

Electroanalysis and coulometric analysis

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Electroanalysis and Coulometric Analysis

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THIS PAPER surveys the literature and developments during 1968 through December 1969; a few papers published before 1968 which have not appeared in previous reviews in this series have also been included.

BOOKS AND REVIEW ARTICLES

A number of books containing material of interest in electrochemical methods of analysis and basic principles of electrochemistry have appeared. Electrochemical methods in general are treated in Donbrow (71) and the English translation of Damaskin's monograph

(64). The book "Electrochemistry at Solid Electrodes" by Adams (2) critically and exhaustively reviews the principles of applying solid electrodes in electroanalytical methods, particularly with applications to the electrochemistry of organic substances in both aqueous and nonaqueous solutions. Two additional volumes in the monograph series "Electroanalytical Chemistry—A Series of Advances," have also appeared (28). Robin has edited a French language book on electrochemical methods (241); the chapter in it by Breant (40) reviews electrometric end-point methods and coulometric titrations. The monograph "Coulom-

etry in Analytical Chemistry" by Milner and Phillips (183) gives a brief introduction to coulometric methods and also includes reprints of many of the fundamental papers in the field.

Several reviews have been concerned with the application of coulometric methods to drug (163, 214), clinical and toxicological (234), and industrial (42) analysis. Reviews on electroanalysis have included discussions of coulometry and other electrolytic methods (1, 117, 273, 301, 306). Discussions of different methods of analysis of plutonium (253) and the noble metals (34) include evaluations of different electrochemical meth-

RECENT TRENDS

Trends in electroanalysis continue away from the older methods, such as electrogravimetric methods, and toward coulometric ones. Interest has continued in the application of electrochemical methods of different types to studies of organic systems. Electrochemical methods can indicate the presence of oxidizable and reducible groups, generate reactive intermediates, and even provide information about structure and energy levels in molecules. Coulometric methods are of special interest in electroorganic chemistry, since the amounts of material and time scale in these experiments approximates those in electrosynthesis. This renewed interest in electroorganic chemistry has led to several meetings and symposia devoted to the field, including one by the Faraday Society during April 1968 at Newcastle-upon-Tyne and one sponsored by the Army Research Office and held in Durham, N. C., in October 1968. Adams' recent book (2) also stresses applications to organic systems.

The decade began with increased application of operational amplifiers to electrochemical instrumentation; their use in potentiostats, coulometers, and waveform generators is now routine. The next decade will probably find increased application of digital instrumentation to electrochemical measurements, with completely automated coulometric analysis of several components just around the corner. The digital computer, which has been widely used for data treatment and computation for the past several years, will find increased application in electrochemical problems. The powerful technique of digital simulation [see (87) and references therein] has and will allow many complex mechanisms to be treated theoretically, for many electroanalytical techniques, even by scientists not conversant with advanced numerical methods.

ELECTROSEPARATIONS AND ELECTROGRAVIMETRY

Electrolytic Sample Dissolution and Preparation. Electrolytic methods have been shown to be useful in the dissolution of refractory metals, including Ta, Nb, W, Zr, V, Hf, Ti, and their alloys. In this method the metal sample is made the anode and a Pt or Ta cathode is employed (8). Electrodeposition methods continue to be useful in preparation of samples for spectroscopic techniques. Emission spectrographic techniques were used to determine traces of Ag on glassy-carbon (186) and traces of Rh on a rotating Cu disk (293). Samples of actinides for α -spectrometry have also been prepared by electrodeposition (32, 107). An interesting method has been proposed for

determining trace elements in Pt by separation on a cation exchange resin column and elution with HCl into an electrolysis cell. The elements Ag, Cu, Ni, Pb, and Pd are then deposited on a Au cathode and determined by spark source mass spectrometry (11).

Other Separations. Jones and Miere (131, 179) have described a novel electrogravimetric technique suitable for determination of traces of metals and based on electrodeposition on a Au-plated quartz crystal. The change in frequency of a crystal oscillator (nominally 3 MHz) following electrodeposition from solutions for 2 to 20 minutes was shown to be a linear function of concentration of the deposited metal (e.g., Cd). The main disadvantage of the technique appears to be the necessity of rinsing and drying the crystal before determination of the frequency. Increased attention has been paid to how

the electrical double layer structure parameters affect separations of metals (23, 24). Electrolytic methods continue to be useful in the preparation of very pure inorganic substances (263) or in the preparation of unusual oxidation states of metals, such as solutions of In(I) by anodization of In wire in HClO₄ media (278). Gosman (105) studied the homogeneous isotope exchange rate of Tl(I) and Tl(III) by simultaneous electrodeposition of Tl from both components in a solution containing ²⁰⁴Tl. Table I summarizes other work in electroseparations and electrogravimetric methods.

CONTROLLED POTENTIAL COULOMETRY

A summary of controlled potential coulometric determinations is given in Table II. The use of coulometric methods in the elucidation of electrode reac-

Table I. Electroseparations and Electrogravimetric Determinations

Separation of	From	Method	Reference
Ag, Cu	Pb, Zn	Electrodeposition of Ag or Cu from acidic solution on glassy-carbon electrodes	(185)
Ag, Cu	Cu, Co Ni	Application of complexing agents and double layer structure studies in controlled potential electrodeposition	(24)
Ag	Zn	Electrodeposition on glassy-carbon from HNO ₃ solutions	(186)
Am		Preparation of sources for α -spectrometry by electrodeposition from dimethylsulfoxide solutions	(107)
Ba, Ca, Sr		Controlled potential deposition on mercury electrodes	(256)
²¹⁰ Bi, ²¹⁰ Pb		Deposition by internal electrolysis using a lead electrode	(124)
Cs, Rb		Deposition from aqueous solutions on liquid gallium cathode	(223)
Cu, Co Ni, Fe	Nb, Ti	Deposition on Pt- or Cu-coated Pt prior to spectrophotometric analysis	(25)
Cu	Co, Ce, other metals	Investigations of optimum conditions for electrodeposition	(26, 69, 229)
Cu, Pb	Re	Electrodeposition on Pt from citrate-tartrate solutions prior to polarographic determination of Re	(196, 197)
In	Zn, Fe Ni, Cr	Electrodeposition on Pt electrode by internal electrolysis with a Zn anode	(307)
Mo	Fe, V	Electrodeposition on a mercury cathode	(99)
Mo	W	Electrodeposition on Pt electrode from (NH ₄) ₂ SO ₄ solution	(101)
Mo, Re		Application of EDTA solutions and internal electrolysis with Zn anode to electrodeposition on Pt electrode	(166)
Pb	Cu	Deposition of PbO ₂ from HNO ₃ solution at a vibrating Pt anode	(85)
Pu		Electrodeposition on stainless steel disk prior to α -spectrometry	(32)
Rare earths		Investigations of electrodepositions on a Hg cathode	(16, 149, 282)
Eu	Cd	Co-deposition of Cd and Eu at Hg electrode followed by controlled potential stripping of Eu	(283)
Gd, Tb		Electrodeposition on Hg cathode from acetate-tartrate solutions	(17)
Rh		Electrodeposition on rotating Cu disk cathode followed by spectrographic determination	(293)
Zr	Be	Deposition as the hydroxide on a Pt electrode by pH change produced electrochemically	(100)

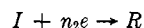
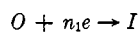
Table II. Controlled Potential Coulometric Determination

Substance determined	Method	Reference
Am	Electrolytic reduction to the III state followed by coulometric oxidation Am(III) → Am(V) at tin oxide conducting glass electrode	(225)
Am	Persulfate oxidation to Am(VI) followed by coulometric reduction to Am(V) at Pt electrode in HNO ₃	(267)
Bi, Pb	Deposition of Bi and Pb on Hg electrode followed by coulometric oxidation of the amalgam in tartaric acid medium	(271)
Ca, Cu, Zn	Indirect coulometric method based on electrolysis of Hg(II)-DTPA complex at Hg-coated Pt electrode	(137)
Cu	Determination of ng amounts in undivided capillary microcell in NH ₂ OH-H ₂ SO ₄	(111)
Cu, Na, Li	Reduction at Hg electrode in acetonitrile-0.1M Et ₄ NCIO ₄	(37)
Cl	Use of Ag-AgCl electrode in a pCl-stat for determination of free chloride in presence of cations	(205)
Mn	Coulometric oxidation Mn(II) → Mn(III) in 0.25M Na ₄ P ₂ O ₇ , pH 2, at Pt electrode	(110)
Mo	Reduction Mo(VI) → Mo(V) in 0.2M (NH ₄) ₂ C ₂ O ₄ , pH 2.1, at Hg electrode	(237)
Pu	Dissolution of PuO ₂ by Na ₂ O ₂ -NaOH fusion, reduction to Pu(III), and coulometric oxidation Pu(III) → Pu(IV)	(182)
Re, Mo, W	Electrochemical oxidation and coulometric determination in Re alloys	(284)
Ru	Ru(IV) as binuclear complex [Ru ₂ O] ⁶⁺ reduced to Ru(III) at Pt electrode in 5M HCl	(298)
U	Determination in Al-U alloys	(77)
U, Fe	Reduction at Hg cathode	(39)
U, Np	Determination in U-Np alloys	(222)
V	Determination by oxidation V(IV) → V(V) or reverse reduction at Pt electrode in 1.5M H ₃ PO ₄ following chemical adjustment of V oxidative state	(238)
ORGANIC SUBSTANCES		
Sulfur compounds	Oxidation in aqueous buffers of phenylthiourea (n = 1), thioglycolic acid (n = 2), and cysteine (n = 2) at Pt electrode	(248)
O-phenylene-diamine	Oxidation (n = 2) at Pt electrode in H ₂ SO ₄	(257)

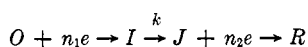
tion mechanisms, where analytical determinations were not devised, are discussed below.

Electrode Mechanisms. Coulometric methods continue to enjoy an important role in the study of electrode reactions, both in the determination of overall *n*-values and in detailed studies of the rates and mechanisms of chemical reactions associated with the electrode reactions. Bard and Santhanam (29) have given a complete survey of the theory, experimental methods, and applications of coulometry to the study of electrode reactions. Meites (176) also reviewed this field, with special attention to the determination of the rates of homogeneous reactions. Although theoretical treatments in this area have been less frequent, two studies have appeared which examine the role of the reactions which occur in the diffusion layer and their effect on coulometric *n*-values and current-time behavior. Karp and Meites (136) pointed out that in reaction schemes in which electroactive interme-

diates are formed in the first electron transfer step, such as the sequence

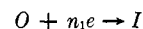


that previous treatments gave incorrect results because they neglected the occurrence of the homogeneous reaction within the diffusion layer. The authors presented a theoretical treatment for this reaction and also for simple stepwise electron transfer and derived corrected equations for these mechanisms. They point out, however, that in cases where the product *I* is not itself electroactive, for example in the ECE scheme



the occurrence of reaction in the diffusion layer is not of importance, even for ratios of *k* to the overall mass transfer rate coefficient (*p* or *β*) of 100. When *k/p* is greater than 100, detection of the intervening chemical reaction by cou-

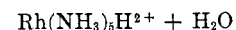
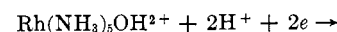
lometry will be difficult. They conclude that in these cases "the extent of a chemical reaction in the diffusion layer is not worth taking into account if the reaction is slow enough to detect." This is fortunate, since the necessity of including the homogeneous chemical reaction terms in the equations for calculating the flux at the electrode surface considerably complicates theoretical treatments. For example, Rangarajan (235) considered the case



in the light of the work of Karp and Meites, and was able to solve the theoretical equations only with some approximations concerning the relative rate of the dimerization reaction to that of the electrode reactions.

Tenygl (279, 280) proposed a technique, which, although called "pneumatic polarography," is actually more closely related to a coulometric method involving gas evolution described by King and Bard. The method is based on electrolysis in two cells connected in series, one containing only supporting electrolyte solution while the other also contains the electroactive substance of interest. Evolved gases from both cells are led to a differential recording manometer where the difference in volumes is determined. For example, in the blank cell H₂ and O₂ are produced by the electrolysis of water. In the sample cell less gas is evolved, since some of the current goes to electrolysis of the electroactive substance, e.g., SO₂²⁻. Although the selectivity of this method is poorer than more conventional coulometric methods, it will probably be useful for the continuous analysis of substances undergoing oxidation or reduction at potentials near those for the background processes.

Parry and Oldham (212) showed that the reduction of Pd(II) in media containing ammonia or pyridine occurs in a two-electron reaction. Johnston and Page (130) studied the reduction of the Rh-species Rh(NH₃)₅OH²⁺ in an ammoniacal medium at a Hg electrode. By measuring *n*_{app} and the amount of H⁺ consumed during the electrolysis, they concluded that the reaction mechanism was



The product of this reaction reacted slowly with solvent and more rapidly with oxygen to yield Rh(III)-O-O-H²⁺, which could be reduced cleanly in a two-electron reaction. Ru(IV) was shown to exist in HClO₄ solutions as a tetrameric species which could be reduced in two one-electron steps (295). The

Ru(III) species formed from the product of the electrolysis could be reduced further to Ru(II) which is immediately oxidized by ClO_4^- . In another study of a Ru species, Itzkovitch and Page (120) found that $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$ is reduced with $n = 1.02 \pm 0.02$ in an acid sulfate medium to a stable Ru(II) species, which reacts with N_2 to form the complex $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$. Connery and Cover (58) employed coulometric techniques to study the electrode reactions and species present in NaOH solutions of Os(IV) and Os(VI). In a reinvestigation of the reduction of pertechnetate ion in 1M NaOH, Kissel and Feldberg (143) found a three-electron reduction at -1.00 V vs. SCE, but a very large value of n_{app} and a catalytic reaction for reduction at -1.27 V. Propst (224) studied the reduction of Po(IV) and suggested a six-electron reduction to polonide ion. Propst and Hyder (228) also used scanning coulometry with a conducting tin oxide glass electrode to investigate the oxidation of Cf(III) in H_2SO_4 solutions. Re(III) showed complicated current-time behavior during reduction in 0.5M HCl, with n_{app} values between 0.75 and 1.11. The results were explained in terms of a one-electron reduction of a trimeric complex (193). McCullough and Meites (160) used coulometry, among other electrochemical methods, to examine the complex electrochemical behavior of Nb(V) in HCl media. Davis and Montalvo (65) showed that the reduction of Mn(III)-hematoporphyrin IX occurs in a one-electron step at pH 6.2.

Coulometry also continues to play an important role in electrochemical studies in nonaqueous solvents. The reduction of several Ni(II) complexes of cyclic amines in acetonitrile (MeCN) was shown to involve transfer of one electron (207). Controlled potential electrolysis was also employed to study the reduction of ZrCl_4 in MeCN (208). Goolsby and Sawyer (103) studied the electrochemistry of Au species in MeCN solutions and found that in the presence of chloride ion, Au(III) is reduced in a three-electron step to the metal. In the absence of chloride ion, Au is oxidized with $n = 1.00 \pm 0.03$ to form stable Au(I) solutions. These authors also studied the reduction of superoxide ion to OH^- (102) and the oxidation of hydroxylamine to N_2O ($n_{\text{app}} = 2.00$) (104) in dimethylsulfoxide (DMSO). Decaborane (14) in MeCN was shown to be reduced in a one-electron reaction (51). Matsui and coworkers (173) studied the reduction of HgBr_2 in *N,N*-dimethylformamide (DMF) and suggested first reduction to Hg and HgBr_3^- ($n_{\text{app}} = 0.67$), followed by further reduction to Hg ($n_{\text{app}} = 2$). Cauquis and Pierre investigated the oxidation of both SCN^- (49) and SeCN^- (50) in MeCN and showed both involved $n_{\text{app}} = 1$ with

formation of $(\text{SCN})_2$ and $(\text{SeCN})_2$, respectively. The oxidation-reduction behavior of Cl^- and HCl in nitromethane was investigated and shown to involve one-electron transfer to form chlorine (167). Tsuji and Elving (285) investigated the reduction of different acids, such as HNO_3 and $\text{H}_2\text{C}_2\text{O}_4$ in pyridine and provided coulometric evidence for one-electron reductions at a Hg-coated Pt electrode. Coulometric methods have also proved useful in studies in fused salts. The +2 states of Sm, Eu, and Yb were prepared in a LiCl-KCl eutectic melt by electroreduction of the trihalides at a W electrode (128). Fulton and Swofford (95) demonstrated that the oxidation of I^- at a Pt electrode in a NaNO_3 - KNO_3 eutectic occurred with $n = 1.06 \pm 0.04$, with formation of I_2 and concomitant decomposition of NO_3^- to NO_2^- and O_2 .

The current interest in electroorganic chemistry and the similarity between electrolyses performed for coulometric and synthetic purposes continues to produce many studies in controlled potential electrolysis of organic compounds. Several investigations of quinones have been reported. O'Brien and Olver (204) showed that the biologically interesting molecule ubiquinone-6 is reduced at a Hg electrode in methanolic solutions with $n = 2.01$. Similarly, the durohydroquinone in MeCN at a Pt electrode was shown to involve an overall two-electron reaction (211). Interest also continues in aromatic nitro compounds. The reduction of nitrobenzene in ethanolic solutions in 0.1M HCl showed the usual $n_{\text{app}} = 4.0$ and reduction to the hydroxylamine (290). In alkaline solutions nonintegral and time-dependent n_{app} values were obtained, however. The reduction of a number of dinitronaphthalenes were also shown to be the nitrohydroxylamine (133), except for the 1,8-dinitronaphthalenes which undergo 10-electron transfers and internal azo- or hydrazo-compound formation (158). The coulometric reduction of a number of *m*-dinitrobenzenes also substituted with alkyl or halide groups have also been reported and appear to show n_{app} values near 4 for aqueous electrolytes (276). The reduction of nitrobenzylhalides in MeCN, however, shows a one-electron reduction to the anion radical which loses halide ion and dimerizes (155). A study of the reduction of *N*-nitro and nitroso derivatives of guanidine and urea in aqueous buffers has also been reported (154).

Miller and Riekema (181) studied the reduction of triphenylbromoethylene in DMF solution and demonstrated a first step two-electron reduction to triphenylethylene. Further reduction at more negative potentials yields triphenylethane.

Erickson and coworkers (82) reported an interesting stereochemical study of

the reduction of geminal dihalocyclopropanes in alcoholic or DMF solutions. In all cases the reactions involved two-electron reduction with removal of Br^- (in Br-Cl compounds); the stereospecificity of the reactions was the same as that found for metallic reductions. In another study of the stereochemistry of electrode reactions, Puglisi, Clapper, and Evans (230) investigated the reduction of benzaldehyde in acidic aqueous solutions at a Hg electrode. The authors found that $n_{\text{app}} = 0.96$ and that the coupled product of the electrode reaction, hydrobenzoin, had a ratio of *dl* to *meso* form of about the same as that obtained in the photolysis of benzaldehyde (about 1.1 to 1.3). However, in the presence of surface active substances, such as tetra-*n*-butylammonium perchlorate, the *dl/meso* ratio was significantly lower, suggesting perhaps that the dimerization occurs within the electrical double layer. Buchta and Evans (41) carried out the reduction of dibenzoylmethane (DBMH) in a DMSO medium and found an overall n_{app} of 0.55. This value fitted the proposed mechanism involving reduction of 4 molecules of DBMH to yield the coupled pinacol and 2 moles of the enolate with the transfer of 2 electrons. The current-time curves obtained in this reduction were unusual in that the current after undergoing the usual monotonic decay increased again and formed a peak. This behavior was said to result from the decomposition of the pinacol to benzil and acetophenone, followed by the reduction of benzil to its anion radical. The peak in current was caused by the catalysis of the pinacol decomposition reaction by benzil anion radical; the authors coined the name "electrolytic autocatalysis" for this type of reaction. In a study of the reduction of perinaphthenone in basic media, Cardinali, Carelli, and Trazza (47) found two one-electron steps; the final reduction product was the dihydro compound.

The electrochemistry of amines and other organo-nitrogen compounds continues to be of interest. Bacon and Adams (22) investigated the oxidation of substituted anilines, such as *p*-chloroaniline, in aqueous media and showed that the reaction occurred with one faraday of electricity consumed per mole of aniline, and produced coupled products. Smith and Mann (258) found that tertiary aliphatic amines oxidized in MeCN containing some water with $n_{\text{app}} = 0.999 \pm 0.001$. In the absence of water slightly lower n_{app} values were obtained because of the reactions which the electrogenerated cation radical can undergo. The electrochemical oxidation of *p*-dimethylaminophenol in acidic aqueous media was shown to occur in a two-electron reaction followed by slow hydrolysis of the quinoneimine species

to benzoquinone (168). At higher pH's the dimethylamine formed as a hydrolysis product can add in a 1,4-addition to the quinoneimine, producing new electroactive species. Ambrose and Nelson (12) studied the oxidation of carbazole and *N*-substituted carbazoles and found that n_{app} was 2.5 to 2.8 for carbazole itself, but was essentially 2.0 for methyl, ethyl, isopropyl, and phenyl substituents. They proposed an initial one-electron oxidation followed by coupling with loss of protons and a second one-electron oxidation of the coupled product. The reduction of phenazine in aqueous acidic solutions was shown to occur with n_{app} of one for reduction at the first polarographic wave (27). In alkaline solutions only a single drawn-out polarographic wave is observed, and n_{app} is about two. Sadler and Bard (243) studied the reduction of several aromatic azo compounds in DMF solutions at a Hg electrode. Reduction at the first polarographic wave showed n_{app} values of one, with formation of the fairly stable anion radical in all cases. Coulometric oxidation (reversal coulometry) of the anion radicals was employed to demonstrate their stability. Reduction at the second polarographic wave showed that an additional electron was added to form the dianion. This species was unstable and probably was protonated. The protonated species, however, was oxidizable back to the parent azo compound in a single two-electron step. In a related study, these authors investigated the reduction of 4,4'-azopyridine-1,1'-dioxide in DMF (244). They found that reduction at the first wave gave n_{app} values of 1.4 to 1.9 which was caused by slow decomposition of the anion radical followed by further reduction to azopyridine. At the second polarographic wave, $n_{app} = 5.88 \pm 0.04$, with reduction all the way to the protonated azopyridine dianion occurring. Cottrell and Mann (59) studied the oxidation of aliphatic sulfides, such as dimethyl sulfide, in MeCN and showed that in dry MeCN n_{app} was 0.84 ± 0.02 with primary formation of a cation radical which undergoes secondary deprotonation and coupling reactions. In the presence of 1% H₂O, n_{app} was 4.0 ± 0.1 . The oxidation of 1-hydroxypyridine-2-thione occurred in a one-electron transfer reaction at a Hg electrode in aqueous buffers and produced the organo-mercury compound as a product (153). Donahue and Olver (70) examined the reduction of 8,8'-diquinolyldisulfide (RSSR) in methanolic solutions at a Hg electrode and found $n_{app} = 1.99 \pm 0.05$. The reaction was said to occur by reaction of RSSR with Hg to form (RS)₂Hg, followed by a two-electron reduction to form 8-mercaptoquinoline, RSH. Yousefzadeh and Mann (305) studied the reduction of alkyl esters of *p*-toluenesulfonic acid in

MeCN at Hg and C electrodes and showed that the primary process is a one-electron reduction leading to the alcohol and toluene. McKinney and Rosenthal (161) showed that the reduction of triphenyl sulfonium ion at an Hg electrode gave n_{app} values between one and two. The reaction products were Ph₂S and Ph₂Hg.

In other studies of organic systems, formate ion was shown to be oxidized in DMSO in a one-electron reaction to CO₂ and formic acid (122). Aromatic carboxylic acid esters formed stable anion radicals in a one-electron reduction in DMF solutions (118). In a study of the electroreduction of dieldrin and aldrin in methanolic solutions, the authors concluded that coulometry was not a convenient method of analysis for these compounds (270).

A number of electrochemical studies of organometallic compounds have included coulometric investigations. DiGregorio and Morris (68) found that the reduction of diphenylthallium(III) cation at a Hg electrode in aqueous solutions at potentials corresponding to its first polarographic wave yields $n_{app} = 1.20 \pm 0.02$ and proposed a reduction of Ph₂Tl⁺ to Ph₂Hg and Tl, with side reactions contributing to the non-integer n_{app} value. Reduction at the second polarographic wave yielded n_{app} values of 2.00 ± 0.02 and produced Ph₂Hg, Tl, and benzene. A very similar mechanism was found for the reduction of the monophenylthallium(III) dication, which shows $n_{app} = 1.02 \pm 0.02$ and the formation of Ph₂Hg and Tl(I) at the first wave and $n_{app} = 2.05 \pm 0.02$ at the second (86). Similar mechanisms are found with other organometallic compounds. For example, triphenyltin fluoride reduces in acid ethanolic solutions in a one-electron reaction to produce F⁻ and Ph₃SnSnPh₃ (288). Morris (191) also found that the aquodiethyllead(IV) ion reduces in 0.5M HClO₄ at a Hg electrode with $n_{app} = 1.96 \pm 0.07$ and produces tetraethyllead, lead metal, and small amounts of diethylmercury. Dessy and coworkers (67), continuing their extensive study of the electrochemistry of organometallic compounds, investigated the behavior of nitroaromatic mercury compounds, such as bis(*p*-nitrophenyl)mercury, at a Hg electrode in dimethoxyethane solutions. The coulometric reduction shows $n_{app} = 2.1$, with stepwise oxidation of the product, *via* a radical anion, to the parent compound possible. The reduction of cyclopentadienyl iron benzene hexafluorophosphates or tetrafluoroborates in ethanolic solutions occurred in a two-electron step producing cyclopentadiene, benzene, and Fe (18). Rollmann and Iwamoto (242) investigated the reduction of Co, Ni, Cu, and metal-free sulfonated phthalocyanines in DMSO at a Hg electrode and showed that suc-

cessive one-electron steps were involved. Santhanam and Bard (247) studied the coulometric reduction of triphenylphosphine and triphenylphosphine oxide in DMF solutions at Hg electrodes and found evidence of a catalytic reaction, with the steady electrolysis current much higher than the background value. This was attributed to the decomposition of the initial anion radical to bi-phenyl, which then undergoes reduction, followed by catalytic reoxidation.

Coulometric methods have also been employed to investigate compounds of biological interest. Dryhurst and Elving (74) studied the oxidation of adenine in aqueous solutions at a pyrolytic graphite electrode and found that n_{app} was 5.6 to 5.8 for the overall oxidation. The oxidations took two days to reach completion, indicating a very slow intermediate step in the process or severe filming of the electrode. Dryhurst also studied the reduction (73) and oxidation (72) of 6-thiopurine (TP) in aqueous buffers. The reduction of TP itself at a Hg electrode gave evidence of a catalytic reaction and high n_{app} values, but 6-TP-sulfonic acid showed smooth reductions to purine with an n_{app} of two. The oxidation of TP in 1M acetic acid at a pyrolytic graphite electrode occurred with $n_{app} = 0.98$ on formation of the disulfide. The oxidation in ammoniacal solutions was more complex and required four faradays per mole of TP and produced purine-6-sulfonic acid and purine-6-sulfonamide. In a continuation of their studies of nicotinamide salts, which are model compounds for the biologically important pyridine coenzymes, Underwood and coworkers (159) studied the reduction of 1,1'-ethylenebis(3-carbamidopyridinium bromide) and related compounds in aqueous buffers. Coulometry showed that all of the compounds reduced in a two-electron process which produced an internally coupled product which could be oxidized back to the starting material at more positive potentials. Oxidation of the coupled reduction product with oxygen, however, led not to the starting material, but to a free radical and then to a species similar to 1,1'-ethylene-2,2'-dipyridylum dibromide (Diquat). Riboflavin was shown to be reduced in DMSO solutions at a Hg electrode with $n_{app} = 0.99 \pm 0.01$ (277). Reversal coulometry showed that the anion radical was not stable, however, and the authors proposed that it decomposed in parallel reactions to produce another anion radical and a second, nonoxidizable substance. The study of biologically interesting substances by electrochemical techniques with the hope of gaining a greater understanding of biological oxidation-reduction processes has been a fruitful one. However, one must be aware of the differences between electrochemical processes, where elec-

tron transfer is the major mode of reduction and biological ones where hydrogen atom or hydride transfer may also be involved. Although much useful electrochemistry has been performed on these systems and valuable electro-analytical techniques have been devised, the real relevancy of these studies to elucidation of biological electron transfer mechanisms as they exist in organisms has not yet been demonstrated.

CONTROLLED CURRENT COULOMETRY— COULOMETRIC TITRATIONS

Determinations. The application of coulometric titrations to high precision determinations continues to be of interest. Marinenko and Taylor (170) performed careful titrations of primary standard benzoic and oxalic acids with electrogenerated base, and found purities of 99.995 and 99.987%, respectively. Based on these values they calculated values of the faraday of $96,486.7 \pm 2.5$ and $96,485.4 \pm 3.4$ coulombs per g.-equivalent, in good agreement with values determined by other methods. The authors again reiterate Tutundzic's proposal that the faraday be made the primary chemical standard and point out that "the uncertainty of the faraday is about one order of magnitude smaller than that of chemical standards commonly used." Knoeck and Diehl (145) showed that high precision titrations with electrogenerated Fe(II) were possible, and found that assay of $K_2Cr_2O_7$ and $(NH_4)_2Ce(NO_3)_6$ yielded values of 99.976 and 99.972, respectively. These authors also proposed a cell for high precision coulometry with external reagent generation in which two external chambers are employed (146). One chamber was used to generate titrant sufficient for 99.9% of the titration, and then the titration was completed using a second, continuous flow, generating electrode chamber. Yoshimori and Hikawa (302) recommended coulometric titration with electrogenerated acid or base to test the purity of some standard reagents with very high precision.

Several new coulometric titrants or methods of electrogeneration have been proposed. Durst and Ross (78) electrochemically generated F^- by transference through a solid state Eu^{2+} -doped LaF_3 membrane. The transference was accomplished by using the membrane to separate the test solution from a 1M NaF (pH 5.5) solution containing a Pt cathode. Upon electrolysis, reduction of H^+ occurs and electroneutrality in the NaF solution is primarily maintained by passage of F^- ions through the membrane into the test solution. The "current efficiency" for the process was 99.2%. Fletcher and coworkers suggested the oxidation of metal borides

as sources of metal ions for coulometric titrations. However, in the generation of La(III) by oxidation of LaB_6 (61-63), the current efficiency depended upon the particular piece of LaB_6 employed and was near 109%. A similar difficulty was found when CrB was employed as a source of Cr(VI) (90), when a current efficiency of only 79.5% was found. The need for specific calibrations of electrode material and the current efficiencies which deviate significantly from 100% probably make these methods useful only in special circumstances. Kostromin and Akhmetov (152) proposed another method of generating Cr(VI), by anodization of a Cr electrode, and found current efficiencies near 100% in 0.1 to 2M HCl solutions at current densities of 0.3 to 70 mA/cm². Electro-generation of unusual oxidation states of metals, in cyano complexes, such as

$Mn(CN)_6^{5-}$ (177) and $Mo(CN)_8^{3-}$ (178), was reported by Mendez and Conde.

Coulometric methods have also been employed for generation of species in solid electrolytes at high temperatures. Several studies involving variation of the Fe:O ratio and determination of the composition of wustite (nonstoichiometric iron oxides) have been reported (180, 239, 240). Another study dealt with a determination of point defects in NiO, CoO, FeO, and $Co_xFe_{3-x}O_4$ by coulometric titration in a calcia-stabilized zirconia solid electrolyte at 1200 °C. (259). Analysis of oxygen in oxide materials, such as Al_2O_3 , SiO_2 , TiO_2 , and FeO, by heating at 2000 °C in Ar or vacuum and coulometric determination of oxygen, has also been described (148). A number of other reported coulometric titrations are listed in Table III.

Table III. Electrogenerated Titrants and Substances Determined by Coulometric Titration

Electrogenerated titrant	Substance determined	Reference
OXIDANTS		
Chlorine	Reinecke salt, papaverine (indirectly)	(135)
	Thio[tris(1-aziridinyl)-phosphine sulfide]	(119)
	Si-H groups in organosilicon compounds	(281)
Bromine	Antimony(III)	(66)
	Europium(II)	(7)
	Nitrites	(164)
	Methylene blue	(134)
	Tetraalkyl lead compounds	(220)
	Amines, amino acids, diamines	(275)
	Si-H groups in organosilicon compounds	(281)
Iodine	Double bonds	(33)
	Cyclohexene	(83)
	Mercury fulminate, by reaction with thiosulfate ion and titration of excess	(239)
	Copper(II), by addition of excess thiosulfate ion and back-titration	(46)
	Sulfuric acid aerosol, by conversion to SO_2 with hot copper	(251)
Hypobromite	Water, by conversion to NH_3 with $NaNH_2$	(303)
	Nitrogen in steel and metallic titanium by conversion to NH_3 in Kjeldahl apparatus	(304)
Manganese(III)	Iron(II)	(20)
Chromium(VI)	Iron(II)	(90)
	Iron(II), Tin(II), Antimony(III)	(152)
REDUCTANTS		
Iron(II)	Potassium dichromate	(145)
	Nitrate ion	(98)
	Plutonium(VI), with back-titration with electrogenerated cerium(IV)	(268)
	Selenium(IV), tellurium(IV), by treatment with excess $KMnO_4$ and back-titration	(3)
	Titanium(III)	Selenium(IV), tellurium(IV)
Hexacyano-manganese(I)	Tellurium(VI), tellurium(IV)	(53)
	Molybdenum(VI)	(200)
	Ferricyanide ion	(177)
Octacyano-molybdenum(V)	Thallium(I)	(178)
Tin(II)	Selenium(IV), tellurium(IV)	(6)
PRECIPITATING AND COMPLEXING AGENTS		
Silver(I)	Chloride ion	(52, 232, 233)
	Chlorine and bromine in organic compounds and polymers	(48)
	Sulfide ion	(44, 45)
	Thioacetamide	(142)
	Tetraphenylborate ion and indirect determination of potassium ion	(189)
	Tetraphenylborate ion and indirect determination of alkaloids, nitrogenous organic bases, quaternary ammonium salts	(213)

Continued

Table III. Electrogenerated Titrants and Substances Determined by Coulometric Titration (Continued)

Electrogenerated titrant	Substance determined	Reference
PRECIPITATING AND COMPLEXING AGENTS		
Aluminum(III)	Fluoride	(194, 203)
Ferricyanide ion	Cobalt(II)	(112)
Ferrocyanide ion	Zinc(II), dipropyltin, and dibutyltin perchlorates	(165)
Copper(II)	Anthranilic acid	(286)
Lanthanum(III)	Fluoride and oxalate ions	(63)
	EDTA, and indirect determination of nickel(II), zinc(II), cobalt(II)	(61, 62)
Iodide ion	Mercury(I), mercury(II)	(162)
ACIDS AND BASES		
Base	Potassium acid phthalate	(269)
	Carboxylic acids	(129, 146, 170)
	Dichromate ion	(146)
	Boric acid	(169)
	Ammonium salts, by passage through cation exchange resin column	(201)
	Weak acids, in nonaqueous solvents	(93, 96)
	Carbon in alloys, by combustion to CO ₂	(300)
	Zinc(II), iron(II) and iron(III), copper(II), by titration of H ⁺ liberated on electroreduction or hydrolysis (indirect coulometric determination)	(215-217)
Acid	Sodium tetraborate	(269)
	Carbonates	(254)
	Lithium hydroxide	(97)
	Weak bases, in concentrated salt solutions	(54)
	Weak bases, in nonaqueous solvents	(287)
	Organic nitrogen compounds, by conversion to NH ₃	(206)
Karl Fischer reagent	Water, in various samples	(116, 132, 144, 198, 199, 274)
FUSED SALTS		
Iodine	Iodate, in NaNO ₃ -KNO ₃ melt by adding I ⁻ and excess arsenic(III) and back-titration	(94)
Mercury(I)	Halide, chromate and "oxide" in molten LiNO ₃ -KNO ₃	(175)
Tungsten(II)	Ytterbium(II) in LiCl-KCl eutectic	(127)

Table IV. Galvanic Analyzers and Continuous Coulometric Titrators

Substance determined	Method	Reference
Cl ₂ in gases	Reduction of Cl ₂ at Au electrode vs. Ag-AgCl counter electrode	(294)
F ₂ in atmosphere	Reaction of F ₂ with LiCl electrolyte and reduction of Cl ₂ at Pt electrode vs. Ag-AgCl counter electrode	(138)
Mercaptans in gases	Continuous titration with electrogenerated Ag(I) in ammoniacal electrolyte	(79)
O ₂ in gases or liquids	Applications and improvements in membrane-covered electrodes or other electrodes for reducing O ₂	(81, 121, 174, 188, 190, 260, 261)
O ₂ in gases, Na, and steels	Solid electrolyte (ZrO ₂ -MgO or ThO ₂ -Y ₂ O ₃) galvanic cells with metal-metal oxide electrodes	(88, 184, 195)
O ₂ , peroxides and hydroperoxides in liquids	Galvanic detector with wire metal (<i>e.g.</i> , Au, Pt) indicator electrode and hollow tubular anode (<i>e.g.</i> , Pb, Zn) in KOH electrolyte	(147)
H ₂ in gases	Oxidation in fuel-cell arrangement at porous Pd electrode with air-Pt black cathode	(43)
H ₂ in solids and gases	Conversion to HCl on catalyst column (<i>e.g.</i> , PdCl ₂) and galvanic detection of acid	(246)
H ₂ in gases	Reduction to hydride at cathode with metal hydride electrolyte	(115)
N-compounds in gases or water	Conversion to NH ₃ by passing over Ni catalyst in H ₂ stream and titration with electrogenerated H ⁺	(9, 172)
SO ₂ in gases	Continuous titration with electrogenerated I ₂ using internal electrolysis with C-MnO ₂ cathode	(10)
Acidic or basic substances	Galvanic detectors or continuous coulometric titrators	(36, 89, 245)
Water in various samples	Applications and improvements in galvanic or coulometric hygrometers by electrolysis of water in P ₂ O ₅ or metal oxide electrolytes	(15, 31, 106, 187, 250, 252)

Other Applications. Coulometric and galvanic detectors for analysis of gas and liquids streams continue to be improved and developed; a number of recent devices are summarized in Table IV. Coulometric methods also continue to be applied to C and H determinations in organic substances. Hersch (114) has received a patent for an apparatus in which O, C, and H are all ultimately converted to CO which is reacted with electrogenerated I₂. Another technique involves conversion of C and H to water and determination with an electrolytic hygrometer (14). In a similar method, C and N were determined by gas chromatography and H by conversion to H₂O and coulometric electrolysis (56). The H content could also be determined by measuring the chromatographic O peak produced by electrolysis of the water; however, the accuracy of the chromatographic H determination was only ±0.2% compared to that of the coulometric determination, ±0.03%. Coulometric and galvanic detectors also continue to find application in chromatographic systems; several detectors have been reviewed (113, 262). Alcohols and aldehydes can be detected by a fuel-cell type of detector employing a KOH electrolyte, a Ag oxide cathode and a porous Pt anode at which oxidations of the organics occur (60). The sensitivity of this detector was said to be two orders of magnitude higher than a thermal conductivity detector. Littlewood and Wiseman (157) determined hydrogenatable material in gas chromatographic effluent by continuous reaction with electrogenerated H₂ maintained at a constant level. Standard samples of O₂ or H₂ for gas chromatographic analysis of gases were prepared electrolytically (13). A coulometric method of detection of amino acids in liquid chromatography employing a Cu working electrode has also been described (272).

Anodic stripping methods and related techniques continue to be applied to metal deposits and metallic samples. Constant current anodic dissolution of Ni-Fe-Cu electroplates in KCNS solution has been employed (150). The measurement of the thickness of metal deposits of Sn, SnFe₂, Zn, and a number of other metals has been described (151). Agasyan and Khamrakulov (4) carried out the analysis of solutions of Cu(II) and Ag(I) by plating the metals on a solid electrode followed by coulometric stripping at a constant current. A similar method for Cu in Zn solutions has also been reported (236). Extensions of previously described methods for the determination of H in Fe, Ni, Cd, and other deposited metals by coulometric oxidation have been described (91, 92). Cathodic reduction of metal salts also has been employed.

Several Ag compounds, such as AgNO₃ and AgCl were determined by placing them in a Pt crucible, adding NaOH solution to convert them to solid AgOH, and reduction at constant current (291). By observing the potential of the cathode vs. a Hg/HgO and noting the time when an inflection in potential occurs, the coulombs required for the reduction could be determined. Barikov and Songina (30) report a similar method for the determination of metal sulfides by sample dissolution into a carbon paste electrode.

The application of controlled current coulometry to studies of reaction kinetics has been reviewed by Janata and Mark (123). Coulometric methods were applied to measure the rates of bromination of aliphatic ethylenic compounds in acetic acid (76). Paris and Gregoire applied coulometric titrations with electrogenerated base to the study of complexes, and investigated both the hydrolysis of Be(II) (209) and the complexation of Ti(III) with picolinic acid (210) with this technique.

APPARATUS

During the last two years, a number of commercially available multipurpose electroanalytical instruments have become available. Several of these incorporate provision for both controlled current and controlled potential operation and include integral coulometers. Ewing (84) has reviewed the characteristics of several of these. A description of a number of commercially available potentiostats and a general discussion of instrumentation, cells, and methodology in controlled potential coulometry has also been given (29). Schroeder and Shain (255) have extended the treatment of design criteria for optimum response and stability of potentiostats. Bewick (38) has discussed the effect of the increasingly popular positive feedback iR-compensators on potentiostat performance and claimed that severe overcompensation can readily be produced. However, another recent paper (57) discusses methods of determining the uncompensated ohmic resistance by determining the current vs. frequency curve and extrapolating to infinite frequency, and reports successful correction of uncompensated iR at frequencies of 0-10 KHz. Pilla and coworkers (219a) also considered models for iR compensation and conclude that "stable overcompensation cannot take place in any practical system." From a practical standpoint, we have found that positive feedback iR compensation is a necessary and very useful technique for electrochemical studies in nonaqueous solvents and other highly resistive solutions, even for measurements at rather slow times.

Several discussions of cell design have

been given. Peltier and Moinet (218) discussed electric field asymmetry in electrolysis cells and demonstrated that with improper cell geometry, H₂ can be evolved at some points of a Hg cathode even when the control potential is set at a value too positive to expect H₂ evolution. Christian and Feldman (55) described a microcell with a solution volume of about 1 ml. and containing sealed-in Pt electrodes which is useful for coulometric titrations. Berlandi and Mark (35) designed a cell constructed from pyrolytic graphite and useful with solution volumes of 5 to 250 μ l for selective controlled potential electro-deposition of radioactive isotopes. Har-rar described cells for controlled potential coulometry with either platinum (109) or mercury (108) working electrodes. An apparatus for simultaneous spectrophotometric, potentiometric, and coulometric measurements has been designed (171). The optical cell was fixed to the side-arm of the coulometric cell, and solution was circulated into it by means of bubbling nitrogen gas. A convenient cell for student electro-deposition experiments has also been suggested (21).

Coulometric Titration Apparatus.

A transistorized automatic coulometric apparatus for determination of S and C in metallic samples has been designed (221). The method employs potentiometric end-point detection and uses the voltage difference between the indicator electrode potential and the end-point potential, through a voltage-to-frequency converter, to introduce current impulses into the solution until the end point is reached. Several patents have been awarded for improvements in the design of automatic coulometric titrators (125, 126, 202, 231). Simple transistorized constant current supplies, especially suitable for student coulometric titrations have been suggested (265, 292). Stock's paper (265), as well as that of Evans (83), also suggest some simple titrations appropriate for student experiments.

Potentiostats and Coulometers.

Potentiostat design continues to be aimed at all solid-state component devices with higher output power, improved stability and shorter response time. Will (299) described a potentiostat based on a Philbrick P85AH control amplifier and a P25AH follower with a rise time of about 3 μ sec, 10¹² ohm input resistance and with provision for iR compensation. The transistorized booster amplifier employed was capable of delivering ± 3 amperes at ± 10 volts. Stock (264) has designed a very simple potentiostat for student work which is composed of an integrated circuit and two transistors. The output for this unit is not specified, but it is probably below 100 mA at 10 volts. Modifications of the popular ORNL

Model Q-2564 controlled potential coulometry unit have been discussed (192). Several other potentiostats and coulometry circuits have also been described (19, 75, 80, 141, 249, 296). Phillips and Milner (219) have designed a modular coulometry apparatus designed for routine and automatic determinations and with provision for automatic sample changing and data print-out. The unit employs a digital voltmeter as a voltage-to-frequency converter for current integration and a clock pulse generator to control the sampling rate of digital voltmeter and timing. In a typical determination the integrator is cleared, a new solution is cycled into place and deaerated, the sample is electrolyzed at a pre-electrolysis potential for a time t_1 , then coulometry carried out for t_2 minutes, the results are printed out, and a new sample is cycled into place. The authors report determination of Mg amounts of Fe, U, Pu, and Cu with a coefficient of variation of about 0.2%. Stock (266) has described an apparatus for automatically adding the electroactive species to a controlled-potential electrolysis cell during the electrolysis. Propst (227) has received a patent for a previously-reviewed scanning coulometry circuit in which the voltage scan rate is inversely proportional to changes in the electrolysis current and has reported some applications of this method (226, 228).

Lingane previously recommended a fixed-field (permanent magnet) low inertia dc motor-counter as an inexpensive (ca. \$150) and convenient coulometer. The difficulty with its application was a drop in the count rate calibration factor at lower input voltages. He has now devised a simple compensation circuit which adds a small constant voltage into the input of the motor (156). With compensation, the unit is capable of measuring the current-time integral to $\pm 0.04\%$ for a 20:1 current range, and to $\pm 0.1\%$ for a 200:1 range. Several coulometers based on electrochemical cells, but of less use in electroanalytical determinations, have also been reported (139, 140, 297).

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Electrophoresis

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BECAUSE OF SPACE limitations, it has been necessary to curtail the number of references in this review. Those given have been selected from more than 3000 articles, most of which seemed to deserve notice. In choosing the articles to be cited, preference has been given to those concerned with analytical advances through electrophoresis. Industrial applications, patents on apparatus, and iontophoresis have been entirely excluded on this basis, despite the fact that each of these categories included important contributions. Other topics that have been severely restricted are hemoglobin research and enzymology. It is believed that the list of newly dis-

covered hemoglobins is comprehensive, but examples of advances in hemoglobin analysis are merely representative. In enzymology the literature has been so extensive that only papers of outstanding importance have been mentioned, and even some of these have been omitted. Considerable weight has been given to the accessibility of journals to chemists in the United States, but exclusion of papers on this basis has sometimes been undesirable; in such instances the *Chemical Abstracts* reference number accompanies the listing. Reviews are mentioned in the appropriate sections rather than being grouped under a single heading.

The wide scope of electrophoresis makes a comprehensive critical review impractical; selected sections where important progress has been made include discussions, while others where progress has been less dramatic are treated in bibliographic style.

This writer thanks all persons who responded to the request for reprints made in the 1968 review, and asks once again for reprints from authors who would like to have their work considered for citation in the next review.

This review extends the coverage of a previous one (1243), with most of the references dating between the latter part of 1967 and the first half of 1969.