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Analytical Electrochemistry: Methodology and Applications of Dynamic Techniques

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Photoelectrochemistry has come of age. Long a laboratory curiosity with few proponents, the field has become the most active and potentially the most important area in modern electrochemistry. A number of papers have recently appeared which bear on the photoassisted (or "photocatalyzed") electrolysis of water, metal complexes, and organic compounds. There is great interest in perfection of an efficient regenerative liquid-junction solar cell for direct conversion of light into electrical or chemical energy. The economic implications of this effort are obvious. As a result of this challenge for a practical breakthrough, a highly competitive new spirit has taken hold of a number of research groups around the world. Major efforts are underway in Japan, Germany, and the United States. Work in this area is outside the scope of the present review; however, the implications for analytical chemists are substantial. We have already learned a great deal about the chemistry of semiconductor electrodes and how these surfaces can be modified for a variety of purposes. We have also learned how light can be used to stimulate certain electrochemical reactions which might otherwise be difficult to carry out. Those who have not been following developments in photoelectrochemistry are missing out on some very exciting work.

Novel theory and methodology in the area of dynamic electroanalytical chemistry continues to evolve at a decreasing rate while reports of routine applications are accelerating rapidly. In the present review, we have selected references which have appeared from January 1976 through December 1977 in several areas which are of particular interest to analytical chemists. This review is by no means exhaustive (e.g., many important papers in the foreign literature are not mentioned). We hope to have achieved a fair assessment of the more recent developments in experimental implementation of the dynamic ($i \neq 0$) techniques.

CHEMICALLY MODIFIED ELECTRODES

As predicted in the previous review (*1A*), work in the area of chemically modified electrodes (CME's) continues at an accelerating pace. There can be little doubt that CME's are at the forefront of experimental electroanalytical chemistry. Not since the advent of the operational amplifier has there been a development of such far-reaching importance to the use of electrodes for practical problem solving. Perhaps the greatest limitations of finite-current electrochemistry is the slow rate of electron transfer exhibited by most molecules and ions at electrode surfaces. One of the important goals of research on CME's is the design of electrodes which afford more rapid electron transfer rates for pre-selected solutes. The implications of these surface-bound catalysts for analytical chemistry, electrosynthesis, and energy conversion are obvious. The ebullient competitive spirit of workers in this field is well justified!

Electrodes have been unwittingly modified by strong adsorption for many years. It is now apparent that this process may finally prove to be useful. Lane, Hubbard, and co-workers have added to their series of publications on surface modified

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platinum electrodes. In one of the first analytical applications of a CME, a platinum microelectrode coated with chemisorbed iodide was used to detect catecholamines in living rat brain using small amplitude pulse voltammetry techniques (2A, 3A). This approach is advantageous in that the catecholamines can be selectively detected in the presence of the large excess of ascorbic acid encountered in the mammalian brain. In a related fundamental paper, Johnson and Resnick have studied the electrocatalysis of iron(III) reduction by adsorbed halides using a rotating disk electrode (4A). Platinum electrodes modified by adsorbed iodide also exhibited an extended useful potential range and decreased charging current in perchloric acid solutions.

Lane and Hubbard have reported that many of the commonly used solvents for nonaqueous electrochemistry chemisorb irreversibly on Pt electrodes and thus inhibit the well established halide-assisted electrochemical reactions of Pt(II) and Pt(IV) complexes (5A). The adsorbed solvent blocked interaction of the surface with iodide preventing the modification mentioned above. On the other hand, if the iodide treatment was carried out before exposure of the electrode to the nonaqueous solvent, solvent adsorption was prevented and the reactivity of the platinum complexes was not blocked. It was feasible to determine the fractional surface coverage of solvent by use of thin-layer coulometry to measure iodine adsorbed on the remaining surface. There are a number of interesting observations noted in this excellent report. Schoeffel and Hubbard studied the adsorption of ethylene and substituted alkenes on clean structurally ordered Pt(100) surfaces prepared in an ultrahigh vacuum Auger spectrometer (6A). The Auger instrument was calibrated for surface coverage measurements by oxidizing adsorbed alkene in 1 M $HClO_4$ using thin-layer chronocoulometry.

Hawkridge and co-workers have been pursuing electrochemical and spectroscopic studies of electron transport components of the plant photosynthetic apparatus (e.g., the ferredoxins). In the course of this work, it was accidentally discovered that the popular redox mediator methyl viologen (1,1′-dimethyl-4,4′-dipyridyl dichloride) could be used to chemically modify a gold electrode by means of a stable

adsorbed film (presumed to be polymeric) (7A). A gold "minigrid" electrode modified in this manner was capable of exchanging electrons with spinach ferredoxin at a much faster rate than for an unmodified electrode. Thus thin-layer spectroelectrochemical studies of the ferredoxin can be undertaken without need for a large excess of mediator in the solution, minimizing the problem of spectral interference between mediator and protein (7A). Davis and Murray have reported strong chemisorption of iron porphyrins and Fe(III) on SnO_2 electrodes resulting in voltammetric waves at negative potentials in nonaqueous solvents which apparently involve catalyzed reduction of the SnO_2 surface (8A). The detailed mechanism appears to be quite complex.

Brown, Koval, and Anson have discovered that a number of organic redox reagents and complexes can be irreversibly bound to graphite electrodes by strong spontaneous adsorption while maintaining excellent redox characteristics (9A). Small amplitude differential pulse voltammetry was noted to be a far more sensitive method than cyclic voltammetry for study of the bound reactants. A later paper extends the experimental work and presents theoretical models for both voltammetric techniques (10A). The "fit" between theory and experiment was excellent, where tested, and it is clear that the pulse technique is adequate for studies of sub-monolayer coverage by the adsorbed reactants. Much of this work should be generally applicable to a variety of CME's with attached redox components, including those which are covalently bound by design. Brown and Anson have focused on the application of their rather straightforward CME approach to electrocatalytic processes involving bound transition metal complexes. As a first step to this end they devised a ligand, [1-(9-phenanthrene)-2-(4-pyridine)-ethene], which can be irreversibly adsorbed on graphite, presumably through the aromatic hydrocarbon "anchor", allowing the "pendant pyridine" to swing free for coordination to various metal complexes (11A). A ruthenium complex was hung from the pendant in this initial study on freshly cleaved basal-plane pyrolytic graphite. The authors note that their approach does not require an extensively oxidized graphite surface and thus the background currents are less complex than for other bonding schemes. Mazur et al. have also advocated the use of oxide-free carbon surfaces as a CME substrate (12A). These workers reacted oxide-free carbon fibers with alkenes. The experimental evidence supports the contention that the "irreversible adsorption" takes place via formation of a six-membered cyclic adduct of the alkene across a phenanthrene-like reactive center on the surface. This provides a practical synthetic entry to all sorts of CME's.

To date, the most common route to chemical modification of electrodes has been by covalent reactions at functional groups containing oxygen. Although the surface chemistry is often not entirely clear, both surface carboxyl and hydroxyl groups have been used. Miller et al. were the first to report the use of an amide linkage to bond organics to thermally oxidized carbon surfaces (1A). The surface is treated with $SOCl_2$ to form the acid chloride which is then reacted with an amine. This approach was originally used to prepare a chiral surface bonded with a nonelectroactive aminoacid ester. It was possible to use this electrode to induce asymmetry in the product of an electrode reaction (e.g., reduction of a lactone to an alcohol or oxidation of a sulfide to a sulfoxide). Highly ordered pyrolytic graphite (HOPG) has been used to assess the influence of edge surfaces vs. basal surfaces (13A). As would be anticipated, the edge surface is more easily oxidized and therefore can accommodate more amide-linked modifier. Lennox and Murray have reported on the use of amidization to link an electroactive substance to a glassy carbon electrode (14A). Tetra(p-aminophenyl)porphyrin was found to exhibit reversible electrochemical properties when bonded. It was demonstrated that Co(II) could be inserted in the attached porphyrin and that the Co(II) metalloporphyrin electrochemistry closely parallels that for unbound complex. A number of electrocatalytic applications of CME's with attached ligands are now likely to be feasible.

The most common approach to CME preparation was originally reported by Royce Murray's team at the University of North Carolina (1A). Surface hydroxyl groups are silylated to form rugged surface–O–Si–C–R linkage. The stoichiometry of the bound entity depends on the silylation reagent, the original surface state, and the reaction conditions. As many

as three surface oxygens may be bound to a single silicon atom. Firth and Miller used this approach to prepare chiral dimensionally stable anodes (DSA, containing tantalum and iridium oxides) and SnO_2 film electrodes (15A). The electrodes were reacted with α-aminopropyltriethoxysilane and the amide linkage was formed by reaction with (−)-camphoric anhydride in dry benzene. Osa and Fujihira used the same reagent to bond rhodamine B to SnO_2 or TiO_2 semiconductor surfaces (16A). A new electrochemical photocell was based on these electrodes abrogating the need for sensitizer in the electrolyte solution. Burt et al. used an analogous modifying reagent for SnO_2 surfaces with a sulfhydryl group substituted for the amine function and then used this handle for attachment of an iron–sulfur cluster $[Fe_4S_4(SR)_4]^{2-}$ (17A). These electrodes should prove to be useful models for the ferredoxins and related iron–sulfur proteins.

Murray's group has been busy preparing and characterizing all sorts of CME's. They describe the covalent attachment of dinitrophenylhydrazine and several organosilane reagents to graphite and glassy carbon electrodes (18A), binding of methylpyridinium to SnO_2 and TiO_2 electrodes (19A), nitrobenzamides to RuO_2 (20A) and Pt (21A). The latter paper may generate pangs of incredulity, but there is little doubt that alkylamine silanes can be covalently attached to PtO surface sites produced by anodization (+1.1 V vs. SCE in H_2SO_4). The silanized surface no longer exhibits the characteristic cathodic stripping peak for PtO reduction and is stable in nonaqueous solvents. Using 3-(2-aminoethylamino)-propyltrimethoxysilane as the modifying reagent followed by treatment with 3,5-dinitrobenzoyl chloride, a platinum electrode was produced with the following surface chemistry (where n = 1–3).
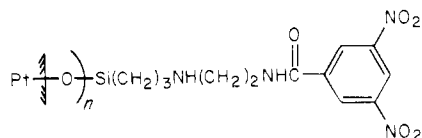
Cyclic voltammetric studies on the attached dinitrobenzamide in DMSO revealed excellent reversible behavior not unlike that for a solution of n-butyl-3,5-dinitrobenzamide at an unmodified Pt surface. It is not difficult to appreciate why these results are cause for thunderous applause!

Kuwana's group at Ohio State have long been in pursuit of ways to encourage biological electron transport components to rapidly exchange electrons with electrode surfaces. The CME may well hold the answer and the Buckeye group has been in rapid pursuit. Armstrong et al. report on the electrochemical and surface characteristics of bare and silanized SnO_2 and In_2O_3 thin film electrodes (22A). Current–potential, charge–potential, and surface conductance–potential data have been correlated with scanning electron microscopy, x-ray fluorescence, Auger, and x-ray photoelectron spectroscopy. More recently Lin et al. have described a new bonding approach based on the reactions of cyanuric chloride (trichloro-s-triazine) with both graphite and metal oxide electrodes to form an ether linkage which is stable in both organic and aqueous media (pH 3–7) (23A). Hydroxymethylferrocene was attached to the modified surfaces which were then characterized by cyclic voltammetry, differential pulse voltammetry, and x-ray photoelectron spectroscopy. As an alternate to high temperature air oxidation, Evans and Kuwana recommend treatment of graphite with a radiofrequency oxygen plasma in order to introduce oxygen-containing groups as points of attachment for covalent surface modification (24A). In a previous series, Evans et al. demonstrated electrocatalysis of solution species using CME's (25A).

Many of the papers mentioned above utilize a number of techniques to characterize CME surfaces. In addition, sheet resistivity measurements have been advocated using a four-point probe (26A), inelastic electron tunneling spectroscopy (IETS) has been proposed as a means for obtaining vibrational information on silylated surfaces (27A), and capacitance and electron spectroscopy has been used to study amidized carbon CME's (28A). Jeanmaire and Van Duyne have reported on an extensive investigation of amines adsorbed on silver using normal and resonance Raman spectroelectrochemistry (29A). In our view, this approach can provide much more detailed molecular information about

CME's than has been obtained with the various electron spectroscopies. It looks easy, therefore we predict extensive applications of Raman to CME work in the near future.

An intriguing family of chemically modified electrodes has been fathered by Santhanam, Jespersen, and Bard who recently described a "thermistor mercury electrode with adsorbed enzyme" (30A). Enzyme adsorbed on mercury (urease and alcohol dehydrogenase) was found to maintain its catalytic activity. Using a small mercury electrode covering a thermistor, it is possible to monitor temperature changes accompanying conversion of substrate and also to control the electrode potential. A number of fundamental as well as analytical possibilities exist. The use of an enzyme as a heterogeneous electrocatalyst is an accomplishment of the first order and therefore wins the "greatest thing since sliced bread" award of 1976–1977.

HYDRODYNAMIC TECHNIQUES

The advantages of electrochemistry in flowing streams and at rotating electrodes have been long recognized. Nevertheless, it was not too long ago that amperometric titrations represented the only well recognized application of hydrodynamic voltammetry to the practicing analytical chemist. In the recent past we have seen a burgeoning of various amperometric devices for gas analysis, trace metal determinations, chromatographic detection, enzyme activity measurements, and so forth. The use of hydrodynamic mass transport for fundamental studies is also increasing in popularity although it remains true that relatively few electroanalytical chemists have ever used a rotating disk (RDE) or ring-disk electrode (RRDE). Now that this field has reached both an experimental and theoretical maturity, it is appropriate to expect more widespread application to chemical problem solving. Stan Bruckenstein and Barry Miller have presented a brief but lucid review on "Unraveling Reactions with Rotating Electrodes" (1B). The authors review fundamentals and then illustrate, by example, how modern concepts of rotating electrodes can be applied to mechanism studies of both heterogeneous and homogeneous reactions. It is unfortunate that some attention could not be devoted to organic reactions, although relatively little literature exists in this area. Among the more adventuresome applications of the RRDE was the one described by Memming who developed an electrode with a semiconductor disk and a platinum ring (2B). The new electrode was used for study of photoinduced charge transfer processes at the semiconductor. Attention was focused on the anodic dissolution of the semiconductor which can occur in these photoelectrochemical systems rather than the more desirable oxygen evolution. A number of applications of the RDE and RRDE to stripping voltammetry have been reported and these are described in the following section. Hydrodynamic mass transport is also becoming an important tool in spectroelectrochemical experiments, particularly those involving biological electron transport components. Phillips et al. described a new RRDE for use in molten salts (3B) and Fischer and Brasme developed a seal for the use of rotating electrodes in a cell with a controlled atmosphere (4B).

Ten years ago flow-through electrochemical cells were a rare laboratory curiosity. In the present day they have achieved some importance in laboratory and commercial electrosynthesis; liquid and gas chromatographic detection; and determination of redox enzyme activity, substrates, and cofactors.

The electrosynthesis area is outside the scope of the present review; however, two papers will be mentioned because of their possible relevance to analytical applications. Fleet and Das Gupta briefly described a reactor based on packed vitreous carbon fibers of 5–10 μm diameter which is noteworthy in the favorable electrode surface area per unit volume, good potential range, and uniform potential control (5B). Clark and Evans reported on a more traditional reactor based on a bed of glassy carbon particles in a porous Vycor tube (51D).

Tubular electrodes continue to be attractive for a variety of applications and now may be considered to be at the mature stage of both theoretical and experimental development. Stulik and Hora have described a new Teflon flow cell containing tubular platinum electrodes (6B). They advocate "cleaning" the surface by periodic application of short potential pulses during the course of prolonged studies at a fixed potential. Coles et al. developed a novel five-electrode system

for control of the working electrode potential in closed loop flowing systems (7B). It is suggested that this new approach will permit the study of rapid heterogeneous reactions with tubular electrodes operated at high velocities, where ohmic potential losses have been a problem in the past. Blaedel and Schieffer have examined the ferricyanide/ferrocyanide couple under a variety of conditions using both rotating and tubular electrodes (8B). Particular attention was paid to the influence of electrode material. Platinum, gold, glassy carbon, carbon film, and boron carbide electrodes were examined. The concept of pulsing or sinusoidally oscillating a convective flux to an electrode has some advantages as pointed out by Miller and Bruckenstein for the rotating disk electrode (1A). Blaedel and Iverson now suggest that pulsed flow provides improved sensitivity for tubular electrodes when the difference between the steady-state currents at each of two flow rates is plotted versus concentration (9B). Excellent performance was obtained at the micromolar level for a ferricyanide test solution.

Thin-layer flow cells have been extensively used in chromatographic detection under amperometric conditions with relatively low conversion efficiency. Siegenthaler and Schmidt recently developed a coulometric thin-layer flow cell (thickness $<10^{-2}$ cm) which they operate at very low volume flow rates (10^{-5}–10^{-3} cm^3/s) (10B). Since the cell is capable of detecting picomole amounts of material, it was useful for measurement of adsorption isotherms (10B) and for determination of trace concentrations of metal ions (11B).

Electrochemical detectors for chromatography continue to be developed, although many applications are now routine. Although interesting gas chromatography applications have been reported, such as the detection of H$_2$S at the part-per-billion level (12B), by far the greatest progress has been made in liquid phase systems. Amperometric and coulometric detectors for liquid chromatography have been reviewed (1A, 13B). Blank has described an inexpensive dual electrode amperometric system based on thin-layer carbon paste electrodes (14B) while Buchta and Papa reported on use of an amalgamated Pt wire electrode (15B) as an alternate to use of a mercury pool (16B) for detection of reducible compounds (15B) or those which oxidize to form mercury complexes, such as glutathione (16B). Lankelma and Poppe have characterized a coulometric detector using a large planar glassy carbon electrode in a thin channel of electrolyte (17B). The usefulness of this cell was demonstrated by application to the determination of phenothiazine drugs in blood by reverse phase liquid chromatography (18B). Electrochemical detection is not well suited to normal phase chromatography due to the fact that the mobile phase is often not sufficiently polar to support the ionic strength necessary to maintain good potential control. Lemar and Porthault have attacked this problem by designing a cell with provision for mixing a polar nonaqueous electrolyte solution with the column effluent upstream from a glassy carbon electrode (19B).

Thin-layer amperometric detectors have been used for a wide variety of practical purposes from the examination of cockroach infestation in cereal products (20B) to the study of phenolic components in beer (21B) and β-cetotetrine in plasma and urine (22B). Aromatic amines are particularly well suited to amperometric detection at graphite electrodes and several important examples of this wisdom have now been published (23B, 24B). Tyrosine metabolism continues to be an important focus in the development of LC/EC techniques. Among the many noteworthy papers published in the past two years, those devoted to study of the metanephrines (25B) and catecholamines (26B) in urine are mentioned because they illustrate the significant symbiosis of amperometric detection and reverse-phase microparticle chromatography (27B). Chemically bonded silica-based stationary phases can be tailored to permit separation of almost anything with spectacular efficiency, but without recourse to nonpolar mobile phases.

Swartzfager demonstrated the use of potential–pulse current–sampling methodology to improve the selectivity of LC/EC for compounds which react at a higher potential than other components which have not been separated by the chromatograph (13B, 28B). Freed and Asmus developed a modification for a commercial LC/EC detector cell to permit collection of fractions (30B). A small silver tube was used as a low volume silver–silver chloride reference through which the eluted zo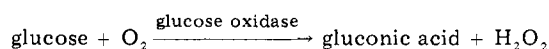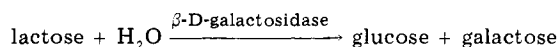nes could pass. Several publications have described systems in which the chromatographic separation process is achieved with a packed bed of conducting particles which serve as an electrode. Fujinaga and Kihara review the principles and various experimental approaches whereby differential migration of metal ions can be accomplished when an injected sample is passed through a glassy carbon bed with an axial potential gradient (30B).

As noted in the previous review (1A), one of the potentially most rewarding areas of investigation for hydrodynamic electrochemical techniques involves the coupling of redox enzymes to amperometric sensors. In most such experiments, convection is used primarily for transport of the sample (as in tubular electrodes) and for mixing of reagents (as for membrane electrodes in stirred solution). While important, the hydrodynamics are rarely varied during the course of an experiment and it is fair to say that other factors are more often the source of difficulty. A great many papers have been published in this area over the past two years and only a selected few will be reviewed here.

Gary Christian's group at the University of Washington has been catalyzed into a frenzy of activity by a variety of enzymes. They have explored the use of carbon electrodes to monitor ferrocyanide and NADH at carbon electrodes. The latter may be a handle for following many enzymatic reactions; however, its electrochemistry is often unfavorable due to slow kinetics. Ferrocyanide can be generated by reduction of ferricyanide by NADH in homogeneous solution. The reaction is not fast, but can be sufficiently rapid for analytical purposes, and ferrocyanide is more suitable than NADH for direct amperometry because of its faster kinetics and chemical reversibility. Thomas and Christian used these features to advantage in a method for serum lactate dehydrogenase (LDH) (31B). The same authors have also explored a number of factors related to the successful use of amperometric oxygen electrodes for measurement of enzyme catalyzed reactions (32B). Oxygen electrodes can be coupled to NADH by various peroxidases which catalyze the aerobic oxidation of NADH (33B).

$$2NADH + O_2 + 2H^+ \xrightarrow{\text{peroxidase}} 2NAD^+ + 2H_2O$$
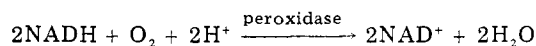
When oxygen is used as the electrochemical "handle" on an enzyme reaction Clark-type membrane electrodes can be used. Thus the electrode is isolated from the biological milieu by a hydrophobic membrane and rendered more reliable for continuous use. Advantage can be taken of a number of enzymes to accomplish the necessary involvement of oxygen. For example, lactose concentration in foods can be indirectly determined by measuring the rate of oxygen consumption in the following reaction sequence (34B):

$$\text{lactose} + H_2O \xrightarrow{\beta\text{-D-galactosidase}} \text{glucose} + \text{galactose}$$

$$\text{glucose} + O_2 \xrightarrow{\text{glucose oxidase}} \text{gluconic acid} + H_2O_2$$

The H$_2$O$_2$ was catalytically reduced to water by I$^-$ and ethanol to prevent disproportionation and regeneration of oxygen. An analogous method for maltose in foods is based upon the hydrolysis of maltose to glucose by α-glucosidase (35B). Serum alkaline phosphatase activity was measured by using tyrosinase to aerobically oxidize phenol (released from phenolphosphate) to o-quinone (36B).

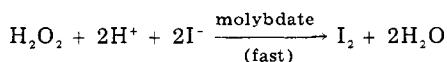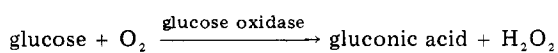$$\text{phenol} + O_2 \xrightarrow{\text{tyrosinase}} o\text{-quinone} + H_2O$$
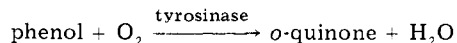
In yet another example, total serum cholesterol was determined by measuring oxygen consumption by the cholesterol oxidase reaction following saponification (37B).

Guilbault et al. have also described an amperometric approach to cholesterol oxidase (38B). A unique rotating porous cell was designed to hold immobilized cholesterol esterase and cholesterol oxidase and a platinum electrode at +0.60 V vs. SCE was used to monitor the hydrogen peroxide released.

Wallace and Coughlin explored the use of amperometry for assay of the activity of aqueous solutions of lactate dehydrogenase, alcohol dehydrogenase, and malate dehydrogenase (39B). They used a bare platinum electrode at high pH to monitor NADH produced in a stirred incubation mixture. We all have our opinions and it is mine (PTK) that this approach will not be viable for useful clinical methods.

Blaedel and Jenkins have gone all-out to prepare a "reagentless" electrode for lactate (40B). They used two approaches. In one scheme, a complex of LDH and NAD was bound to a celluose membrane via glutaraldehyde and, in the other, a mixture of the enzyme and agarose-bound NAD was trapped in a thin-layer between a glassy carbon electrode and a cellulose membrane which would permit transport of lactate (in) and pyruvate (out) while retaining the enzyme and co-enzyme. The latter system was found to be advantageous for several reasons. It provided greater stability and also the agarose-bound NADH (a product of the LDH catalyzed oxidation) could be electrochemically recycled to the NAD form with greater facility than could the glutaraldehyde-bound coenzyme. In principal, an electrode of this type could be used indefinitely without need for either additional enzyme or coenzyme and would therefore be "reagentless" as advertised. There are a number of experimental difficulties; however, the concept is sound and we can expect to hear more from the busy Badgers at Wisconsin.

George Wilson's group has reported on a novel "rotating ring disk enzyme electrode" in which an enzyme is chemically bound to the disk surface and a bare Pt ring is used (41B, 42B). Glucose oxidase was bound to a carbon paste disk. The carbon paste was formulated from mineral oil and graphite powder with the addition of n-octadecylamine. Exposed amine groups on the surface were linked to glucose oxidase using a combination glutaraldehyde and bovine serum albumin to form imine bridges to the enzyme. The following sequence of events was studied at both the disk and ring electrodes with I_2 providing the amperometric handle:

$$glucose + O_2 \xrightarrow{\text{glucose oxidase}} gluconic\ acid + H_2O_2$$

$$H_2O_2 + 2H^+ + 2I^- \xrightarrow[\text{(fast)}]{\text{molybdate}} I_2 + 2H_2O$$

The ring-disk approach to amperometric enzyme studies provides a number of advantages. In addition, the authors have developed a rather novel and quite straightforward approach to preparation of chemically modified electrodes which will be useful for a variety of other purposes (see previous section). Once again the carbon paste electrode is vindicated and outlives the shouts of its most virulent critics.

Mell and Maloy have used the same model reactions as Wilson to evaluate experimentally and theoretically the advantages of operating a glucose oxidase amperometric membrane electrode in the pulse rather than steady-state mode (43B). In this case, the reaction is allowed to proceed within the membrane phase and I_2 is detected periodically by application of a potential pulse. The waiting period between pulses permits the I_2 concentration to rise and a significant enhancement of sensitivity is achieved. Both chronoamperometric and chronocoulometric experiments were carried out and analyzed by detailed finite difference simulations.

STRIPPING VOLTAMMETRY

The remarkable sensitivity of stripping voltammetry together with the capability for multielement analysis has stimulated significant activity in method development and applications of this versatile electrochemical technique. The book "Electrochemical Stripping Analysis" by Vydra, Stulik, and Julakova combines a useful description of techniques with a comprehensive survey of applications according to element (1C). The stripping analysis of macro- and microsubstances has been reviewed (2C). Cahill and Van Loon compared some of the features and problems of trace analysis by anodic stripping voltammetry (ASV) and atomic absorption spectroscopy (3C).

Various electrodes have been evaluated for use in stripping voltammetry. The search continues for improved substrates for the frequently used mercury film electrode (MFE). Graphite-epoxy (4C) and radiation-cured polymer impregnated graphite (5C) have proved suitable for MFE substrates. Stojek et al. evaluated graphite based thin MFE's prepared in situ (6C) and silver based MFE's (7C, 8C). Vydra has reviewed stripping analysis with the glassy carbon rotating disk electrode (9C). In the area of solid electrodes, graphite cloth was evaluated as a porous electrode for use in flow-through systems (10C). A carbon pyroceramic material was used in a determination of lead by stripping chronopotentiometry, voltammetry, and coulometry (11C, 12C).

With regard to the hanging mercury drop electrode (HMDE), Moorhead and Doub studied the diffusion of electrodeposited cadmium into the mercury thread leading to the mercury drop (13C). By integrating anodic dc stripping currents for successive sweeps on a single drop following one deposition period, and for successively extruded drops following one deposition, they found that less than 0.1% of the deposited cadmium was lost into the drop-thread.

Several new ideas in cells have been reported. The feasibility of combining the excellent analytical sensitivity of differential pulse ASV with the small volume capabilities of the thin-layer cell was demonstrated by Heineman et al. (14C, 15C). A microcell with a rotating mercury-plated glassy carbon electrode has been used in conjunction with anodic stripping coulometry (16C). Magjer and Branica developed a cell in which mass transport of electroactive species to the electrode during deposition was achieved by a conically perforated vibrating disk (17C). Stulik and Bedros designed cells which permit ion-exchange or solvent extraction separation simultaneously with the deposition step (18C). A variety of other cells have been reported including a rotating cell with a stationary electrode (19C), a small volume polyethylene cell (20C), and a multiple cell system for more rapid analyses (21C).

Several researchers have explored the potentialities of combining ASV with flow-through cells. Wang and Ariel obtained high sensitivity and excellent precision with a flow-through cell containing an MFE with glassy carbon substrate (22C). Schieffer and Blaedel reported on a twin tubular electrode flow cell for ASV with collection (23C). Andrews and Johnson determined Se(IV) in chromatographic effluent by ASV at a flow-through tubular gold electrode (24C). Igolinskii and Zheleznyak obtained good results for cadmium and zinc with continuous- and pulsed-flow thin-layer cells containing a mercury-coated gold electrode (25C).

Osteryoung et al. have investigated staircase voltammetric stripping from the thin mercury film electrode (26C, 27C). The sensitivity of the method is comparable to that of differential pulse voltammetric stripping. However, the staircase technique is much faster, requiring less than 2 seconds as compared to several minutes for differential pulse. The advantages of square-wave ASV for fast analysis and discrimination against charging currents was evaluated on a computer-controlled data acquisition system (28C). Several papers have discussed strategies for optimizing the performance of ASV. Valenta et al. considered the influence of a variety of voltammetric parameters on differential pulse ASV at the MFE (29C). A new version of the standard addition approach which circumvents exceeding the limited solubility of metals such as Cu in the MFE was demonstrated. Computer-assisted optimization of ASV to provide specified signal-to-noise and signal-to-background ratios with a minimum analysis time has been explored (30C). Bond and Grabaric minimized the problem of overlapping stripping waves with a microprocessor-controlled instrument (31C). Matson et al. discussed the optimization of conditions for ASV with a programmable instrument (32C).

Seelig and Blount evaluated the real-time digital optimization technique known as the Kalman filter for its ability to return optimal values of analyte concentration from noise corrupted synthetic data for ASV (33C).

An inherent difficulty with ASV is the formation of intermetallic compounds between metals deposited in the mercury electrode. Shuman and Woodward found that several Cu-Zn intermetallic compounds form during ASV analysis of solutions containing both Cu and Zn (34C). Ostapczuk and Kublik confirmed formation of the intermetallic compounds AuCd, Au_3Cd, AuZn, and CuAu in mercury, although they found no evidence for previously reported compounds between Ag and Cd, Ag and Zn, and Cu and Cd (35C). They also found that Ag exerts a catalytic effect on the reduction of NO_3^- giving rise to an anodic peak which was formerly interpreted as evidence for the formation of AgZn and AgCd intermetallic compounds (36C). Gumunski and Galus studied the AuZn intermetallic compound by a variety of techniques at a hanging gold amalgam drop electrode (37C). Heineman et al. demonstrated the elimination of interferences due to the Cu-Zn intermetallic compound by using a twin-electrode thin-layer

cell in which Cu and Zn are exhaustively deposited on separate mercury film electrodes with independent potential control (15C).

Dissolved organic material can also adversely affect stripping voltammetry. Batley and Florence studied the influence of dissolved organics on ASV and CSV analysis of seawater (38C). The effect of sorption by natural and model organic compounds on trace metal analysis has also been reported (39C). Effects included depressed peak currents, positively shifted peak potentials, and broader peaks.

Nghi and Vydra have investigated the stripping voltammetric determination of metals in aqueous and nonaqueous media after solvent extraction to improve selectivity. This approach has been evaluated on bismuth (40C), lead (41C), and tin (42C).

An important feature of stripping voltammetry is its potential for the chemical speciation of trace metals in natural waters. This capability for differentiating among free and bound forms of a metal ion has been discussed in several articles dealing with the general applicability of voltammetry to marine and aquatic chemistry (43C–45C). Batley and Florence found the major proportion of Cd, Pb, and Zn in seawater to be associated with organic and inorganic colloidal species (46C, 47C). They have devised a scheme for the classification of heavy metal species in natural waters (48C). The method is based on the ASV measurement of labile and total metal in variously treated samples. Duinker and Kramer studied the speciation of dissolved Zn, Cd, Pb and Cu in Rhine River and North Sea water (49C). They also investigated the complexing capacity of dissolved organic material. Branica et al. applied ASV to determining the state of complexation of metal ions at low concentration levels (50C). O'Shea and Mancy characterized trace metal–organic interactions by titrating solutions of metal ions with organic ligands and vice versa in a system chosen to simulate natural water systems (51C). Monitoring the titrations by ASV permitted differentiation of free metal from labile and nonlabile metal complexes. ASV was used to determine stability constants of hydroxo and carbonato complexes of lead, copper, and cadmium at concentration conditions which approximate those of natural water (52C).

The analysis of seawater for copper, lead, cadmium, and zinc by ASV continues to be studied (43C, 53C–55C). The determination of mercury in seawater by ASV with a graphite electrode (56C) and twin gold rotating disk electrodes operating in the subtractive mode (57C) has been reported. Trace mercury(II) has also been determined in 0.1 M perchloric acid at a rotating gold disk electrode (58C).

Several articles have dealt with the determination of metals in biological samples, especially lead in blood (15C, 59C–64C).

Numerous applications of ASV have appeared in the past two years. Some typical determinations include cadmium in the presence of humic acid (65C), cadmium in alloy steels (66C), copper in silicon (67C), copper in thiocyanate media (68C), gallium in thiocyanate media at 60 °C (69C), gold(III) in the presence of iron(III) (70C), lead and antimony in firearm discharge residues on hands (71C), lead using second-harmonic alternating voltammetry (72C), lead and cadmium in pottery (73C), lead in 2-hydroxyethyliminodiacetic acid solutions (74C), ruthenium (75C), zinc in acidic media (76C), and trace elements in zinc plant electrolyte (77C). Automated differential pulse ASV was used to investigate the problem of dilute solution storage (78C).

The applicability of stripping voltammetry continues to expand into the realm of organic analysis by means of cathodic stripping voltammetry (CSV). Typical determinations by CSV include thioamide drugs in biological fluids (79C), water-soluble mercaptans by phase-selective CSV (80C), thiourea-containing pesticides (81C), and sulfide and thiols in the presence of vitamin B_{12a} (82C). The determination of inorganics by CSV continues to be explored. Selenium (83C, 84C) and iodine (85C) have both been determined at the ppb level. Laitinen and Watkins have studied the cathodic stripping of PbO_2 on tin oxide electrodes (86C). Halides have been determined (87C) including bromide and chloride in airborne particulate matter (88C).

SPECTROELECTROCHEMISTRY

Activity in spectroelectrochemistry continues to expand as more spectral information is acquired in conjunction with electrochemical experiments. New methodology in transparent electrodes, cells, and spectroelectrochemical techniques has been developed and applied to a variety of chemical systems.

Kuwana and Heineman recently reviewed spectroelectrochemistry involving the optically transparent electrode, OTE (1D). New developments in OTE's involve carbon and mercury. A carbon OTE prepared by vapor depositing a thin film of carbon onto a glass or quartz substrate has been evaluated (2D). The electrode properties are similar to those of a conventional graphite electrode with a higher resistance due to the thin film required to retain good optical transparency. This carbon OTE served as a substrate for deposition of a thin mercury film to form a mercury OTE. Such a mercury OTE was shown to be useful for investigating oxidation waves (e.g., for cysteine) which involve oxidation of the mercury electrode rather than of the solution species. Scanning the potential into the oxidation wave gives an increasing transparency of the OTE due to loss of mercury. Gold minigrids continue to be the most popular OTE's used in optically transparent thin-layer cells. The negative potential range can be extended by electrochemically depositing a thin film of mercury on the gold minigrid (3D). Norvell and Mamantov obtained good electrochemical and optical properties on an OTE consisting of reticulated vitreous carbon (4D). The transparency of this intriguing material is due to its porosity. In the area of rotating electrodes, a semitransparent rotating disk electrode facilitated photochemical generation of species close to the electrode surface (5D).

A variety of spectroelectrochemical cells have been reported in the past two years. Hawkridge et al. constructed a small-volume cell from a machinable glass-ceramic for use with nonaqueous solvents (6D). Anderson's cell enables the anaerobic transfer of biological samples for low temperature EPR measurements (7D). A cell in which the optical path length can be varied by the position of a light pipe is useful for spectroelectrochemical kinetic measurements on appreciably absorbing solutions (8D). Small-volume thin-layer cells which can be maintained anaerobic have been developed for the study of biological redox components (9D, 10D). A flow cell has been used for the identification of unstable compounds by simultaneous electrochemical and spectrophotometric measurements (11D).

The ease with which spectroscopic techniques can be combined with the rapid electrolysis feature of thin-layer electrochemistry has stimulated activity in the development and application of optically transparent thin-layer electrode (OTTLE) techniques. Several papers have shown thin-layer spectroelectrochemistry to be a viable kinetic technique for monitoring slow homogenous reactions coupled to electrode processes. The reactive species is quantitatively generated within about 20 s in the thin solution layer by a potential step, and the subsequent chemical reaction is monitored spectroscopically. Owens and Dryhurst used this approach to monitor the reaction of an electrogenerated diimine with water (12D). McCreery showed how faster reactions can be slowed into the thin-layer time window by using potential control to adjust the oxidized/reduced ratio of the reactive species (13D). The method was applied to the hydrolysis of electrogenerated p-quinoneimine. The thin-layer approach complements other electrochemical kinetic methods by allowing slower reactions to be studied. This was nicely demonstrated by Mark et al. with the very slow homogeneous oxidation of electrogenerated Cob(I)alamins (14D, 15D).

The thin-layer spectropotentiostatic technique has seen increasing application to the measurement of spectra and redox potentials of metal complexes and biological redox components. In this experiment, the redox component is incrementally converted from one redox state to another by a series of applied potentials. Each potential is maintained until an equilibrium ratio of oxidized/reduced is achieved and a spectrum is recorded. A Nernst plot from the potentials and corresponding spectra gives accurate values for reduction potentials and n values. The capabilities of this technique were illustrated for a cobalt and copper schiff base complex in dimethylformamide (16D) and for the water soluble tetrakis(4-N-methylpyridyl)porphinecobalt(III) (17D). The technique has proved to be especially useful in the study of vitamin B_{12} (18D, 19D). In this case, the first one-electron step for reduction is unusually slow and consequently not

observed by most voltammetric techniques. However, this wave is observable by the spectropotentiostatic technique in which each potential is maintained until equilibrium is reached. Murray et al. used the OTTLE to obtain spectra in a study of 1,8-dihydroxyanthraquinone and anthraquinone anion radicals in dimethylformamide (20D). Hawkridge et al. used the technique to study a surface modified gold minigrid (7A). A laboratory experiment has been developed for teaching thin-layer spectroelectrochemical techniques to students (21D).

Biocomponents which exchange electrons very slowly with electrodes can be studied via the spectropotentiostatic technique by adding a mediator-titrant to couple the biocomponent to the electrode. Hawkridge and Ke have used this approach to study photosynthetic electron-transport components by light-induced absorption changes, fluorescence yield changes, and circular dichroism (10D). Kreishman et al. used the precision inherent in this method to observe a biphasic behavior in the temperature dependence of the redox potential of cytochrome c (22D).

The indirect coulometric titration with optical monitoring of biocomponents as developed in Kuwana's laboratory has been applied to the measurement of the $E^{0'}$ values of the two copper atoms in cytochrome c oxidase in the presence of CO (23D). Since the two copper atoms were not observed optically, the redox potentials were determined by their influence on the shape of absorbance–charge plots obtained by optically monitoring the two heme irons during reduction and oxidation. This study clearly demonstrates the unusual capabilities of this technique—the spectroelectrochemical measurement of a redox component which is not electroactive and not observed optically. Kuwana et al. have reported a comprehensive evaluation of mediator-titrants, an important feature of both the indirect coulometric titration and the thin-layer spectropotentiostatic technique (24D). The indirect coulometric technique has also been used to measure fluorescence yields of photosystem (II) in the photosynthesis mechanism (25D). Hendler et al. have reported a coulometric technique for performing potentiometric titrations (26D, 27D).

The spectroelectrochemical techniques for the study of rapid homogeneous chemical reactions coupled to electrode processes have seen further development and application. Van Duyne, Ridgway, and Reilley have developed the theory of double-potential step spectroelectrochemistry for the first-order, one-half regeneration mechanism and for first-order E.C. processes with product and reactant adsorption (28D, 29D). Mackey and Kuwana investigated the rates of electron transfer between electrogenerated species and the heme proteins, cytochrome c and cytochrome c oxidase (30D). Problems associated with the spectroelectrochemical method when applied to fast rates involving slowly-diffusing macromolecules were discussed. Blount and Evans have studied reactions of cation radicals of EE systems by a combination of spectroelectrochemistry and stopped-flow kinetics with electrogenerated reactants (31D–33D). Yacynych and Mark used a rapid scanning spectrometer to investigate the oxidation of 1,2-diaminobenzene, alone and in the presence of Ni(II) (34D). Steckhan has studied the mechanism of olefin oxidations (35D, 36D). Spectra of short-lived intermediates were obtained using a computer controlled rapid scanning spectrometer. The reduction of nitrobenzene and substituted benzaldehydes in sulfolane were studied by transmission spectroelectrochemistry (37D, 38D).

The capabilities for obtaining high resolution vibrational spectra by resonance Raman for electrogenerated intermediates and products continue to be demonstrated in Van Duyne's laboratory (39D–41D). Resonance Raman spectra have been obtained for the electrogenerated dianion of naphthacene (42D). The remarkable sensitivity of Raman spectroscopy for adsorbed heterocyclic, aromatic, and aliphatic amines on silver electrodes suggests that this technique will become extremely powerful in the study of adsorption (43D–45D). High resolution spectra of adsorbed species and millisecond time response to potential changes have been reported (44D). Surface phenomena at platinum (46D, 47D), copper (48D), and lead (49D) electrodes have been investigated. Fujihira and Osa have observed adsorbed dye layers by internal reflection resonance Raman spectroscopy (50D).

Some spectroelectrochemistry in the infrared region has been reported. Clark and Evans used a porous bed of glassy carbon particles as a flow cell to generate quinone radical anions and dianions (51D). The electrolyzed solution passed into an infrared cell for optical measurements. Mattson and Jones used infrared internal reflection spectroscopy to observe the adsorption of fibrinogen at an OTE consisting of a thin carbon film on germanium (52D).

Electron spin resonance spectroscopy continues to be used for characterizing electrogenerated organic radicals and metal complexes. This important aspect of spectroelectrochemistry was recently reviewed by McKinney (53D).

Reflection techniques for studying the interfacial region has been reviewed by Parsons (54D), Blondeau and Yeager (55D), and Muller (56D). Representative studies with ellipsometry include the adsorption of quinoline (57D) and DNA (58D) at mercury and the oxidation of nickel electrodes (59D). Typical studies using reflectance spectroscopy are the electroreflectance at lead electrodes (60D), the adsorption of water at mercury (61D), the electroreflectance of single crystal silver (62D), and the oxidation of cuprous sulfide (63D). Gottesfeld et al. have used combined ellipsometric and reflectometric measurements of surface processes on gold, platinum, and palladium electrodes (64D).

Emission Mössbauer spectroscopy has been used for in-situ studies of the passivation and oxidation of cobalt electrodes (65D).

The use of x-ray photoelectron spectroscopy (XPS, ESCA) and Auger spectroscopy to characterize electrode surfaces has increased dramatically. Winogard et al. have used both techniques to study the oxidation of platinum electrodes in sulfuric and perchloric acids (66D) and to study the underpotential deposition of silver and copper on platinum electrodes (67D, 68D). Murray et al. have made extensive use of ESCA in characterizing their chemically modified electrodes, vida supra. Kuwana et al. have employed both ESCA and Auger to study tin and indium metal foil and oxide electrodes (69D, 70D) and plasma etched pyrolytic graphite electrodes (71D). Schoeffel and Hubbard used thin-layer coulometry for calibration in an Auger study of substituted hydrocarbon monolayers on platinum (72D).

Thin-layer electrochemistry was combined with low-energy electron diffraction by Ishikawa and Hubbard to study the relationship between electrochemical reactivity of platinum and the electrode surface structure with an adsorbed layer of electrolyte (73D).

The electrodeposition of metals on graphite electrodes has been used as a preconcentration step to enhance sensitivities in analysis by atomic absorption spectrometry (74D–76D), energy dispersive x-ray fluorescence spectrometry (76D), and counting α radioactivity (78D).

MISCELLANY

The media in which electrochemical reactions are performed was the subject of considerable innovation a decade ago; however, there remains little activity in terms of new solvent–electrolyte systems. Detailed reviews with recommendations for the purification of sulfolane (1E) and dimethylformamide (2E) have been reported. Voltammetric half-wave potentials have also been reported for these same two solvents (3E, 4E). Collecting reference data of this sort is clearly not the most exciting research; however, more effort in this direction is sorely needed for both fundamental and analytical purposes. Fawcett and Caton have made a detailed analysis of the errors encountered in the capillary method for determining diffusion coefficients (5E). Reliable reference data on diffusion coefficients of electroactive substances in various media is another area deserving more attention. The accuracy of available data is often outside the capability of modern electrochemical instrumentation and can be limiting in some experiments. As described in previous reviews, more attention should be placed on the electrochemistry of various solvents and electrolytes per se. These reactions are commonly participants in the mechanisms of the electrochemical conversion of numerous substances which oxidize or reduce near the background limits of the supporting medium. Sawyer et al., for example, have applied a number of techniques (a style worth imitating) to studies of the electrochemical oxidation of tetraethylammonium hydroxide in dimethyl sulfoxide (6E).

Davis described a straightforward approach to the electrochemical study of slightly soluble compounds (especially metalloporphyrins) involving evaporation of a film of the

compound on an electrode prior to immersion in the solvent of interest (7E). Yamaguchi and Tsukamoto studied a phenomenon which might eventually also aid in solubilizing uncooperative substances. They examined the influence of cyclodextrins on the polarographic reduction of p-nitrophenol and reported dissociation constants for the clathrate complex (8E). Yeh and Kuwana have been very successful at solubilizing ferrocene in aqueous phosphate buffer by use of a nonionic detergent (9E). Micelles entrapping ferrocene apparently can exchange electrons both with an electrode and with heme proteins. They therefore serve nicely as redox mediators for study of biological electron transport components. Franklin and Sidarous have used micelles and emulsions in preparative anodic oxidations of aromatic alcohols (10E). In this case, it was useful to enhance the solubility of reactant as a means to scale up the synthesis. In addition, the percent yield could be enhanced.

Electrochemical studies at low temperatures would seem to provide a number of advantages; however, such work is almost as rare as the Carolina Parakeet. Deming et al. did nice things with 1,4,8,11-tetraazacyclotetradecanemercury(II)$^{2+}$ which they oxidized to the mercury(III)$^{3+}$ complex in propionitrile at –78 °C (11E). They describe a low temperature electrolysis cell useful for both ESR and UV/visible spectroscopy. Nelson et al. have presented new information on the conformational analysis of cyclic tetraalkylhydrazines by low temperature cyclic voltammetry (12E).

There is nothing new about mercury pools; however, the area of such electrodes has never been clearly defined on a mathematical basis. Keith Oldham has developed a theoretical approach for the area and curvature of a mercury pool occupying a cylindrical vessel (13E). Another interesting report on mercury electrodes was prepared by Hanley and Peters who used an amalgamated platinum wire in a cylindrical thin-layer cell (14E). They were able to isolate products from microcoulometric experiments for examination by gas chromatography. Liquid–liquid extractions were carried out on microliter volumes using sealed melting-point capillaries. For example, 2–3 µL of diethylether and 10 µL of water could be partitioned with excellent precision!

Adams and the troops at the University of Kansas have continued to explore the use of microvoltammetric electrodes for in-vivo monitoring of neurochemical events. They have now demonstrated that it is possible to detect the dopamine (a neurotransmitter) metabolite homovanillic acid in cerebrospinal fluid following electrical stimulation of the nigrostriatal pathway (15E). Less esoteric perhaps, but equally stimulating, is "Doing Chemistry with Electrodes" which is the inevitable bottom line (16E).

ELECTROCHEMICAL NOMENCLATURE, FINITE CURRENT TECHNIQUES

Voltammetry. Finite current methods in which a current response is measured as a function of a potential waveform increasing in amplitude in a positive or negative direction. The waveform may be a ramp, a pulse train, a sine wave, or various combinations thereof.

Polarography. Voltammetric methods carried out using the dropping mercury electrode.

Hydrodynamic Voltammetry. Voltammetric techniques in which mass transport is controlled by convection as well as by diffusion, including stirred solution voltammetry and rotating disk voltammetry among others.

Amperometry. An electroanalytical approach in which current is measured at a fixed potential under conditions where the faradaic reaction is mass transport limited. The current may be constant (e.g., some amperometric oxygen or enzyme electrodes) or may vary as a function of time (e.g., chronoamperometry) and/or added reactant (e.g., amperometric titration).

Anodic Stripping. Techniques (usually voltammetric) in which an analyte is preconcentrated by reduction onto or into an electrode and is subsequently determined by electrochemical oxidation to form a soluble species.

Cathodic Stripping. Techniques (usually voltammetric) in which an analyte is preconcentrated by oxidation onto or into an electrode and is subsequently determined by electrochemical reduction to form a soluble species.

Differential Techniques. (Not subtractive). Require measurement of a difference between two signals either in-

stantaneously or separated by a fixed time period (as in differential pulse polarography).

Derivative Techniques. (Not differential). Those in which a rate of change is continuously measured.

Anodic Current. The rate of charge flow in a direction which results in oxidation of an electrode material or solution component.

Cathodic Current. The rate of charge flow in a direction which results in reduction of an electrode material or solution component.

Positive Potentials. (Not "anodic potential"). Potentials positive with respect to a specified reference electrode or redox couple.

Negative Potentials. (Not "cathodic potentials"). Potentials negative with respect to a specified reference electrode or redox couple.

Quasi-Infinite Diffusion Techniques. Methods in which a concentration gradient does not extend from an electrode to the walls of its container.

Restricted Diffusion Techniques. A concentration gradient extends from an electrode surface to the walls of the container or occurs in the pores of a packed bed electrode.

Thin-Layer Techniques. Restricted diffusion methods in which the concentration gradient exists perpendicular to parallel walls (two electrodes, or one electrode and a diffusion barrier).

Working Electrode. (Not "indicator" or "test" electrode). The electrode at which the reaction of interest takes place.

Auxiliary Electrode. (Not "counter" electrode). The electrode in three-electrode experiments which provides a current path in series with the solution and the working electrode. The potential of the auxiliary electrode is not controlled with respect to the reference electrode.

ACKNOWLEDGMENT

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