FUNDAMENTALS OF ELECTRO-ANALYTICAL CHEMISTRY

Paul Monk
Manchester Metropolitan University, Manchester, UK

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Series Preface

There has been a rapid expansion in the provision of further education in recent years, which has brought with it the need to provide more flexible methods of teaching in order to satisfy the requirements of an increasingly more diverse type of student. In this respect, the *open learning* approach has proved to be a valuable and effective teaching method, in particular for those students who for a variety of reasons cannot pursue full-time traditional courses. As a result, John Wiley & Sons Ltd first published the Analytical Chemistry by Open Learning (ACOL) series of textbooks in the late 1980s. This series, which covers all of the major analytical techniques, rapidly established itself as a valuable teaching resource, providing a convenient and flexible means of studying for those people who, on account of their individual circumstances, were not able to take advantage of more conventional methods of education in this particular subject area.

Following upon the success of the ACOL series, which by its very name is predominately concerned with Analytical *Chemistry*, the *Analytical Techniques in the Sciences* (AnTS) series of open learning texts has now been introduced with the aim of providing a broader coverage of the many areas of science in which analytical techniques and methods are now increasingly applied. With this in mind, the AnTS series of open learning texts seeks to provide a range of books which will cover not only the actual techniques themselves, but *also* those scientific disciplines which have a necessary requirement for analytical characterization methods.

Analytical instrumentation continues to increase in sophistication, and as a consequence, the range of materials that can now be almost routinely analysed has increased accordingly. Books in this series which are concerned with the *techniques* themselves will reflect such advances in analytical instrumentation, while at the same time providing full and detailed discussions of the fundamental concepts and theories of the particular analytical method being considered. Such books will cover a variety of techniques, including general instrumental analysis, spectroscopy, chromatography, electrophoresis, tandem techniques, electroanalytical methods, X-ray analysis and other significant topics. In addition, books in the series will include the *application* of analytical techniques in areas such as environmental science, the life sciences, clinical analysis, food science, forensic analysis, pharmaceutical science, conservation and archaeology, polymer science and general solid-state materials science.

Written by experts in their own particular fields, the books are presented in an easy-to-read, user-friendly style, with each chapter including both learning objectives and summaries of the subject matter being covered. The progress of the reader can be assessed by the use of frequent self-assessment questions (SAQs) and discussion questions (DQs), along with their corresponding reinforcing or remedial responses, which appear regularly throughout the texts. The books are thus eminently suitable both for self-study applications and for forming the basis of industrial company in-house training schemes. Each text also contains a large amount of supplementary material, including bibliographies, lists of acronyms and abbreviations, and tables of SI Units and important physical constants, plus where appropriate, glossaries and references to original literature sources.

It is therefore hoped that this present series of textbooks will prove to be a useful and valuable source of teaching material, both for individual students and for teachers of science courses.

Dave Ando
Dartford, UK

Preface

This present book is no more than an *introduction* to electroanalytical chemistry. It is not a textbook, but is intended for those wanting to learn at a distance, or in the absence of a suitable tutor. Accordingly, the approach taken is that of a series of tutorial questions and worked examples, interspersed with questions for students to attempt in their own time. In no way is this meant to be a definitive text: students who have mastered these topics are recommended to consult the books and articles listed in the Bibliography at the end.

Electroanalysis is a relatively simple topic in concept, so the first few chapters are intended to be extremely straightforward. Some aspects of the later chapters are more challenging in scope but, as students build on the earlier sections, these latter parts should also appear relatively painless.

A word about errors. I have used the phrase 'treatment of errors' fairly liberally. A few of my colleagues take this phrase to mean the statistical manipulation of data once the latter have been obtained. I have followed a different tack, and mean here those errors and faults which can creep into an actual experimental measurement. Indeed, this book is not long enough to describe the actual manipulation of data.

Perhaps I should mention a few of these colleagues. I am delighted to work with such professionals as Dr Brian Wardle and Dr David Johnson of my own Department, namely Chemistry and Materials, at the Manchester Metropolitan University (MMU). They have both read this book in manuscript form from end to end. Additionally, my friends Dr Séamus Higson of the Materials Science Centre, University of Manchester Institute of Science and Technology (UMIST) and Dr Roger Mortimer of the Department of Chemistry, Loughborough University, have also read the entire manuscript. The kind encouragement of these four, together with their perceptive and shrewd comments, have made the preparation of this book much more enjoyable. I also wish to thank Professor Arnold Fogg of Loughborough University and Dr Alan Bottom for their comments within the context of a stimulating correspondence. I have incorporated just about all of the comments received from these wise men, and I extend my heart-felt thanks to all of them. Nevertheless, all errors remaining are entirely my own.

I also wish to thank Dr Lou Coury and Dr Adrian Bott of Bioanalytical Systems, Inc. for their enthusiasm, and permission to reproduce Figures 6.16, 6.18, 6.19, 10.1 and 10.3. I gladly thank Dr Manfred Rudolph for his description of the DigiSim^{TM} program, Dr Mike Dawson of E G & G for his help concerning the Condecon program, and Dr Keith Dawes of Windsor Scientific for his help, and the permission to reproduce Figure 10.2.

Further thanks are also in order, namely to Professor Derek Pletcher of Southampton University for permission to reproduce Figures 6.12, 6.23 and 6.25 and the first two of the three computer programs presented in Chapter 10, to Elsevier Science for permission to reproduce Figures 7.14, 8.1, 8.5 and 8.16, to The Royal Society of Chemistry for permission to reproduce Figures 7.11, 8.3, 8.6 and 8.7, to Wiley-VCH for permission to reproduce Figure 4.3, and to John Wiley & Sons, Inc. for permission to reproduce Figures 3.12, 4.9, 4.10, 6.7, 6.8 and 6.28, plus the third computer program given in Chapter 10. In addition, I wish to acknowledge the following organizations for permission to reproduce further material used in the text, namely The Electrochemical Society, Inc. for Figure 8.14, Oxford University Press for Figure 7.8, the American Chemical Society for Figure 6.27, and the International Society for Optical Engineering (SPIE) for Figure 6.14.

Finally, I would like to thank John Wiley & Sons Ltd and Dave Ando (Managing Editor of the AnTS Series) for commissioning this book, the second title in this series of texts, my friends who have not seen very much of me over the past year, and not least, my precious wife Jo.

Paul Monk
Manchester Metropolitan University

Acronyms, Abbreviations and Symbols

General

A	ampere (amp)
AC	alternating current
ASV	anodic stripping voltammetry; adsorptive stripping voltammetry
AU	absorbance unit
C	coulomb
CE	counter electrode
CME	chemically modified electrode
CSV	cathodic stripping voltammetry
CT	charge transfer
CV	cyclic voltammogram
DC	direct current
DME	dropping-mercury electrode
EIS	electrochemical impedance spectroscopy
EPR	electron paramagnetic resonance
ESR	electron spin resonance
F	farad (unit of capacitance)
G	gauss
HMDE	hanging mercury-drop electrode
IR	infrared
ISE	ion-selective electrode
IUPAC	International Union of Pure and Applied Chemistry
J	joule
LSV	linear-sweep voltammetry
m	metre

MFE	mercury-film electrode
min	minute
NMR	nuclear magnetic resonance
OTE	optically transparent electrode
Pa	pascal
RDE	rotated disc electrode
RE	reference electrode
RRDE	rotated ring-disc electrode
s	second
SCE	saturated calomel electrode
SHE	standard hydrogen electrode
SI (units)	Système International (d'Unités) (International System of Units)
STP	standard temperature and pressure
TIR	total internal reflection
TISAB	total ionic strength adjustment buffer
UV	ultraviolet
UV–vis	ultraviolet and visible
V	volt
WE	working electrode

a	activity
A	area
Abs	absorbance
$\boldsymbol{B}$	magnetic field strength (flux density)
c	concentration of analyte
$c^{\ominus}$	standard concentration under standard conditions, i.e. 1 mol per unit volume
C	capacitance
D	diffusion coefficient
e	electronic charge (charge on an electron)
E	potential; electrode potential; energy
$E^{0'}$	formal electrode potential
$E^{\ominus}$	standard electrode potential
$E^{\ominus}_{\mathrm{O,R}}$	electrode potential for the O,R couple under standard conditions
E_{b}	baseline potential in pulse voltammetry and polarography
E_{f}	final potential in a voltammogram
E_{i}	initial potential in a voltammogram
E_{in}	electrode potential of a redox indicator
$E_{\mathrm{O,R}}$	electrode potential for the O,R couple
E_{λ}	switch potential in cyclic voltammetry
$E_{1/2}$	polarographic half-wave potential
emf	electromotive force
f	linear rotation rate

F	Faraday constant
G	Gibbs function (Gibbs energy)
G'	Gibbs function (Gibbs energy) at frustrated equilibrium
$G^{\ominus}$	standard Gibbs function (Gibbs energy)
H	enthalpy
H'	enthalpy at frustrated equilibrium
i	current density
I	current; ionic strength; intensity of an EPR absorption
I_{circuit}	current through a circuit
I_{d}	diffusion current in polarography
I_{D}	current at a disc electrode
I_{K}	kinetic current
I_{p}	peak current in a voltammogram
I_{R}	current at a ring electrode
j	flux
k	general constant, e.g. calibration constant
k_n	rate constant of a chemical reaction (the subscript, where indicated, gives the order of reaction)
k'	rate constant of a pseudo-order reaction
k_{ct}	rate constant of electron transfer
K	equilibrium constant
K_{S}	solubility constant (solubility product)
l	length; optical path length
L	inductance; Avogadro constant
m	mass
n	number of electrons transferred
N	collection efficiency at an RRDE
N_0	RRDE collection efficiency when no homogeneous reaction occurs
N_{κ}	kinetic collection efficiency at an RRDE
p	pressure
$p^{\ominus}$	SI standard pressure
q	electric charge density
Q	electric charge
r	radial distance from the centre of an electrode's surface
R	resistance; molar gas constant
R_{cell}	resistance of a cell
s	selectivity coefficient of an ion-selective electrode
S	entropy; intensity of an EPR signal
S'	entropy at frustrated equilibrium
t	time; transport number
T	thermodynamic temperature; optical transmission (transmittance)
v	velocity
V	volume; applied potential

V_f	flow rate of solution
X	width coefficient of a channel electrode
z	charge on a particle
Z	impedance
Z'	real component of Z^*
Z''	imaginary component of Z^*
Z^*	overall impedance
Z_W	Warburg impedance
α	transfer coefficient; irreversibility coefficient
$\gamma_\pm$	mean ionic activity coefficient
δ	thickness of Nerst depletion region (layer)
ε	extinction coefficient
η	overpotential
η_S	viscosity
θ	phase angle between current and potential in impedance
λ	wavelength
Λ	ionic conductivity
ν	scan rate ('sweep rate') in polarography and voltammetry; stoichiometric number
ξ	extent of reaction
ρ	density
σ	electronic conductivity
τ	time-scale of observation; length of a cycle, e.g. lifetime of a dropping-mercury electrode drop
υ	kinematic viscosity
ω	angular rotation rate
Ω	ohm

Standard Electroanalytical Prefixes and Suffixes

a	anodic
c	cathodic
D	disc
et	electron transfer
f	flow
j	junction
lim	limiting
p	peak
R	ring

Chemical Species

bipm	4,4′-bipyridine
bipy	2,2′-bipyridine
cp	cyclopentadiene
det	diethylenetriamine
DMF	*N*,*N*-dimethylformamide
DPB	diphenyl benzidine
e^-	electron
EDTA	ethylenediaminetetraacetic acid
EtOH	ethanol
GC	glassy carbon
HV	heptyl viologen (1,1′-diheptyl-4,4′-bipyridilium)
ITO	indium–tin oxide
M	general metal species
MB	Methylene Blue
MV	methyl viologen (1,1′-dimethyl-4,4′-bipyridilium)
PC	propylene carbonate
X	general anion species

About the Author

Paul Monk

The author was brought up in Hastings, on England's south coast, where he attended a local comprehensive school. Despite this education, he achieved entrance to the University of Exeter to read Chemistry. Having obtained a B.Sc. degree and then a doctorate (in 1989) on the electrochemistry of the viologens, he was awarded a fellowship at the University of Aberdeen to study the electrochromism of thin films of tungsten trioxide.

He joined the staff of the Department of Chemistry and Materials, Manchester Metropolitan University in 1991 as a Lecturer in Physical Chemistry. He was promoted to Senior Lecturer in 1998.

He enjoys writing, and is also the author of the books *Electrochromism: Fundamentals and Applications* and *The Viologens*, both of these published by John Wiley & Sons.

Paul Monk is married, in which state he is instructed to profess great happiness, and is also a Methodist Local Preacher.

Chapter 1

Explanatory Foreword

Learning Objectives

- To appreciate that electroanalysis is an analytical tool in which electrochemistry provides the analytical methodology.
- To understand the fundamental differences between potentiometric and amperometric electroanalytical measurements, namely potentiometric measurements are those of the potential made at zero current (i.e. at equilibrium), while amperometric measurements are of the current in response to imposing a perturbing potential (dynamic, i.e. a non-equilibrium measurement).
- To learn the standard nomenclature of electroanalysis.
- To appreciate that while the majority of electroanalytical variables follow the IUPAC system of units, a majority of the common electrochemical equations, if containing variables of length (or units derived from length), will still use the unit of centimetre.
- To appreciate that the fine-detail of electroanalytical nomenclature is important, for example, the way an electrode potential or concentration is written has important implications.
- To notice that the way in which a complicated electrochemical word or term can be split up into its component parts will aid the understanding of its meaning.

1.1 Electroanalysis

Analysts always ask questions such as ‘what is it?’, ‘how much of it is present?’, and sometimes, ‘how fast does it change?’. Electrochemistry is an ideal analytical tool for answering each of these questions – sometimes simultaneously. Here,

Table 1.1 Comparisons between potentiometry and amperometry

Feature	Potentiometry	Amperometry
Property measured	Potential of electrode (at zero current)	Current through an electrode
Analytical methodology	Quantitative and monitoring	Qualitative and quantitative
Concentration range	10^{-7} to 1 mol dm^{-3}	Generally 10^{-8} to 10^{-4} mol dm^{-3}, but can be as low as 10^{-15}
Relative precision	0.1 to 5%	2 to 3%, and lower detection limits
Particular advantages	Useful for titrating coloured or turbid solutions (and also for direct measurements in these solutions)	Can readily follow kinetics of fast reactions. More versatile than potentiometry for the elucidation of reaction mechanisms
Major disadvantages	The measured quantity is activity and not concentration	Apparatus can be expensive (but much cheaper than many non-electrochemical alternatives). Measurements sensitive to contaminants
	Measurements are slow (unless automated)	Measurements sensitive to dissolved oxygen (although this is not true for *square-wave* voltammetry)

we will use the word 'electroanalysis' to mean the use of electrochemistry in an analytical context.

In this present book, we will look at the analytical use of two fundamentally different types of electrochemical technique, namely potentiometry and amperometry. The distinctions between the two are outlined in some detail in Chapter 2. For now, we will anticipate and say that a **potentiometric** technique determines the **potential** of electrochemical cells – usually at zero current. The potential of the electrode of interest responds (with respect to a standard reference electrode) to changes in the concentration[†] of the species under study. The most common potentiometric methods used by the analyst employ voltmeters, potentiometers or pH meters. Such measurements are generally relatively cheap to perform, but can be slow and tedious unless automated.

An **amperometric** technique relies on the **current** passing through a polarizable electrode. The magnitude of the current is in direct proportion to the concentration of the electroanalyte, with the most common amperometric techniques being polarography and voltammetry. The apparatus needed for amperometric measurement tends to be more expensive than those used for potentiometric measurements alone. It should also be noted that amperometric measurements can be overly sensitive to impurities such as gaseous oxygen dissolved in the solution, and to capacitance effects at the electrode. Nevertheless, amperometry is a much more versatile tool than potentiometry.

The differences between potentiometry and amperometry are summarized in Table 1.1. It will be seen that amperometric measurements are generally more precise and more versatile than those made by using potentiometry, so the majority of this book will therefore be concerned with amperometric measurements.

1.2 Nomenclature and Terminology (IUPAC and Non-IUPAC)

The experimental practice of electrochemistry has a long history. For example, more than 200 years have passed since Volta first looked at the twitching of animal tissues in response to the application of an electric impulse. The literature of electrochemistry was huge even before the International Union of Pure and Applied Chemistry (IUPAC) first deliberated in a systematic code of electrochemical symbols in 1953. Accordingly, many of the IUPAC recommendations will not be followed here.

We will now look at each of the major variables in turn.

Redox couple. Two redox states of the same material are termed a 'redox couple', e.g.

[†] Strictly speaking, it responds to changes in **activity**, as defined in Chapter 3.

$$AgCl_{(s)} + e^- = Ag_{(s)} + Cl^-_{(aq)}$$

The electron in this equation will come from (or go to) an electrode if current flows.

Electrode potential. Potentiometric experiments determine potentials. The two components of the redox couple are only together at ***equilibrium*** at a single energy specific to the system under study and at the conditions employed. This energy, when expressed as a voltage,[†] is termed the **electrode potential**, E. The 'electrode potential' is also known as the 'redox potential' or 'reduction potential'. Some texts for physicists call E the 'electrode energy'.

Unless stated otherwise, we normally assume that the solution is aqueous.

E is normally written with a subscript to indicate the two redox states involved. $E_{Fe^{2+},Fe}$, for example, is the electrode potential for the ferrous ion–iron metal system. Note that we expect a different electrode potential if different redox states are involved, so $E_{Fe^{2+},Fe} \neq E_{Fe^{3+},Fe}$. It is the usual practice to write the oxidized form of the couple first.

SAQ 1.1

Write symbols for the electrode potential for the following couples:

(a) bromine and bromide;
(b) silver and silver cation;
(c) ferrocene, $Fe(cp)_2$, and the ferrocene radical cation, Fe $(cp)_2^{+\bullet}$.

There are several different electrode potentials we shall need to use, for example, E, which is the potential of a **half-cell** reaction. It is not usually described with any form of superscript, but will have subscripts, as shown above.

$E^\ominus$ is the **standard electrode potential**, and represents a value of E measured (or calculated) when all activities are 1, when the applied pressure[‡] p is 1 atmosphere and with all redox materials participating in their standard states. As for E, $E^\ominus$ should be cited with subscripts to describe the precise composition of the redox couple indicated. Note that $E^\ominus$ is often written as E^0, thus explaining why standard electrode potentials are commonly called 'E nought'. The symbol '$\ominus$' implies standard conditions i.e. 298 K, $p^\ominus$ and unit activities throughout.

[†] This exposition has been greatly simplified. At equilibrium, the sums of the electrochemical potentials, $\bar{\mu}$, within each of the two half cells comprising the overall cell are the same, and $\bar{\mu}$ is related to the chemical potential μ a by the relationship $\bar{\mu} = \mu + nF\phi$. The occurrence of a potential E at the electrode is a manifestation of the difference in electric field, $\Delta\phi$ between the electrodes and their respective couples in solution, as a function of their separation distances.

[‡] The SI unit of pressure is the pascal, Pa. The SI standard pressure is 1 bar (10^5 Pa) and is denoted by the symbol $p^\ominus$. For historical reasons, the electrochemical standard pressure is taken as being 1 atmosphere of pressure; $p^\ominus$ for the electroanalyst is therefore 101 325 Pa, a 1% difference from the SI value, which causes negligible differences in $E^\ominus$.

Related to $E^\ominus$ is the **formal electrode potential**, $E^{0\prime}$ (as discussed in Chapter 6), which can be called 'the standard electrode potential at 298 K, $p^\ominus$ and unit *concentrations* throughout'. The differences between $E^\ominus$ and $E^{0\prime}$ are discussed in Chapter 6.

The electrode potential obtained with linear-sweep polarography, for example, at a dropping-mercury electrode (DME), is different again and is called the **half-wave potential**, $E_{1/2}$, which is also discussed in Chapter 6.

The phrase 'electrode potential' implies a single electrode, but such potentials are in fact determined or calculated from measurements of **cells** comprising two or more electrodes. This procedure is necessary since it is not possible to measure the energy of a single redox couple at equilibrium:[†] in practice, we have to measure the *difference* or *separation* in energy between two (or more) electrodes. This separation is termed the ***emf***, following from the somewhat archaic expression 'electromotive force'.[‡] In other texts, the alternative name E_{cell} is sometimes given to the *emf*; some texts (rather confusingly) call it just E.

The magnitude of E does not depend on the size of the electrodes – nor does it depend on the material with which the electrode is made, or on the method of measurement. It is therefore an intrinsic quantity.

Current. Amperometric experiments measure current. The **current** I is the rate at which charge is passed, while the **current density** is symbolized as i. Current density is defined as the current per unit electrode area A, so we can write the following:

$$i = \frac{I}{A} \tag{1.1}$$

where current has the unit of the ampere (or 'amp', for short).

Note Both area and ampere have the symbol A, but A for ampere is shown in upright script, while *A* for area is shown as italic – because it's a variable.

SAQ 1.2

What is the current density if an electrode of area 0.35 cm^2 is passing a current of 12 mA?

[†] While this potential cannot be determined for a single electrode, a potential *can* be derived if the potential of the other electrode in a cell is defined, i.e. the potential of the standard hydrogen electrode (SHE) is arbitrarily taken as 0.0000 V. In this way, a potential scale can then be devised for single electrode potentials – see Section 3.2.

[‡] The abbreviation '*emf*', in upright script, is often used in other textbooks as a 'direct', i.e. non-variable, acronym for the electromotive force. Note, however, that in this present text it is used to represent a variable (cell potential) and is therefore shown in italic script.

DQ 1.1

Why use current density at all?

Answer

Current is not measured at equilibrium. Each electroanalytical laboratory will own its own set of electrodes, some large and some small. The current actually measured will be a simple function of the electrode area since charge is passed when electrolyte impinges on a electrode (if it is sufficiently polarized). We see that current is an extrinsic *quantity because its value depends on how much 'something' we employ during the measurement. In this case, the 'something' i.e. the current, relates to the electrode area.*

In contrast, current density is intrinsic *and does not depend on the electrode area, since, by its definition, the current measured has been adjusted to compensate for differences in area.*

In a similar manner to current density, we next distinguish between charge and charge density. The charge that flows is Q, while the charge density, i.e. the charge per unit area, Q/A, is symbolized by q.

Length. It is when we come to units of length that the problems begin. The SI unit of length is the metre, m. Accordingly, the SI unit of concentration is mol m^{-3}. Interconversion between concentration in mol m^{-3} and concentration expressed in the more familiar[†] units of mol dm^{-3} is simple, i.e.

$$\text{concentration in mol m}^{-3} = 10^3 \times \text{concentration in mol dm}^{-3} \qquad (1.2)$$

because there are 1000 cm^3 in 1 dm^3, and thereby 1000 litres in one cubic metre. We see that concentrations in SI units appear as larger numbers.

SAQ 1.3

11 g of solid KCl are dissolved in 250 cm^3 of water. What is the concentration when expressed with the units of mol m^{-3}?

It is rare for electrochemists to use SI units in this way, so, like most analysts, they will usually talk in terms of the concentration units that are most convenient.

Unfortunately, many of the standard equations encountered in electrochemistry require the concentration unit of mol cm^{-3} (moles per cubic centimetre). The conversion between mol cm^{-3} and the familiar mol dm^{-3} is as follows:

$$\text{concentration in mol cm}^{-3} = 10^{-3} \times \text{concentration in mol dm}^{-3} \qquad (1.3)$$

[†] Many texts use the symbol 'M' for mol dm^{-3}. We will not use 'M' here in order to emphasize the requirement for interconversion.