RSC Detection Science

Electrochemical Strategies in Detection Science

Edited by Damien W. M. Arrigan

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Edited by

Damien W. M. Arrigan
Curtin University, Perth, Australia
Email: d.arrigan@curtin.edu.au

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Preface

Electrochemical methods of chemical analysis have been widely used for many years. This is seen most especially with the trusty pH electrode and conductivity meter, which are used widely in industrial and environmental applications. The everyday analyses of clinical samples for electrolytes, performed with ion-selective electrodes, and the mass-manufactured glucose test strips which place routine electrochemical measurements into the hands of non-scientists are further examples of the extensive use of electrochemical measurements. These examples illustrate that electrochemical methods and devices built on sound principles and evaluations serve vital functions outside of the research laboratory. Electroanalytical chemistry and electrochemical methods have the great advantage that they are sensitive and selective, can be easily made portable and miniaturized, and are often adaptable to new applications.

The purpose of this volume is to discuss recent advances in electrochemical methods and materials that may bring new strategies to bear on chemical and biochemical detection problems. The scope of the volume is to survey contemporary research and development advances within the areas of electrochemical detection based on new and re-vitalised methods, new materials with enhanced properties, and new devices that achieve better electroanalytical signal generation. As a result, the chapters collected here, written by leading researchers in the field, encompass advances in electrodes and devices, from microscale to nanoscale, electrochemical nanomaterials, and electrochemical behaviour and applications of soft interfaces and materials.

Chapter 1 deals with advances in stripping voltammetric detection of metals and addresses the replacement of mercury electrodes for this application. Chapter 2 continues the discussion of electrode devices, dealing specifically with microfabricated electrodes and their use in biomedical

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detection, while Chapter 3 discusses the use of electrodes in conjunction with microfabricated chips for chemical/biochemical separations and detection. Microelectrodes also feature in Chapter 4, in terms of scanning electrochemical microscopy, especially for biological systems characterization. Chapters 5–8 bring the discussions to the nanoscale, dealing with detection of nanoparticles (Chapter 5), nanofabricated electrode devices (Chapter 6), carbon nanomaterials (Chapter 7), and dispersible nanoparticle electrodes (Chapter 8). The final two chapters discuss electroanalytical opportunities derived from soft (liquid–liquid) interfaces (Chapter 9) and from room temperature ionic liquids (Chapter 10).

It is hoped that this collection of chapters will provide the interested reader with an introduction to some of the recent hot topics in electrochemical detection research and provide a platform for the design and development of further improvements in this area of detection science.

Damien W. M. Arrigan
Perth, Australia

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CHAPTER 1

Advances in Stripping Analysis of Metals

ANASTASIOS ECONOMOU*[a] AND CHRISTOS KOKKINOS[a,b]

[a] Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, Athens 157 71, Greece; [b] Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece
*Email: aeconomo@chem.uoa.gr

1.1 Introduction

Electrochemical stripping analysis (SA) has been established as a successful trace analysis technique for more than three decades. Stripping analysis is a general term that encompasses a wide family of electroanalytical techniques that make use of a "preconcentration" step of the analyte on the surface of the working electrode. In SA, the preconcentration step is followed by the detection step in which the accumulated analyte is detected and quantified by means of a voltammetric or chronopotentiometric scan. While in solution-phase electrochemical detection the redox signal is determined by the rate of mass transport of the electroactive analyte to the electrode surface, in SA the redox signal is determined by the amount of the accumulated analyte. Therefore, the accumulation step is responsible for the high sensitivity of SA whereas the different potential methods of accumulation of the analyte on the working electrode (discussed in Section 1.2) and the multi-parametric nature of SA provide versatility, wide applicability and enhanced selectivity. Typical metals and semi-metals that can be determined with SA are listed in Table 1.1. The theory and practice of SA are described in specialized monographs[1,2] and general review articles.[3–5]

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Table 1.1 Metals and semi-metals that can be determined by SA (in italics are the species that are normally determined only after electrolytic accumulation, underlined are the species that are normally determined after non-electrolytic accumulation and in bold are the species that can be determined after either electrolytic or non-electrolytic accumulation).

											Al						
		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	**Cu**	**Zn**	Ga	Ge	**As**	*Se*		
		Y	Zr		Mo	Tc			Pd	**Ag**	**Cd**	**In**	**Sn**	**Sb**			
		La	Hf						Pt	**Au**	**Hg**	*Tl*	**Pb**	*Bi*			

Ce	Pr				Eu			Dy	Ho			Yb	Lu
Th		U											

A brief account of the birth and gradual evolution of SA is provided in earlier work.[1,5,6] SA was first conceptualized and applied in 1931 by Zbinden to determine low concentrations of copper at a platinum electrode.[7] However, not until the 1950s was SA revisited when the hanging mercury drop electrode was developed by Kemula. In the same decade, the remarkable sensitivity of SA was stressed by many workers and new types of thin mercury-film electrodes were introduced. In the 1960s, the theory for SA and pulsed potential–time waveforms was developed. The commercial availability of low cost multi-purpose apparatus and the expanding use of SA to many new analytical applications took place in the 1970s. The development of non-electrolytic preconcentration approaches and of automated flow-through manifolds, together with the introduction of microelectrodes for SA, dominated the 1980s and 1990s. Recent advances in SA are concentrated on research on new eco-friendly electrode materials, the extended use of microfabrication technologies and miniaturization and the development of integrated devices for on-site monitoring. Therefore, this chapter will not focus on specific applications but will try to highlight developments in sensor types, fabrication and materials.

1.2 The Principle of Stripping Analysis

The distinctive feature of SA in comparison to other electroanalytical techniques is the accumulation/preconcentration step. In most applications involving analysis of metals, preconcentration is carried out with electrolysis of the target metal cations to the respective metals (and some special cases to metal oxides) and deposition on the surface of the working electrode[1,2] (Figure 1.1A). Following accumulation, the accumulated metals are oxidized (or the metal oxides reduced) to the respective cations and stripped back into the solution. Depending on the nature of the working electrode surface, the

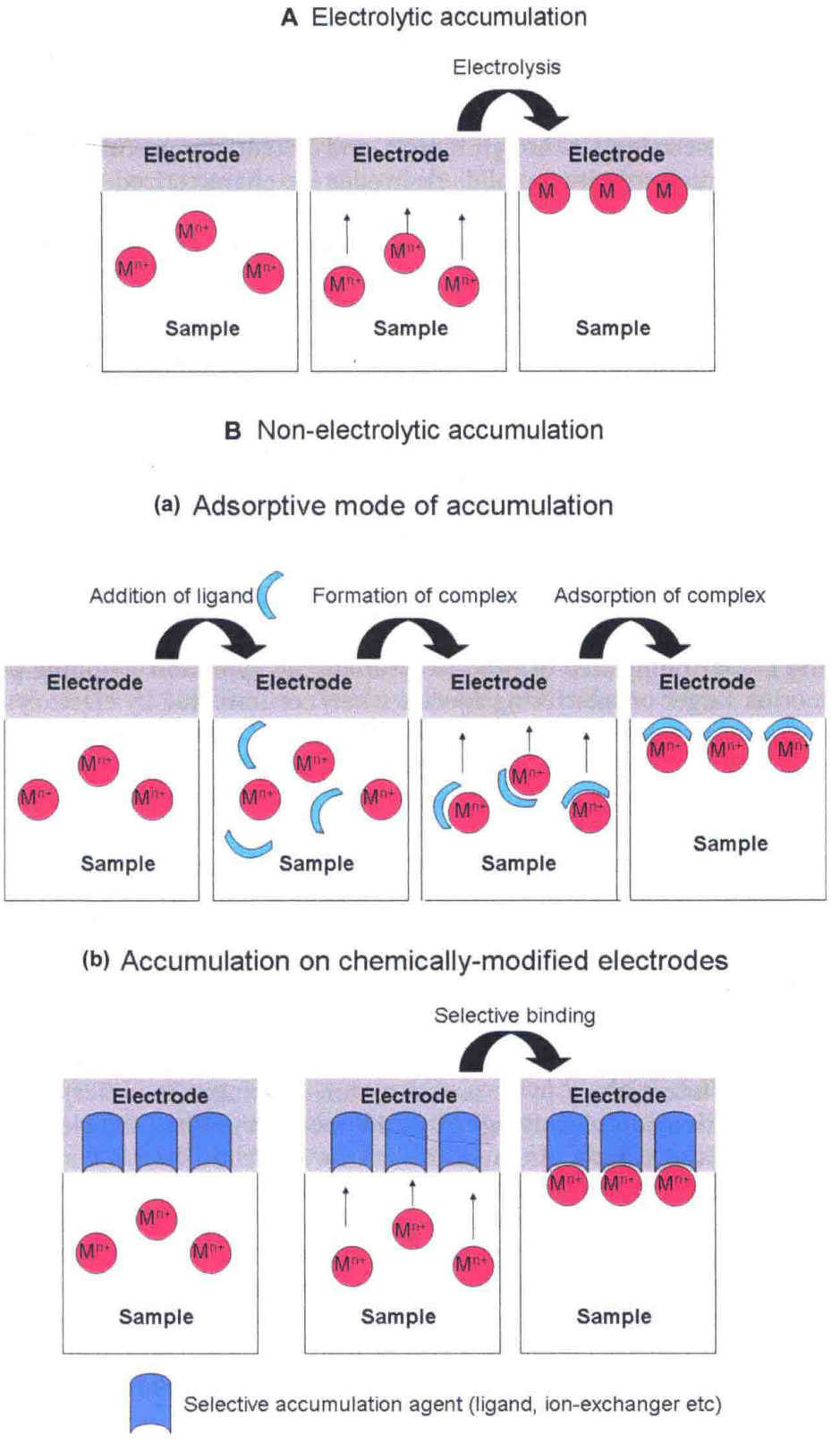

Figure 1.1 Modes of accumulation in SA of metals.

deposited metal can form a thin film, an amalgam or an alloy with the electrode. Reduction of metals on inert electrodes (such as carbon, platinum or boron-doped diamond) proceeds *via* the formation of a monolayer of the target metal (underpotential deposition, UPD) followed by the deposition of the bulk-phase metal. Although simple and potentially useful, electrolytic preconcentration on inert solid electrodes is characterized by multiple stripping peaks that are hard to interpret.[8,9] This is due to the easy formation of intermetallic compounds on the electrode surface and to the different oxidation (stripping) potentials associated with the different states of the metal deposits. Amalgams are typically generated when heavy metals deposit on mercury electrodes or during the deposition of mercury on gold electrodes. Finally, alloys are formed when bismuth, tin or antimony electrodes are used for electrolytic accumulation of alloy-forming metals. Amalgamation and alloying facilitate the electrolytic deposition and stripping of metals and lead to stripping signals that are easier to interpret. Following electrolytic accumulation, the stripping step can be performed by an anodic voltammetric scan, a constant oxidation current or by a chemical oxidizing agent.[1,2]

Non-electrolytic accumulation can be alternatively employed for metals that are not amenable to electrolytic deposition, are not readily oxidized during the stripping step or produce overlapping oxidation stripping peaks with other target or interfering species when accumulated by electrolysis.[10] The adsorptive mode of accumulation involves addition of a selective complexing ligand (such as dimethylglyoxime, catechol, 8-hydroxyquinoline) with surface-active properties in the sample[10–13] (Figure 1.1B-a). The metal cations form a complex with the ligand and the complex is then physisorbed on the electrode surface. The stripping step is usually based on the reduction of the metal cation in the accumulated complex but the reduction of the ligand or catalytic effects can be also exploited.[13,14] A second strategy is based on the utilization of chemically-modified electrodes.[10,15,16] In this case, the working electrode is bulk- or surface-modified with a suitable agent that can selectively bind the target metal cation. In the context of SA of metals, accumulation at chemically-modified electrodes can proceed by electrostatic interactions (with a clay or ion-exchanger modifier) or complexation (with a complexing ligand as the modifier). When the electrode is immersed in the sample, the modifier on the electrode interacts and binds with the target metal cations, which are accumulated on the electrode surface in their native oxidation state (Figure 1.1B-b). In the simplest scenario, the stripping step can be a reductive scan in which the accumulated metal cations are reduced.[9] A more complex protocol involves potentiostatic reduction of the accumulated metal cations followed by an anodic stripping step in which the target metals are oxidized.[9] Again, stripping can be performed by either a voltammetric scan or a (reductive or oxidizing) constant current.

The nomenclature in SA is not standardized and usually more or less established empirical abbreviations define a technique by reference to the