Analysis with Ion-Selective Electrodes

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ANALYSIS
WITH ION-SELECTIVE
ELECTRODES

ELLIS HORWOOD

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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A. Durst and published by the National Bureau of Standards, Washington 1969, is a classic in the field but is already outdated.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.

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* 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).

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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;
E^0	standard potential		degree of dissociation
$E^{0'}$	normal potential	γ	activity coefficient
F	Faraday constant	λ	equivalent conductivity
h	hydration number	Λ	equivalent conductivity at
I	ionic strength		a given concentration
J	material flux	μ	stoichiometric coefficient;
k	distribution coefficient		chemical potential
k_{IJ}^{Pot}	selectivity coefficient	μ^0	standard chemical potential
K	equilibrium constant	$\tilde{\mu}$	electrochemical potential
K_s	solubility product	φ	internal electrical potential
m	molality	$\Delta\varphi$	potential difference
R	universal gas constant	$\Delta\varphi_D$	Donnan potential
S	slope of the dependence of	$\Delta\varphi_L$	liquid-junction potential
	E vs. log a	$\Delta\varphi_M$	membrane potential
t	transport number	Φ	osmotic coefficient
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 ith charged species present in phases 1 and 2,

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

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:

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

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,

$$\Delta \varphi = \varphi(2) - \varphi(1) = \frac{\mu_i^0(1) - \mu_i^0(2)}{z_i F} + \frac{RT}{z_i F} \ln \frac{a_i(1)}{a_i(2)}$$

$$= \text{const} + \frac{RT}{z_i F} \ln \frac{a_i(1)}{a_i(2)} \quad (1.3)$$

Therefore, if the activity of the ith species in one phase and the μ_i^0 values are known, the activity of the ith species in the other phase can be determined by measuring the $\Delta \varphi$ 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 PbS < PbSe < 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 extrac-
tion system or a complexing agent, selective toward certain ionic
species.

The potential difference $\Delta\varphi$, 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 stan-
dard solution containing a suitable reference electrode and the test
species at defined activity. The ion-sensitive material then acts as an
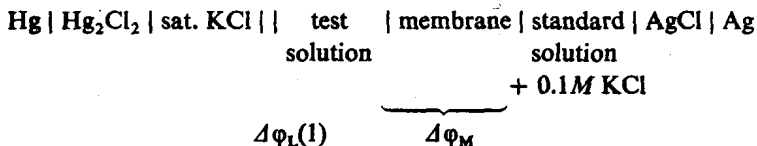electrochemical membrane separating the sample and the standard solu-
tion and the potential difference between two reference electrodes, one
immersed in the test solution and the other in the standard solution, is
measured. The electrochemical cell employed can then be represented e.g.
by the scheme

$$Hg\,|\,Hg_2Cl_2\,|\,sat.\,KCl\,||\,test\,|\quad membrane\quad |\,standard\,|\,sat.\,KCl\,|\,Hg_2Cl_2\,|\,Hg$$

$$\underset{phase\ 1}{solution} \qquad\qquad \underset{phase\ 2}{solution} \qquad\qquad\qquad (I)$$

$$\Delta\varphi_L(1)\ \varphi(1)\quad \Delta\varphi_M\quad \varphi(2)\ \Delta\varphi_L(2)$$
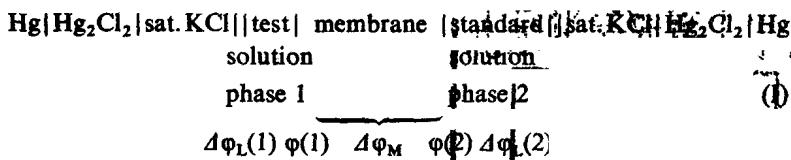
For this system Eq. (1.3) is valid, potentials $\varphi(1)$ and $\varphi(2)$ correspond to
the test and the standard solution, respectively, and their difference is
equal to the membrane potential, $\Delta\varphi_M$. With ion-selective membranes,
the bulk of the membrane and of the solutions is often 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 (I) that the actual potential difference mea-

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

Hg | Hg$_2$Cl$_2$ | sat. KCl || test | membrane | standard | AgCl | Ag
                                  solution   solution
                                                                  + 0.1M KCl

$$\Delta\varphi_L(1) \qquad \Delta\varphi_M$$

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, $\Delta\varphi_L$. 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 ith species travelling along the x-axis, assuming low concentration so that $c_i = a_i$, and the absence of convectional movement,

$$J_i = -U_i RT(\mathrm{d}c_i/\mathrm{d}x) - z_i F U_i c_i(\mathrm{d}\varphi/\mathrm{d}x) \tag{1.4}$$

where U_i is the species mobility, defined by

$$U_i = \lambda_i/(|z_i|F^2) \tag{1.5}$$

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

$$\Delta\varphi_L = \varphi_2 - \varphi_1 = -\frac{RT}{F}\int_1^2 \sum_i \frac{t_i}{z_i}\,\mathrm{d}\ln c_i \tag{1.6}$$