RECENT TRENDS IN ELECTROANALYTICAL CHEMISTRY.

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Introduction

[In view of the heterogeneity of interests represented by the audience, I have chosen to speak in a fairly general vein, rather than discuss my very limited research area. This is also a welcome occasion to make non-electroanalytical chemists aware of some electrochemical techniques which could be useful analytical tools in their own disciplines, especially in studying processes or phenomena at electrical interfaces. Because of time constraints, only a few of the major electroanalytical techniques can be mentioned.]

Electrochemistry has to do with *controlled electrical paths* for producing chemical transformations involving a *net* electron transfer. The electrical parameters that are employed and varied to force specific electrochemical reactions are: potential or voltage (both direct current and alternating current), current, and resistance. The analytical signals or responses observed are current, charge, potential, resistance, or time-dependence of any of these signals. Resistance is often measured in the inverse form, conductance.

Electrochemical methods are generally useful for: (1) quantitative, (2) qualitative, and (3) kinetic characterizations of chemical systems. Knowledge obtained from the last two has made many irreversible reactions available for analytical applications.

The classical electroanalytical methods familiar to many are electrolysis (exhaustive), coulometry, potentiometry, amperometry, and conductimetry. In the late 1920s, J. Heyrovsky (1959 Nobel Laureate in Chemistry) invented polarography, which concerns the measurement of current resulting from an applied potential at a dropping mercury electrode (DME), a spherical microelectrode. From polarography, several *modern* methods have been born and have been loosely referred to as "polarographic methods" (strictly, they are voltammetric methods, dealing with current-potential relationships).

Polarography proved to be a very versatile analytical and thermodynamic tool. It was widely applied for 25-30 years after its invention, although involving

largely inorganic systems. The sixties saw a decline in its popularity because of the method's limitations: the DME is actually an expanding electrode (large charging currents); positive potentials are inaccessible (because of oxidation of mercury), thus excluding many oxidation reactions; the inadequate two-electrode design; and current "damping" problems which arise from oscillations due to the growth and fall of the mercury drop.

The 1970s, however, saw a "renaissance" of polarographic methods (1) and the birth of several new *transient* techniques (i.e., methods involving the application of current or potential pulses, or other signal waveforms of short duration). This revival is attributed to the advent of smaller, cheaper, and more versatile solid-state electronics (especially operational amplifiers). The three-electrode potentiostat came about, which provided precisely-controlled potentials at the working electrode. Other features of the new breed of instrumentation eliminated background current from the analytically significant faradaic current, and presented the analytical response (signal) in the form of a peak, rather than the conventional polarographic wave.

About the same time, new electrode materials (e.g., graphite, glassy carbon) started to be discovered, which extended the potential window of investigation into the anodic region, but without pronounced chemisorptive or catalytic action as in the case of platinum. New electrode designs and configurations (e.g. rotating ring-disk) also helped widen the applications (originally largely limited to the reduction of metal ions) to include many organic and biological reactions.

Present-day electroanalytical methods possess the following attractive features: (1) small volume of test solution; (2) non-exhaustive; (3) short analysis times (a few minutes); (4) high sensitivity, due to greater suppression of background; (5) improved resolving power; and (6) easy automation or computer-interfacing for laboratory control and/or data processing.

The theory for each of the techniques to be described is too mathematical; only the final, established relationship of analytical response to concentration of electroactive species will be cited. In some of the transient techniques, digital simulation has been employed to test the validity of analytical equations derived from first principles. The methods discussed below represent those used mostly in the author's research work.

Selected Electrochemical Methods

1. *Potentiometry at Selective Electrodes*

The first and most widely used ion-selective electrode is the glass electrode which appeared in 1906). It consists of a special glass membrane (about 50 μm thick), which responds to the hydronium ion in a Nernstian fashion. Measurements with ion-selective electrodes are essentially determinations of membrane potentials which themselves comprise junction potentials between electrolyte phases. The

performance of any single system is determined largely by the degree to which the species of interest can be made to dominate charge transport in part of the membrane.

Since the late sixties many different ion-selective electrodes have appeared. The latest review on this area presents a host of new electrode systems, new configurations, new reference electrodes, new routine and non-routine applications (inorganic, organic, biological, and medical), and new measurement systems including automated continuous flow types (2). The pH-sensitive electrode continues to be modified or replaced; one of these is a liquid-membrane type based on tri-n-dodecylamine as neutral carrier, which is claimed very adequate both for intracellular and extracellular hydrogen-ion activity measurements (3). Other new types of selective electrodes reported include solid-state membranes, liquid-ion exchangers, and gas-sensing and enzyme-coupled devices (2). Coated wire electrodes responsive to halo-metal complex anions (4) and chemically modified electrodes for determination of dissolved organic analytes (5) have been developed. These selective electrodes can readily be "home-made" (6, 7).

Development work concerns determination of selectivity characteristics, detection limits, temperature and response time limitations, and potential pitfalls (e.g., chemical interferences, aging, "memory effects," poisoning), prior to application to real analytical situations. Solvent effects and membrane thickness to surface ratios are some critical factors influencing non-Nernstian behavior.

2. *DC and Pulse Polarography*

The family of polarographic techniques has again found widespread applicability since the introduction of low-cost three-electrode potentiostats and more convenient DME designs. In particular, normal pulse and differential pulse polarography have brought down the detection limits from about 1×10^{-5} molar for conventional (dc) polarography to at least 1×10^{-7} molar for the pulse modes. Enhancement in response is due to the improvement from reduced charging current contribution, since currents are sampled under potentiostatic conditions when the charging currents have decayed to the minimum value. Recent applications include trace (inorganic and organic) analyses, determination of oxidation states, detection of complexation, and acid-base chemistry. Biological and pharmaceutical applications have been especially numerous (8, 9), proving that polarography remains the most powerful electroanalytical tool today.

A new concept in dropping mercury electrodes, the static mercury drop electrode (SMDE), was introduced recently by one of the leading manufacturers of polarographs (PARC) and overcomes one formidable limitation in polarography, i.e., measurements are made at an expanding electrode. The SMDE is similar to the conventional DME; however, the electrode assembly includes a valve which allows the mercury flow to be stopped at selected time intervals to produce a stationary rather than a growing drop on the tip of the capillary. The SMDE retains all the advantages of the conventional DME (fresh surface) but avoids the problem of

obtaining data at an electrode with continuously changing area. The SMDE allows "area step" experiments to be performed, which can be considered analogous to potential step experiments. Because of the elimination of charging current from area growth terms, there is essentially no difference in detection limits between DC polarography and differential pulse polarography when using the SMDE (10). This is believed to be a very significant development and could lead to the convergence in the performance of the various polarographic techniques.

3. *Stripping Analysis*

Because of the pre-concentration step, stripping analysis is to date the most sensitive electrochemical method of analysis. It utilizes a bulk electrolysis step of a few minutes' duration to pre-concentrate (by a factor of 100-1000, or more) a substance from solution into the small volume of a mercury electrode (or onto the surface of a solid electrode). After this step, the material is redissolved ("stripped") from the electrode using some voltammetric technique (frequently linear potential sweep voltammetry).

The widest application is in the analysis of trace metals by cathodic deposition, followed by anodic stripping with a linear potential scan (anodic stripping voltammetry, ASV) or together with a differential pulse (DPASV). Mercury, platinum, gold, mercury-film on glassy carbon, etc. can serve as substrate electrodes. The technique is especially useful for the analysis of very dilute solutions, down to 10^{-10} or 10^{-11} molar.

Cathodic stripping voltammetric (anodic pre-concentration step) applications are slowly unfolding, e.g. analysis of Mn (II) as MnO_2, sulfide as Ag_2S (on silver electrode), etc.

A related technique but one which requires simpler instrumentation is potentiometric stripping analysis (PSA), which was introduced by Jagner *et al*. (11, 12). The same pre-concentration step is required; however, the stripping is performed chemically by an oxidizing agent (or reducing agent, in the case of anodic pre-concentration), such as oxygen, Hg(II), Fe(III), etc. (13). In the reductive case, hydroquinone has been employed as stripping agent (14, 15).

In this method the analytical signal for stripping a component is proportional to the time required to redissolve that component. A theoretical analysis of the method was recently reported by Chinese workers (16).

Determinations are generally performed in stirred solutions to improve reproducibility and analytical signal levels.

There are a few problems with this technique, such as finding the suitable oxidizing or reducing agent which does not electrolyze at the potential of pre-concentration. Furthermore, the stripping process may not be entirely transport-controlled. However, good resolution and its applicability in media of low ionic strength are distinct advantages over ASV.

4. *Voltammetry at Rotating Electrodes*

One of the few convective electrode systems for which the hydrodynamic and convective-diffusion equations have been solved rigorously for the steady state

is the rotating disk electrode (RDE). It consists of a disk of the electrode material imbedded in a rod of an insulating material (e.g., glass tubing, teflon, epoxy resin, other plastics). The parameter controlled is the angular velocity of the RDE.

The Levich equation for a totally mass-transfer-limited condition predicts that the limiting current is proportional to the concentration of the electroactive species in the bulk of the solution and to the square root of the electrode rotation speed (17). The RDE has numerous applications not only for analytical determinations but also for measurement of kinetic parameters.

The rotating ring-disk electrode (RRDE) is an even more powerful tool. It consists of a disk electrode combined with a ring electrode, which is concentrically placed around the disk electrode. The current-potential characteristics of the disk electrode are unaffected by the presence of the ring. Independently of the disk (e.g. the disk at open circuit), the ring current can be measured and is related to the geometric parameters of the ring, i.e., the inner and outer radii.

RRDE experiments are usually carried out with a bipotentiostat, which allows separate adjustment of the disk potential and ring potential. However, it is possible to use an ordinary potentiostat to control the ring circuit and a simple floating power supply in the disk circuit.

Two types of experiments are frequently used at the RRDE: (a) collection experiments, where species generated at the disk are observed at the ring; and (b) shielding experiments, where the flow of bulk electroactive species to the ring is perturbed because of the reaction at the disk. The ring current is related to the disk current by the collection efficiency (in the former case) and by the shielding factor (in the latter case), both quantities being predictable from the electrode geometry (17).

The application of transients (e.g. potential step) or hydrodynamic modulation (18) have allowed the study of absorption phenomena at the disk through the currents at the ring. Monomolecular layers of Sn, Pb, Tl, and Hg have been measured on a gold RRDE and are applicable in ultra-trace analyses of these metals (19-22).

5. Cyclic Voltammetry

One very popular tool which deserves mention, not so much for its analytical utility but for the wealth of qualitative information that can be directly visualized from the current-potential curves recorded, is cyclic voltammetry. A triangular potential waveform is employed, and the resulting voltammograms are characterized by peaks. Equations to predict peak current and peak potential for both reversible and irreversible systems have been derived (23).

New systems for study would benefit from initial observations obtained from cyclic voltammetry. Different mechanisms give rise to distinct variations of peak current, peak potential, etc. with the kinetic parameters for both charge transfer and coupled chemical reactions. Diagnostic criteria for establishing mechanisms based on changes of peak potential as a function potential scan rate and concen-

tration are now known and have been utilized in numerous basic studies of electrochemical systems (24).

An interesting application of cyclic voltammetry which was reported is the in vivo monitoring of substances in the kidney or brain, employing a miniature carbon paste electrode (25).

6. *Combination Techniques*

Electrochemical detection methods are becoming very important in liquid chromatography and in continuous flow analysis (26). Ion-selective and voltammetric electrodes are frequently used. The advantage of high sensitivity continues to make electrochemical detectors popular despite the problems of providing electrodes with reproducible surface and low background current. In addition, such detectors must be compatible with the chromatographic requirement of low dead volume and fast response, and the electrochemical requirement of low resistance. The utility of the LCEC detector can be extended by derivatization of analyte molecule with electroactive reagents or by use of electrogenerated reagents.

In recent years, study of electrode processes and electrode surfaces involved other experiments to obtain information that could not be gathered in purely electrochemical measurements. One of these is absorption spectroelectrochemistry, which involves directing a light beam through the electrode surface to measure absorbance changes resulting from species produced or consumed in the electrode process. The obvious prerequisite is an optically transparent electrode (e.g. thin films of semiconductors like SnO_2 or In_2O_3, or Au or Pt deposited on glass, quartz, or a plastic surface). Spectroelectrochemical methods can be especially useful for unravelling a complex sequence of charge transfers, such as in the study of redox proteins (26). Thin-layer (test solutions ca. one microliter) spectroelectrochemistry has been further combined with GC/MS to identify reaction intermediates (27).

Instrumentation

Description of new microprocessor- or microcomputer-based electroanalytical systems comprises the largest number of publications in the field in the past few years. The objectives vary from searching for novel applications, improving the versatility of the system through software modification, to enhancing sensitivity through signal averaging. Several modules and modifications of commercial instruments were reported, e.g. a conversion module which extended the capability of a polarographic analyzer to cyclic voltammetry and derivative polarography, modification of timing sequence to improve performance, etc. (24).

Through microprocessor technology, it is possible to build a low-cost electroanalytical system with flexibility limited only by software capabilities. Enormous amounts of data may be obtained and transformations from one response to another readily performed. At the same time there can be excellent means for

detecting interferences in analytical data and possibly compensating or correcting for them. It has been suggested that instrumentation will be equivalent for the different polarographic techniques if digital approaches were routinely implemented (10).

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Apolinar S. Lorica, Discussant

Speaking as a baseball fan, I would say that Dr. Vicente has touched all the bases and made a homerun in discussing the recent trends in electroanalytical chemistry. So, what is there left to say? Well, maybe I could say something about future trends to justify my presence here.

As Dr. Vicente mentioned, practically all the "happenings" in electroanalytical chemistry for the last 30 years can be traced to a minute electrode aptly called the "dropping mercury electrode". Future trends will be largely dependent on studies on new and modified electrodes. Another metal, gallium, which is a liquid like mercury at our room temperature (M. P.=$30°C$) during the hot months, has been considered as an electrode material and might figure prominently in future developments in the dynamic field of electroanalytical chemistry.

There is considerable interest in the chemical modification of the electrode. Coated wire electrodes and some chemically modified electrodes are already being used in ion-selective electrodes, as noted by Dr. Vicente. Chemical modification has so far been achieved by: 1) covalent attachment of functional groups; 2) adsorption of organic molecules; and 3) adherence of a polymer matrix containing a redox active component.

Chemically modified electrodes are still shrouded in mystery. They are easy to prepare, and can be *home-made* as Dr. Vicente said. This is probably why they are becoming increasingly popular. They appeal to the boy and the scientist in a man. There is, however, much controversy over the exact mechanism of their response. Some exhibit nearly Nernstian response to changes in ion concentration while others show irreproducible and drifting potentials and nobody has come up with a convincing explanation.

It is safe to say that miniaturization will underlie future developments in electroanalytical chemistry. The reason for this is the continuing effort to use very small amounts of sample which is partly fueled by the desire to economize on expensive chemicals. Another reason is the desire to use ion-elective electrodes to monitor *in vivo* important blood electrolytes.

As you may have noticed, electroanalytical chemists use down-to-earth terminology. For example, in polarography, the salt which is added to the solution in great excess, is called the *supporting* electrolyte. It gathers near the electrodes but does not react. The other electrolyte, presumably, the *star* electrolyte, is the one that reacts at the electrode, which, incidentally, is called the *working* electrode. The other electrode only acts as a reference electrode. The current that is used to charge up the electrical double layer around the *dropping* mercury electrode is called the *charging* current, of course, while the current used in the electrode reaction (which is measured in units named after Michael Faraday) is the *faradaic* current. When the potential of the working electrode obeys the Nernst equation, its behavior is termed *Nernstian*. Finally, to end this brief discussion, I'm sure you remember having heard the process of removing a deposit covering an electrode called suggestively, *stripping*.

Amando Kapauan, Discussant

I would just like to add two very recent developments in this area of electro-analytical chemistry. One concerns a paper that is published by Dr. Vicente's old boss, Dr. Bruckenstein just recently, about two months ago, in the March issue of Journal of Electroanalytical Chemistry described a new kind of electrode system called the wall-tube electrode. The reason why this is very important has to do with what Dr. Vicente mentioned earlier.

One of the most powerful electrodes for the study of basic electrode reactions is the rotating disc electrode. The reason for this I won't go into, it is one of those few electrodes, in fact it is the only electrode so far up to last March in the literature, where the current is strictly proportional to the area; if you double the area, the current doubles and there are hydro-dynamic reasons for this. But if you have ever tried to make a rotating disc electrode, you will find that it is so difficult that around the world there are just a few, countable in the fingers of your hand, laboratories that are capable of turning out very good rotating disc electrode results.

Dr. Bruckenstein's paper is a mathematical study of the hydrodynamics of an electrode which is a small electrode embedded as a flat disc then polished exactly to the surface of a container's wall. The electrolyte is conducted to this electrode using a small tubing whose internal diameter is slightly bigger than the micro-electrode embedded on the wall. Under these conditions, with solution flowing from the tube into the wall (that is why it is a wall-tube electrode) the hydrodynamics is exactly the same as in the rotating disc electrode, but with the tremendous advantage that it is stationary. All you need to do is pump the solution through the tube. I expect that there will be dozens of papers in the next few years concerning the applicability of this system to basic electrode phenomena. One of the things that we ought to try our hands in because it is easy to make.

The other is the development of very cheap microprocessor systems which are all available nowadays, even in Binondo. The cheapest Apple-type computer sells for about ₱3,000.00* This includes 64 K of memory, exact operational duplication of all Apple functions. The Apple computer has a tremendous amount of software and hardware available, compatible with it. So that I think there is no excuse for anybody who wants to fool around with microcomputers and microprocessors in terms of expenses here in this country at the present time. In fact, we are doing better than many other developed country in the world. You can't buy anything as cheaply as what is available in Binondo here. Go out there and get yourself one and start fooling around with it. It is the thing to do nowadays. Thank you very much.

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*At printing time up to ₱7,000 because of inflation.