. [6-11]). Rapid development in this field was started in the sixties by construction of working heterogeneous-membrane electrodes [12] and especially by the discovery of the single-crystal fluoride-selective electrode [13]. The field of ISE's was broadened by introduction of liquid ion-exchanger membranes [14, 15], membranes containing electroneutral macrocyclic compounds [16], enzyme electrodes [17] and gas sensors [134]. At present, many kinds of ion can be determined directly and many compounds indirectly with ISE's. Several dozens of manufacturers all over the world make these electrodes and many ISE's can readily be prepared in the laboratory. The main appeal of ISE's lies in the simplicity of the measuring technique and instrumentation and in their suitability for continuous monitoring, which makes them particularly useful in routine control analysis, pollution control and biology and medicine.

1.1 ION-SELECTIVE ELECTRODE POTENTIAL

When two phases containing electrically charged particles (ions, electrons or dipoles) come into contact, an electrical potential difference develops at their interface. The compositions of the phases are characterized by the appropriate electrochemical potentials, $\tilde{\mu}$, the values of which must be equal if the system is in equilibrium. Thus for the i th charged species present in phases 1 and 2,

$$\tilde{\mu}_i(1) = \tilde{\mu}_i(2) \quad (1.1)$$

Under ISE conditions it can be assumed that the chemical properties of the phases are independent of the electrical charges involved and thus Eq. (1.1) can be rewritten in terms of the standard chemical potentials, μ_i^0 , the activities, a_i , the charges, z_i , and the inner electrical potentials of the phases, ϕ :

$$\mu_i^0(1) + RT \ln a_i(1) + z_i F \phi(1) = \mu_i^0(2) + RT \ln a_i(2) + z_i F \phi(2) \quad (1.2)$$

where R is the universal gas constant, T is the absolute temperature and F is the Faraday. Hence, for the potential difference at the interface,

$$\begin{aligned} \Delta \phi = \phi(2) - \phi(1) &= \frac{\mu_i^0(1) - \mu_i^0(2)}{z_i F} + \frac{RT}{z_i F} \ln \frac{a_i(1)}{a_i(2)} \\ &= \text{const} + \frac{RT}{z_i F} \ln \frac{a_i(1)}{a_i(2)} \end{aligned} \quad (1.3)$$

Therefore, if the activity of the i th species in one phase and the μ_i^0 values are known, the activity of the i th species in the other phase can be determined by measuring the $\Delta \phi$ value. It can be seen that an immense number of systems can potentially be used as electrodes for determining the activities of various species in solution. However, in practical measurements not only sensitivity to the particular species, but also satisfactory selectivity, accuracy and reproducibility of the measurement will be required, thus imposing considerable limitations on the selection of useful systems.

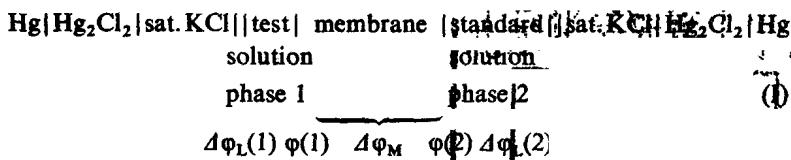
First, most substances exhibiting purely electronic conductivity (chiefly metals, various forms of carbon and some other substances) are excluded as potential ion-selective materials, as they behave as redox electrodes and are sensitive to redox systems and not to individual ions. Substances suitable for use as ion-selective materials therefore exhibit ionic conductivity; in some cases both ions and electrons participate in the transport of electric charge in the material and whether the material will exhibit predominantly ionic or redox sensitivity depends chiefly on the relative values of the transport numbers for the ions and electrons. For example, in the series of chalcogenides the materials have progressively more metallic character in the order $\text{PbS} < \text{PbSe} < \text{PbTe}$, and the sensitivity towards Pb^{2+} decreases accordingly [18].

There are several exceptions where substances with predominantly electronic conductivity exhibit ion-sensitivity and these will be discussed in Section 1.1.2.

Second, the material must differentiate among various ionic species; ideally it should respond to only one of them. This is achieved, e.g. when various ionic species have different mobilities in the material and/or

the material behaves as an ion-exchanger, an adsorbent, an extraction system or a complexing agent, selective toward certain ionic species.

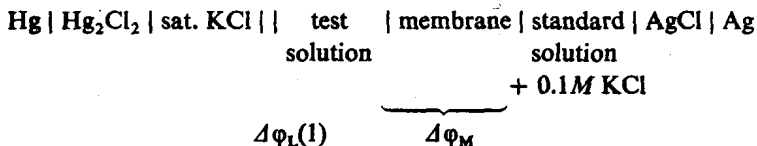
The potential difference $\Delta\phi$, given by Eq. (1.3), cannot be measured directly. Generally, only the potential difference in an electrochemical cell consisting of two electrodes (half-cells) is measurable. Therefore, the ion-selective material must be incorporated into some kind of electrode, the potential of which is then measured against a suitable reference electrode (direct potentiometric measurement). It is possible to connect the ion-selective substance directly to an electronic conductor (e.g. by depositing it on a carbon support or by pressing or plating a metal contact onto it); this principle is, in fact, employed in some types of ISE's (see Section 2.1.3). However, this arrangement, though advantageous from the point of view of electrode construction, has two disadvantages from the theoretical point of view. First, the potential difference formed at the interface of the ion-sensitive material and the electronic conductor is mostly poorly defined thermodynamically and may sometimes be poorly reproducible; second, the activity of the species sensed in the electrode active material is often not defined. The situation is simpler when the ion-sensitive material is placed between the sample solution and a standard solution containing a suitable reference electrode and the test species at defined activity. The ion-sensitive material then acts as an electrochemical membrane separating the sample and the standard solution and the potential difference between two reference electrodes, one immersed in the test solution and the other in the standard solution, is measured. The electrochemical cell employed can then be represented e.g. by the scheme



For this system Eq. (1.3) is valid, potentials $\phi(1)$ and $\phi(2)$ correspond to the test and the standard solution, respectively, and their difference is equal to the membrane potential, $\Delta\phi_M$. With ion-selective membranes, the bulk of the membrane and of the solutions is often not in equilibrium, and mass transport then occurs; if at least the interfaces are in equilibrium, then Eq. (1.3) still applies, but the activity and potential values refer to the close vicinity of the interfaces.

It can be seen from scheme (1) that the actual potential difference mea-

sured will involve the membrane potential, $\Delta\phi_M$, and liquid-junction potentials at the liquid phase interfaces. Potential $\Delta\phi_L(2)$ need not always be present, as for example in the cell:



Cell type (II) is most frequently employed in measurements with ISE's. Nevertheless, it is now necessary to examine the properties of these potentials.

1.1.1 Theoretical Membrane Potentials

The membrane can simply mechanically prevent rapid mixing of two solutions, without hindering the diffusional transport of any species across the interface. Owing to the various diffusion rates of the individual ions, a potential gradient develops across the interface and gives rise to a potential difference between the two solutions, termed the liquid-junction or diffusion potential, $\Delta\phi_L$. This is a limiting case with membrane potentials; in practical electrochemical cells containing ISE's it appears at the porous diaphragm of the external reference electrodes and the diffusion potential across the membrane often contributes to the overall membrane potential.

The value of the diffusion potential can be calculated by starting from the Nernst-Planck equations for the mass fluxes of all the species involved [19-22]; for the i th species travelling along the x -axis, assuming low concentration so that $c_i = a_i$, and the absence of convective movement,

$$J_i = -U_i RT (dc_i/dx) - z_i F U_i c_i (d\phi/dx) \quad (1.4)$$

where U_i is the species mobility, defined by

$$U_i = \lambda_i / (|z_i| F^2) \quad (1.5)$$

where λ_i is the equivalent ionic conductivity. On introducing the condition that no net electric current flows across the interface, and rearranging, the equation for the liquid-junction potential is obtained in the form

$$\Delta\phi_L = \phi_2 - \phi_1 = -\frac{RT}{F} \int_1^2 \sum_i \frac{t_i}{z_i} d \ln c_i \quad (1.6)$$