

POTENTIOMETRIC WATER ANALYSIS

**D. Midgley
K. Torrance**

Potentiometric Water Analysis

Derek Midgley and Kenneth Torrance
*Central Electricity Research Laboratories,
Leatherhead, Surrey, England*

A Wiley-Interscience Publication

JOHN WILEY & SONS

Chichester · New York · Brisbane · Toronto

Copyright © 1978 by John Wiley & Sons, Ltd.

All rights reserved.

No part of this book may be reproduced by any means, nor transmitted, nor translated into a machine language without the written permission of the publisher.

Library of Congress Cataloging in Publication Data:

Midgley, Derek.

Potentiometric water analysis.

'A Wiley-Interscience publication.'

Includes bibliographies.

1. Water -- Analysis. 2. Electrochemical analysis. I. Torrance, Kenneth, joint author.

II. Title.

QD142.M52 546'.22 77-7213

ISBN 0 471 99532 0

Typeset in IBM Press Roman by

Preface Ltd, Salisbury, Wiltshire.

Printed in Great Britain by

Unwin Brothers, The Gresham Press, Old Woking, Surrey

Preface

This book draws on work carried out at the Central Electricity Research Laboratories and the authors are grateful to the Central Electricity Generating Board for permission to publish it. The authors alone, however, are responsible for opinions expressed and for the selection of factual material.

Contents

PART I THEORETICAL AND PRACTICAL BACKGROUND

1 Introduction	3
2 Electrochemical Principles	6
Concentration and Activity	6
Single-ion activity coefficients	8
Ion association	8
Activity as an analytical parameter	9
Cell Potentials and Electrode Potentials	9
Standard potentials	10
Reference Electrodes and Liquid Junction Potentials	10
Reversible Reactions	13
Measurement of the Cell Potential	13
3 Electrodes	16
Metal-based Electrodes	16
Cation-sensitive electrodes	16
Anion-sensitive electrodes	17
Interferences	18
Limit of response	18
Metal-metal oxide pH electrodes	19
Inert metal-redox system electrodes	20
The hydrogen electrode	21
The quinhydrone electrode	22
Membrane Electrodes	23
Solid-state membrane electrodes	24
Glass electrodes	27
Liquid ion-exchange electrodes	29
Indirectly Selective Electrodes	34
Gas-sensing membrane electrodes	34
Construction of gas-sensing membrane electrodes	37
Reference Electrodes	38

The calomel electrode	39
Silver-silver chloride electrodes	40
The Thalamid electrode	41
The mercury-mercurous sulphate electrode	41
Unusual reference electrodes	41
Design and construction of reference electrodes	42
Form of liquid junction	43
Concentration of reference solution	44
Sealed reference electrodes	44
Double-junction reference electrodes	45
Temperature effects	45
Colloidal and suspension effects	46
4 Equipment	49
Types of Meters	49
pH and pIon meters	49
Digital and analogue display	50
Portable pH meters	50
Microprocessor analysers	51
Recorder and printer outputs	51
Matching meter output and recorder input	52
Temperature compensation	52
Additional features	53
Voltmeters and electrometers	54
Industrial Monitoring Equipment	54
pH measurements	54
Measurements with ion-selective electrodes	55
Flow cells	56
Automatic Titration Apparatus	58
5 Analytical Principles	61
Combination of Errors	63
Significance Testing	64
Comparison of means	65
One-sided and two-sided tests	66
Use of the <i>t</i> -test	66
Comparison of standard deviations — the <i>F</i> -test	67
Criterion and limit of detection	68
Within-batch and between-batch errors	69
Testing Analytical Methods	71
Precision	71
Accuracy	71
Recovery tests	71
Interference tests	74
Blanks, baselines and reference solutions	75
Control charts	76

Calibration Graphs	77
Linear regression	77
Correlation coefficients	78
Testing for linearity	78
6 Potentiometric Titrations and Related Methods	81
Titrimetric Procedures	81
Acid-base titrations	81
Precipitation titrations	83
Compleximetric titrations	83
Redox titrations	83
Addition titrations	83
Competitive titrations	86
Finding the Equivalent Volume	86
The titration curve	86
Titration to a fixed potential or pH	87
Derivative titrations	89
Gran titrations	89
Linear titration plots	93
Experimental limitations	95
Single-point Titrations	98
Known addition	98
Known subtraction	102
7 Potentiometric Analytical Practice	105
Ion-selective Electrodes	105
Apparatus	105
Sample Collection	108
Conditioning and Storage of Electrodes	110
Concentration Range and Units	112
Analytical Procedures	112
Temperature	113
Stirring	114
Light	115
Flow-cell analysis	115
Calibration	117
Direct potentiometry	117
Preparation of a permanent calibration graph	117
Nernstian calibration with two standard solutions	119
Nernstian calibration using the direct activity scale of a plon meter	120
Non-Nernstian calibration	121
Known-addition and known-subtraction potentiometry	122
Titrimetry	123
Sources of Error	124
Ionic strength effects	124
Masking	124

Interferences	125
Precision.	125
Accuracy	126
Response Time	126
Tracing Faults	127
Off-scale readings	127
Invariant readings.	128
Loss of sensitivity.	128
Slow response	129
Drift	129
Noise	129

PART II ANALYTICAL METHODS

The Measurement of pH	135
Determination of Acidity and Alkalinity	147
Determination of Lithium	155
Determination of Sodium with a Sodium-responsive Glass Electrode	160
Determination of Potassium	171
Determination of Calcium Using Calcium-responsive Liquid Ion-exchange Electrodes	186
Determination of Water Hardness with Liquid Ion-exchange Electrodes	194
Determination of Silver	205
Determination of Copper	214
Compleximetric Titrations	226
Determination of Cadmium	239
Determination of Lead	243
Determination of Aluminium	248
Determination of Total and Free Carbon Dioxide with a Gas-sensing Membrane Electrode	254
Determination of Nitrite and Nitrogen Oxides with a Gas-sensing Membrane Electrode	263
Determination of Sulphur Dioxide with a Gas-sensing Membrane Electrode.	271
Determination of Ammonia with a Gas-sensing Membrane Electrode	279
Determination of Total Nitrogen Using a Gas-sensing Ammonia Electrode after Kjeldahl Digestion	290
Determination of Free and Total Cyanide Using a Cyanide-selective Electrode	298
Determination of Low Levels of Total Cyanide Using a Silver Sulphide Electrode	306
Determination of Fluoride	313
Determination of Chloride Using Electrodes Based on Silver Chloride.	323
Determination of Low Levels of Chloride	333
Determination of Bromide and Iodide	343
Determination of Thiocyanate	352
Determination of Sulphide.	355
Titrimetric Determination of Sulphate	366

Determination of Nitrate using a Liquid Ion-exchange Electrode	374
Determination of Boron as Fluoroborate using a Fluoroborate-selective Liquid Ion-exchange Electrode	383
Determination of Perchlorate	390
Appendix 1 Theoretical Values of the Nernstian Slope	394
Appendix 2 Debye-Hückel <i>A</i> and <i>B</i> Coefficients for Electrolytes in Water. . .	395
Appendix 3 Equipment Manufacturers	396
Appendix 4 Tables of the Function, $\frac{1}{\left(\text{antilog} \frac{E_2 - E_1}{k}\right) - 1}$	399
Index	403

Part I

**THEORETICAL AND PRACTICAL
BACKGROUND**

Chapter 1

Introduction

With increasing demands on water for industrial, agricultural and domestic consumption, resources are being used and re-used more intensively than ever before. With each cycle of re-use, it becomes more important to check that the water is sufficiently pure for the purpose for which it is intended and that any waste water returned to the common stock does not contain unacceptable levels of pollutants. In the past, non-specific parameters such as conductivity, pH and biological oxygen demand have largely sufficed as measures of water quality, but the need in many circumstances for the determination of specific chemical substances is becoming more pressing.

As a technique, potentiometry has the advantage of being easily adaptable to circumstances. One reason for this is the very wide range of concentrations that can be determined by the same equipment with only a minimum of procedural variations and another is the comparative ease with which measurements can be made either with battery-powered instruments in the field or with automatic apparatus for continuous monitoring inside industrial plant or in remote locations. For both applications, the robustness of many electrodes is an advantage compared with photometric techniques. It is only within the last ten years that a wide variety of ion-selective electrodes has become available, but a number of species are now commonly determined by means of such electrodes: sodium in highly pure water; fluoride and nitrate in potable waters; sulphide and cyanide in industrial effluents; potassium, calcium, and carbon dioxide in biological fluids; and chloride and ammonia in a great variety of media. The fluoride electrode has made its way into standard analytical texts together with the long-established glass electrode for pH determinations, e.g. APHA (1971), DoE (1972), and more recently the nitrate and cyanide electrodes have been tentatively recognized (APHA, 1975). Although a number of books have usefully described the theory behind ion-selective electrodes, e.g. Durst (1969) and Koryta (1975), there has been little attempt to draw together the existing knowledge specifically for the benefit of analysts. Moody and Thomas (1971) provided a valuable summary of electrode properties and in a later review (Moody and Thomas, 1973) gave an extensive list of references, but very often such papers provide too little information from which the analyst can work and fail to indicate such basic attributes of an analytical method as its precision

and accuracy. The same is true of many of the methods published by manufacturers of electrodes.

Our aim has been to bring our experience to bear on published results and to stress particularly those points which are of practical interest to the analyst. We have not discussed experimental electrodes, but only those commercially available. In the analytical methods in Part II we have tried to give as much information as possible on the problems specific to the use of each electrode, but to some extent each type of sample must be considered individually. Although the methods are directed primarily to the analysis of fairly pure waters such as boiler water and feed water for steam-raising plant and of natural waters such as river waters, it is hoped that they will be of interest to analysts occupied either with other types of aqueous samples such as sea water, blood and soil extracts or with the analysis of solid samples after they have been dissolved. In the latter cases, the procedure for the analysis of pure water may need to be modified to take account of a fairly concentrated background of species other than the determinand, but the treatment of pure water samples does indicate the most desirable conditions of pH, ionic strength, etc., for potentiometric measurements.

The methods are described with manual analysis in the laboratory in mind, but the majority should be directly applicable to analysis in the field and many to continuous monitoring of a sample stream. For both of these applications, direct potentiometry often has advantages over other methods, even in cases where the potentiometric method is inferior in precision or accuracy in the laboratory. Our aim has been to make the procedure clear to the non-specialist and to point out the advantages and pitfalls of potentiometry so that the analyst can reasonably judge how useful an electrode can be in his laboratory from the details of the method in Part II taken together with Chapter 7 of Part I. The methods are grouped according to their operational similarities rather than by the nature of the determinand or the type of electrode, although the three types of classification often coincide, e.g. the alkali metals and most of the halides.

Part I contains the background common to the methods in Part II. The theory in Chapters 2, 3, and 6 is aimed at promoting an appreciation of the practical aspects of potentiometry and potentiometric titrations under the analyst's control, so that he can decide the relevance to his particular samples of a method written for a general case and how the method may need to be modified. Electrode mechanisms are not considered except in general terms to bring out the differences between the various types of electrodes. Similarly, Chapter 4 is concerned with what instruments can do and not with how they do it. Consideration should be given to the understanding of analytical results as well as to the means of obtaining them and Chapter 5 describes the basis on which analytical results are assessed before decisions are taken.

Nomenclature

Certain terms are used throughout the text and it is convenient to define them here:

The *determinand* is the substance whose concentration is being measured or determined.

The *calibration slope* of an electrode is the constant relating the observed e.m.f. to the logarithm of the determinand-concentration. It is also called the *slope factor* and is said to be *Nernstian* when it agrees with the theoretical value calculated as in Appendix 1.

In titrations, the *titrant* is the solution of known concentration added to the sample and the *indicator electrode* is that used to follow the course of the titration, whether it responds directly to the determinand or not. The *equivalence point* occurs when an exactly stoichiometric amount of titrant has been added to the sample and it should be distinguished from the *end-point*, which is the operational approximation to it.

A general indication of the purity of water is given by its *specific conductivity*, which is reported in units of microsiemens per centimetre. These units are related to older ones as follows.

$$1 \mu\text{S cm}^{-1} \equiv 1 \mu\text{mho cm}^{-1} \equiv 1 \text{M}\Omega^{-1} \text{cm}^{-1}$$

Pure water has a specific conductivity of about $0.04 \mu\text{S cm}^{-1}$ at 18°C . Otherwise pure water in equilibrium with the carbon dioxide in the air has a specific conductivity of about $0.75 \mu\text{S cm}^{-1}$. Mixed-bed deionization units are capable of producing water with a specific conductivity of less than $0.2 \mu\text{S cm}^{-1}$.

Bibliography

- APHA, 1971, *Standard Methods for the Examination of Water and Wastewater*, 13th ed., American Public Health Association, Washington, D.C.
- APHA, 1975, *Standard Methods for the Examination of Water and Wastewater*, 14th ed., American Public Health Association, Washington, D.C.
- DoE, 1972, *Analysis of Raw, Potable and Waste Waters*, Department of The Environment, HMSO, London.
- Durst, R. A. (ed.), 1969, *Ion Selective Electrodes*, National Bureau of Standards Special Publication 314, US Department of Commerce, Washington, D.C.
- Koryta, J., 1975, *Ion-selective Electrodes*, Cambridge University Press, Cambridge.
- Moody, G. J., and J. D. R. Thomas, 1971 *Selective Ion-Sensitive Electrodes*, Merrow, Watford.
- Moody, G. J., and J. D. R. Thomas, 1973, *Selective Ion-sensitive Electrodes*, Selected Annual Review of the Analytical Sciences, Vol. 3, The Society for Analytical Chemistry, London, p. 59.

Chapter 2

Electrochemical Principles

Potentiometric analysis depends on the relationship between the concentration of the determinand, i.e., the species to be determined, and the e.m.f. of an electrochemical cell in which the determinand is one of the components of an equilibrium system. The ideal relationship is known as the Nernst equation,

$$E = E^{\circ} + k \log (c) \quad (2.1)$$

where E = the measured cell potential, E° = a constant for a given temperature, c = the concentration of determinand and $k = RT \log (10)/nF$ where R is the gas constant, T the absolute temperature, F is Faraday's constant and n is the number of electrons discharged or taken up by one molecule of determinand. Usually, but not necessarily, n equals the charge (with sign) on the ionic form of the determinand. Values of k are tabulated in Appendix 1.

In practice, it may be difficult to achieve the ideal relationship without defining the conditions of measurement very closely. In order to arrange a potentiometric system for the greatest convenience and accuracy, it is necessary to consider the components that make up equation 2.1.

CONCENTRATION AND ACTIVITY

The ideal relationship expressed in equation 2.1 is only approached as the solution approaches infinite dilution. For real solutions we must write

$$E = E^{\circ} + k \log (a) \quad (2.2)$$

where a = the activity of the species in question, related to the concentration by the equation

$$a = c.f \quad (2.3)$$

The activity coefficient, f , is a pure number and the activity therefore has the same units as the concentration.

If equation 2.2 is re-written as follows

$$E = (E^{\circ} + k \log (f)) + k \log (c)$$

it can be seen, that if f can be kept constant, the form of equation 2.1 is regained. The activity coefficient is a measure of the interaction of an ion with all the other ions present and its magnitude depends on the total ionic composition of the solution, in fact on a property known as the ionic strength, usually symbolized as either μ or I

$$I = 0.5 \sum c_i z_i^2 \quad (2.4)$$

where c_i and z_i = the molar concentration and charge, respectively, of the i th species and the summation is carried out over all the ionic species present. In most potentiometric analytical methods, the ionic strength is kept constant by adding to the sample an excess of 'indifferent' electrolyte; i.e., one which has no effect on the equilibria involved in the cell reaction except through the agency of the ionic strength, so that variations in the concentration of the determinand do not affect the activity coefficient significantly and the desired relationship between e.m.f. and concentration is obtained.

It is nevertheless often useful to be able to calculate activity coefficients and to know the limitations of the various ways of doing so. The simplest formula is the Debye-Hückel limiting law equation, in which A is a function of the temperature

$$-\log(f_i) = A \cdot z_i^2 \cdot I^{1/2} \quad (2.5)$$

and the dielectric constant of the solvent. The equation is fairly accurate at ionic strengths up to 10^{-4} – 10^{-3} mol l $^{-1}$, depending on the nature of the ions present, but at higher ionic strengths (up to 10^{-2} mol l $^{-1}$) the extended Debye-Hückel equation is needed

$$-\log(f_i) = A \cdot z_i^2 \cdot I^{1/2} / (1 + B \cdot a \cdot I^{1/2}) \quad (2.6)$$

where B is also a function of the temperature and dielectric constant and a , the 'ion-size parameter', is the distance of closest approach in solution of ions of opposite charge. When more than one electrolyte is present in the same solution, the meaning of the ion-size parameter[†] is ambiguous and it is often adjusted empirically to give good agreement between observed and calculated values. A useful simplification of equation 2.6 is known as the Guntelberg equation

$$-\log(f_i) = A \cdot z_i^2 \cdot I^{1/2} / (1 + I^{1/2}) \quad (2.7)$$

At still higher concentrations, equation 2.6 can be extended by an extra term

$$-\log(f_i) = A \cdot z_i^2 \cdot I^{1/2} / (1 + B \cdot a \cdot I^{1/2}) - b \cdot I \quad (2.8)$$

where b is an empirical coefficient. A particularly useful form of equation 2.8 is the Davies equation, which is reasonably accurate up to $I = 0.1$ mol l $^{-1}$ (Davies, 1962)

$$-\log(f_i) = A \cdot z_i^2 [I^{1/2} / (1 + I^{1/2}) - 0.3I] \quad (2.9)$$

In mixtures of two or more electrolytes, further terms (Guggenheim and Turgeon, 1955) can be added to equation 2.8, but this is of little analytical use. It is possible to calculate activity coefficients at ionic strengths above 1×10^{-1} mol l $^{-1}$

(Robinson and Stokes, 1965), but it is not expected that the formulae would be relevant to the purposes of this book.

Values of the Debye-Hückel coefficients A and B are tabulated in Appendix 2 as a function of temperature for water as solvent. Experimentally determined activity coefficients for many electrolytes have been tabulated by Conway (1952), Harned and Owen (1958) and Robinson and Stokes (1965).

Single-ion Activity Coefficients

So far, we have assumed that the activity coefficient of a single ionic species has a definite meaning, as implied by equation 2.3, but there is no way of measuring such *single-ion activity coefficients* and, thermodynamically, they are neither meaningful nor necessary. The only measurable quantity of this sort is the *mean* ionic activity coefficient, f_{\pm} , and single-ion activity coefficients must be based on some extra-thermodynamic assumption. Whatever convention is adopted, equation 2.10 should be obeyed, i.e., for an electrolyte of general formula $A_m B_n$

$$(f_{\pm})^{m+n} = (f_A)^m (f_B)^n \quad (2.10)$$

Mean ionic activity coefficients can be calculated from equations analogous to 2.5–2.9 by replacing z_i^2 with $z_A \cdot z_B$. If $z_A = z_B$, the calculated values of f_A , f_B and f_{\pm} are the same. The mean ionic activity coefficients calculated from equations 2.5, 2.7, and 2.9 are compared in Table 2.1 with the observed values for aqueous solutions of calcium chloride at 25 °C.

Table 2.1 Mean ionic activity coefficients of calcium chloride in water at 25 °C

Concentration (molal)	Observed	Calculated		
		Equation 2.9	Equation 2.7	Equation 2.5
0.0001	0.962	0.961	0.961	0.960
0.0005	0.918	0.917	0.916	0.913
0.0010	0.887	0.887	0.885	0.879
0.0050	0.783	0.782	0.774	0.750
0.0100	0.724	0.722	0.707	0.665
0.0500	0.574	0.576	0.518	0.402
0.1000	0.518	0.537	0.435	0.276

Ion Association

It is important to note that electrodes respond only to the concentration of the 'free' ion in solution, e.g., the fluoride electrode (p. 313) is sensitive to F^- ions but not to the coexisting species HF and HF_2^- . The concentration, c , in equations 2.1 and 2.3 refers only to the free ions and does not include any associated or complex