

Electroanalysis and Coulometric Analysis

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THIS PAPER surveys the literature and developments during 1966 through December 1967; papers published before 1966 which have not appeared in previous reviews in this series have also been included.

BOOKS AND REVIEW ARTICLES

Several new books and journals containing material of electroanalytical and electrochemical interest have appeared. The newest edition of "Standard Methods of Chemical Analysis" (329) includes chapters discussing the fundamentals of electrogravimetric and coulometric methods. Zozulya has written a brief monograph on coulometric analysis (341) and coulometric titrations in nonaqueous solvents have been discussed (146, 250). A new series of monographs, "Electroanalytical Chemistry—A Series of Advances," (26) has also appeared. Two recent journals containing papers of interest in electrochemistry are the Russian journal *Elektrokhimiya* (available in an English translation as *Soviet Electrochemistry*) and *Analytical Letters*.

The "Encyclopedia of Industrial Chemical Analysis" contains sections on coulometry (111, 187) and electrodeposition (67). Gross and Murray have also reviewed several electroanalytical methods in an encyclopedia article (93), and the application of coulometry (308) and electrodeposition (190) techniques to trace analysis has been discussed. A number of review articles on coulometric titrations (37, 75, 221, 261, 293, 301, 338) and controlled potential coulometry (144, 220, 258) have appeared.

NEW TECHNIQUES

Optical Methods of Observing Electrode-Solution Interface. While spectroscopic investigations of solutions following electrolysis have been carried out for many years, interest has turned recently to direct observation of the electrode surface or the solution at the electrode surface during the electrolysis. One approach involves the use of transparent electrodes so that radiation passes through the layer of solution at the electrode surface as well as the bulk solution.

Kuwana and coworkers (150, 151) have employed both commercially available and laboratory prepared electrodes consisting of a thin layer of semiconducting tin oxide on a glass substrate. They reported successful results for the oxidation of *o*-tolidine (which has apparently become a standard test system for evaluating optical methods), although the unique nature of the electrode surface causes some difficulties. Mark and coworkers (236, 237) prepared transparent electrodes by depositing thin films of platinum on glass using a commercially available "liquid platinum" preparation. The platinum films thus produced were found to adhere well to the glass and to be relatively inert to chemical attack. An electrode which probably comes closest to the conventional electrochemical working electrode, recently described by Murray and coworkers (199), consists of a gold minigrad electrode sandwiched between glass plates. Because the spacing between the glass plates is about 80 microns, the cell also behaves as a thin-layer electrochemical cell.

To obtain higher sensitivities and observe only the layer of solution close to the electrode surface, internal reflection techniques [e.g., attenuated total reflectance (ATR) or frustrated multiple internal reflectance (FMIR) spectroscopy] have also been employed. Probably the most complete discussion of ATR at a tin oxide electrode-solution interface, employing visible radiation, has been given by Hansen, Kuwana, and Osteryoung (96, 97). Those authors discussed factors contributing to absorbance changes during electrolysis, and correlated these changes with electrochemical parameters in different techniques. Although the method appears useful, interpretation of the absorbance changes is quite complicated, see e.g. (281). Internal reflection spectroscopy in the visible region has also been reported on the thin platinum film electrodes (236, 237). Mark and Pons (180) reported preliminary results on internal reflection techniques (FMIR) at a germanium electrode under infrared radiation. Reed and Yeager (243) have mentioned similar experiments in an attempt to determine the extent of adsorption of organic species from aqueous solutions.

A different type of a spectroscopic-electrochemical experiment involves ob-

servation of radiation reflected from or scattered by the electrode surface. Ellipsometric methods, which involve precise measurements on elliptically polarized light to obtain information about the properties and thicknesses of films formed on the electrode surface, have been widely used, see e.g. (82, 148, 242) and references contained therein. Direct measurements of the reflectance of a polished platinum electrode surface have been used to study oxide (137) and iodine (85) film formation. Perhaps the most unique experiments employing optical methods are those described by Walker (326). In these, a continuous specular reflection technique was employed; light from a laser was directed at the inside of a cylindrical silver cathode in such a manner that multiple reflections occurred before the final reflection of the beam to the detector. Absorbance changes observed have been ascribed to the presence of hydrated electrons at the electrode-solution interface. The identification of hydrated electrons resulting from the electrochemical reduction of protons surely will be of great importance in explaining the data of the myriad papers concerned with the hydrogen electrode reaction. Lasers have also been employed in recent interferometric (211) and holographic interferometric (133) experiments. The major contributions of optical techniques to electrochemistry probably lie in the future. However, interest in these topics is demonstrated by talks delivered on these techniques at the Winter, 1968, Gordon Research Conference in Electrochemistry by Genshaw and Muller on ellipsometry, O'Brien on interferometric methods, McIntyre on reflectance studies, and Kuwana and Kruger on other optical methods.

Digital Electrochemical Instrumentation. Electroanalytical instrumentation during the decade 1958-67 was characterized by extensive use of analog computer devices (e.g., operational amplifiers). Although digital techniques were used from time to time, for example, in the construction of coulometers based on analog-to-digital (AD) converters or in digital determination of transition or coulometric titration times, the last years have shown increasing application of digital data acquisition methods and even direct digital control of electrochemical processes. Since digital data acquisition

methods have been used to record voltage signals obtained from transducers in many different fields, with commercially available systems or modules, the extension of these methods to electrochemical experiments is quite straightforward. Generally this involves the use of an AD converter and a multiplexer, so that several channels may be scanned, with output on paper tape (45) or punched cards (47).

For rapidly varying signals, where these methods may be too slow, direct recording into the core storage of a multichannel analyzer may be employed (160). The advantages of these methods are that more precise measurements, not limited by reading an oscilloscope screen or recorder chart, can be made, that the worker is relieved of analyzing recorded data, and that the data are obtained in a form which can be put into a digital computer without further preparation. The procedure can be carried one step farther by using digital modules to produce not only the timing functions for the data acquisition function, but also the wave forms employed in the electrochemical experiment through the use of digital-to-analog converters (41). The most versatile arrangement involves the use of a complete general purpose digital computer. For example, a small general purpose digital computer has been used to initiate the electrochemical experiment, to acquire, digitize, and store the data, to test for completion of the experiment, to perform a functional analysis of the data, and produce output yielding an analysis of the data (158). The decreasing cost of small computers, the growing availability of time-sharing arrangements on larger ones, and the power of digital computer techniques for data reduction, smoothing, functional analysis, statistical evaluation, etc., suggests increasing applications of these techniques. However, the experimentalist must realize that these methods may not be economically feasible or justifiable and that the time and effort expended in the construction of instrumentation must be justified by the experiments and research to be performed.

ELECTROSEPARATIONS AND ELECTROGRAVIMETRY

Electrolytic Sample Dissolution.

Several methods of analysis based upon anodic dissolution of metallic samples have been reported. Automatic anodic dissolution of a metal sample preceding colorimetric analysis was the subject of a recent patent (210). The dissolution of U and the adsorption and deposition behavior of various fission products were also investigated (328). Alternating current electrolysis was shown to be useful for dissolving

noble metals and metals resistant to HCl solutions; rates of solution for Cd, Cu, Au, In, Ir, Pd, Pt, Rh, Ta, and W were studied (43). Electrographic stripping of Au and Ag from different alloys has been reported (270). The anodic solution method for the determination of hydrogen in steel and iron coatings has been discussed; errors occur in the determination because of loss of hydrogen in side reactions and other factors (175, 263). An electrolytic method of determination of Si_3N_4 in silicon steel has also been described (333). Buechel and Effenkammer (48) have suggested that the dissolution of heterogeneous alloys at constant potential has advantages over the constant current dissolution method.

Countercurrent-Exchange Electrolysis. This technique consists of electrolysis at a liquid metal electrode (mercury or an amalgam) with the electrolyte phase and electrode transported in countercurrent directions through a column, with provision for external refluxing of both the electrode and the electrolyte phases. The countercurrent flow is established in columns packed with sand and large numbers of theoretical plates and effective separations can be attained (15, 31) (see the previous review in this series for a discussion of other flow electrolytic methods). The method has

proven effective in the separation of lithium isotopes by electrolysis using lithium amalgam electrodes and dimethylformamide (14, 16) or *n*-propylamine (32) solutions of lithium salts. A Pb-Tl mixture has been suggested as useful in testing the performance of a column (15). In a similar experiment, enrichment of a fused PbCl_2 solution in chlorine-37 by electrolysis in a tube filled with powdered glass employing a liquid lead cathode has been described (265). Electrolytic separation in capillary tubes by a related method has also been discussed (325).

Other Separations. A method of metal ion removal by deposition on a powdered metal cathode for the purpose of solution purification has been patented (196). A method of separating electroactive gases such as oxygen and hydrogen at catalytically activated electrodes has been described (10). Zebreda and Kozlovskii (339) have discussed, in some detail, the separation of metals as amalgams by electrolysis. Anodic oxidation of the amalgams and intermetallic compound formation was discussed. A novel method of simultaneous electrodeposition and spectrochemical excitation at a rotating copper disk has been described (324). In this technique electrodeposition of the metals from a KCl solution occurs at the edges of a varnished copper disk

Table I. Electroseparations and Electrogravimetric Determinations

Separation of	From	Method	Reference
Co	Ce, Pu	Electrodeposition of Co at controlled potential	(68)
Co, Ni	Bi, Cu, Pb, Cd, Sb	Electrodeposition on Pt electrode using internal electrolysis with Zn anode	(173)
Cu	Na, Cd, Zn, Al, V, Mo, Mn, Fe, Co, Ni	Investigation of optimum conditions for electrodeposition	(40)
Cu	Rare earths	Electrodeposition of Cu from HNO_3 solution prior to spectrophotometric analysis of rare earths	(307)
Mn		Electrodeposition on Hg cathode from H_2SO_4 - Na_2SO_4 medium	(86)
Pb	Th, U	Electrodeposition of Pb prior to spectrophotometric determination of Th and U	(284)
Pb	Th	Electrodeposition of Pb on platinized Cu cathode at controlled potential	(23)
Ru	Fission products	Electrodeposition of Ru on Pt cathode from 0.1M HCl solution	(134)
Sb		Electrodeposition on vibrating electrode from H_2SO_4 medium	(76)
Se		Investigation of electrolysis of SeO_2 in H_2SO_4 solution	(218)
Se, Te	Many metals	Electrodeposition on Ni-plated Pt cathode by internal electrolysis employing Zn anode	(172)
Ag, Bi, Cu, Cd, Pb, Sb	Many metals	Investigation of separation by internal electrolysis with various anodes in media containing different complexing agents	(170, 171)

rotating at 5 rpm. This is followed by spark excitation and recording of the emission spectra. A cell designed for the electrodeposition of radioactive isotopes on metal foils has also been described (340). Table I summarizes other work in electroseparations and electrogravimetric methods.

CONTROLLED POTENTIAL COULOMETRY

Determinations. The differential controlled potential coulometric technique, in which electrolysis is carried out in two identical cells connected in series, one containing the sample and the other a known amount of the

substance, has found additional application. Goode and Herrington (87) applied the method to the determination of U by reduction of U(VI) at a Hg electrode in H₂SO₄ solutions. They found that extreme care was necessary in the application of the technique, but that standard deviations of 0.009% were obtainable for 30- to 120-mg amounts of U. The differential coulometric method combined with radioisotope dilution can also be employed (156, 224). In this technique, an equal amount of a radioactive isotope is added to both the sample and standard electrolysis cell (e.g., cadmium-109 for determination of Cd). After a given electrolysis time, not necessarily that needed for completion of the electrolysis, the difference in radioactivity in the sample and standard cells can be employed to calculate the amount of unknown. Using this technique with electrolysis times of 300 sec to 35 min, 3- to 400- μ g amounts of Cd were determined with errors below 1%.

An *in situ* coulogravimetric study of the oxidation of an Ag electrode in 1M KOH has been described (157); similar techniques could prove useful in analysis. Two applications of controlled potential coulometric monitoring of the effluent of ion exchange columns have been reported (302, 303). The apparatus consists of an eluent reservoir, an oxygen removal chamber, the separation column, and an electrolysis cell equipped with a working electrode of large surface area. When an Ag working electrode was employed, halides, CN⁻, SCN⁻, Fe(CN)₆⁴⁻, Fe(CN)₆³⁻, S₂O₃²⁻, and S²⁻ could be determined in amounts of several to hundreds of micrograms (302). Peters and Caldwell (226) employed controlled potential coulometric methods both in the preparation of standard Cu(I) solutions in a bromide medium by reduction of Cu(II) at a Pt electrode and for analysis of the solutions of Cu(I), in a study of the solubility of CuBr in NaBr solutions. Lingane (167) demonstrated that successful coulometric determinations can be performed even in the presence of perturbing side reactions involving the solvent. He found that in the electroreduction of Ba(II) on a Hg electrode, some direct reduction of water and some reaction of the Ba amalgam with water occurs. The extent of these side reactions was determined by analysis for the Ba(II) and the hydroxyl ion in solution after electrolysis. Van Lente (320) described a student experiment in coulometry involving connection of silver, iodine, and hydrogen-oxygen coulometers in series. Other controlled potential coulometric determinations are summarized in Table II.

Electrode Mechanisms. Controlled potential coulometry continues to

Table II. Controlled Potential Coulometric Determination

Substance determined	Method	Reference
Ag, Au, Pt, Pd	Determination in Pd alloy; coulometric reductions in ammoniacal or phosphate media	(304)
Ag, Au	Thin layers on Cu plate determined by anodic dissolution followed by reduction on Hg electrode in KCN medium	(201)
Am	Electrolytic oxidation Am(III) \rightarrow Am(VI), followed by coulometric reduction to Am(V) at Pt electrode	(138)
Ba	Ba(II) \rightarrow Ba amalgam at Hg cathode from aqueous 0.5M tetraethylammonium iodide solution in presence of Sr(II)	(167)
Cd	Cd(II) \rightarrow Cd(0) in microgram amounts by differential, isotope dilution technique	(156, 224)
Cd	Deposition of Cd on Hg electrode followed by coulometric oxidation of amalgam in 0.1M HClO ₄ in presence of Bi	(216)
Cd, Pb, Sn	Reduction of Cd(II), Pb(II), and Sn(IV) on Hg electrode followed by coulometric oxidation	(331)
Cu	Nanogram amounts of Cu(II) determined by coulometric reduction on Hg electrode	(102)
Eu, Yb, Sm	Reduction of Eu(III), Yb(III), and Sm(III) to II state at Hg electrode in acetonitrile	(62)
Fe(CN) ₆ ⁴⁻	Fe(CN) ₆ ⁴⁻ \rightarrow Fe(CN) ₆ ³⁻ at Pt electrode in KCl medium	(272)
Fuel gases, O ₂	Electrolysis at fuel cell-type electrode containing Pd or Pt black	(305)
Pu	Pu(III) \rightarrow Pu(IV) at Pt electrode after NH ₄ H ₂ SO ₄ fusion of refractory Pu-containing materials	(189)
Pu	Review of methods and interferences	(229)
Ru	Reduction of RuCl ₆ ²⁻ in presence of other Pt metals	(288)
Se	Reduction of Se(IV) at Hg electrode in 0.2M HCl or 0.5M citric acid medium	(314)
Te	Reduction of Te(IV) at Pt electrode in presence of Se(IV)	(6)
U	Review of methods U(VI) \rightarrow U(IV) in H ₂ SO ₄ at Hg electrode by differential method Determination of U-oxygen ratio in U oxides by coulometric reduction followed by oxidation with Ce(IV)	(126) (87) (141)
U, Np	Reduction following oxidation with Ce(IV) in H ₂ SO ₄ medium at Pt (Np) or Hg (U) electrode	(231)
U, Fe	Analysis of Pu-UC-Fe cermets	(188)
ORGANIC SUBSTANCES		
Aliphatic amides	Oxidation ($n = 1$) of primary, secondary, and tertiary amides at Pt electrode in 0.2M LiClO ₄ -acetonitrile medium	(213, 214)
Catechol	Oxidation ($n = 2$) at Pt electrode in 1N H ₂ SO ₄ at 3° C	(254, 273)
Nitroso compounds	Reduction of several compounds to amines ($n = 4$); cupferron also reduced ($n = 6$)	(233)
Nitro compounds	Reduction in dimethyl sulfoxide-0.5M LiCl at Hg electrode ($n = 4$ or 6)	(165)

find application in the elucidation of the mechanisms of electrode reactions. Van Loon and Page (321) showed that coulometric reduction of Ir(IV) in alkaline solution occurs in a one-electron reaction. The oxidation of Pt-(NH₃)₄²⁺ in the presence of chloride or bromide at a Pt electrode was investigated (184). The oxidation yields Pt-(NH₃)₄X₂²⁺ (X = Cl⁻ or Br⁻) in an uncomplicated two-electron reaction; the oxidized species is also reducible to the ammine complex. Hubbard and Anson (113) studied the reduction of PtCl₆²⁻ and PtBr₆²⁻ and the oxidation of PtCl₄²⁻ and PtBr₄²⁻ by coulometric experiments in a thin-layer cell. The reduction was shown to occur by a two-electron reaction, without any evidence of a Pt(III) intermediate, as had been previously reported. The reduction of uranyl peroxydicarbonate in Na₂CO₃ solutions at Hg electrodes occurs in an irreversible reaction with $n = 3$ to a U(V) carbonate complex (343). Coulometric experiments were used to study the electroreduction of the bis- and tris-2,2'-bipyridine complexes of Cr(III) at a Hg electrode (315). Stepwise reduction reactions are suggested, but the results are complicated by the presence of different species in sluggish equilibrium and by following disproportionation reactions. The coulometric reduction of glyoxalbis(2-mercaptoanil)-nickel in dimethylformamide (DMF) was shown to occur in a one-electron reaction; the product of a macro-scale electrolysis was the same as that obtained by reduction with sodium amalgam (155).

Coulometric techniques also proved useful in investigating organometallic compounds. Morris (198) showed that the reduction of the aquadiethyl tin(IV) cation in HCl or KCl solutions at a Hg electrode occurs with $n = 1.99 \pm 0.03$. Because the polymeric product coats the electrode surface, electrolysis times were quite prolonged. The coulometric reduction of dicyclopentadienyl titanium(IV) dichloride in various aqueous electrolyte solutions at a Hg electrode was investigated by Valcher and Mastragostino (319); they demonstrated that $n = 1.15 \pm 0.18$ for the reduction. Bednarski and Jordan (30) studied the reduction of ferriheme in various aqueous buffers. They found that reduction occurs in a two-electron reaction to either ferro monomer or dimer, depending upon the pH. Fused salt processes have also been investigated. The reduction of trimetaphosphate in a LiCl-KCl eutectic at a Pt electrode was shown to involve 1.95 faradays per mole of PO₃⁻ (154). The reduction of Nb₅Cl₅ in molten alkali chlorides was said to occur in two consecutive, two-electron steps (249).

Interest in organic electrode reactions in both aqueous and nonaqueous solu-

tions still continues. The reduction of anthracene and 9,10-diphenylanthracene in DMF solutions was shown to occur to the fairly stable anion radicals in one-electron reactions, when sufficient care was taken with purification of the solvent and vacuum line techniques were employed (253). Reversal coulometry was used to study the stability of the anion radicals; reduction to the dianion and in the presence of such proton donors as hydroquinone was also described. The coulometric oxidation of aromatic hydrocarbons in methylene chloride at a Pt electrode was shown to occur by an initial one-electron abstraction to the cation radical (227). When the hydrocarbon was substituted in positions of high charge density—*e.g.*, rubrene or 9,10-diphenylanthracene—the cation radical was fairly stable. For unsubstituted hydrocarbons—*e.g.*, tetracene and anthracene—fast following reactions occur, and larger n -values are observed. The electrochemistry of alkali metal cyclopentadienides in DMF was shown to involve one-electron transfers and reaction with the Hg electrode (185).

Nitrogen-containing organic compounds of several types were investigated. The oxidation of several aromatic amines in acetonitrile (AN) has been investigated (73). Rao and Meites (241) used coulometric techniques in their study of the oxidation of hydroxylamine in alkaline solutions. The oxidation of persantine in AN solution was shown to involve a one-electron reaction producing the cation radical (153). O'Donnell and Mann (213, 214), in a detailed investigation of the oxidation of aliphatic amides in AN, found that the reaction proceeds by a one-electron transfer followed by a fast following reaction with solvent, finally yielding protonated amide and succinonitrile. The separation of the oxidation potentials of primary, secondary, and tertiary amides was large enough to permit differentiation of these in analysis of mixtures. Phenazine and its mono-*N*-oxide were investigated in aqueous solution at several pH's (202). Phenazine was reduced in two one-electron steps in acidic solutions, with formation of a green molecular complex of phenazine and dihydrophenazine as an intermediate. The reduction of benzylidene methylamine *N*-oxides (nitrones) is said to occur by a four-electron process in aqueous solutions (149). Several studies involving coulometry of nitro compounds have appeared. Lindbeck and Freund (165) investigated the reduction of nitrophenols, nitrobenzoic acids, nitroanisole, and nitrotetraphthalic acid in dimethyl sulfoxide (DMSO) solutions containing 0.5M LiCl. Electrolysis on the final reduction wave yielded integral n_{app} -values of 4 or 6 and a procedure for the deter-

mination of micromolar amounts of the compounds with an error of about 1% was described. Coulometric techniques were used in a study of the effect of proton donors, such as *o*-phthalic or trichloroacetic acids, on the electroreduction of *p*-chloronitrobenzene (53). The electroreduction of nitrobenzenes in liquid ammonia solutions has also been studied and mechanisms for the reactions have been proposed (100).

The mechanism of catechol oxidation in H₂SO₄ solution was investigated (273). The suggestion, made in connection with this and other oxidations, that the product of the current and the electrolysis time may be a useful function for characterizing coulometric processes (255) does not seem to be well-taken, however. The coulometric electroreduction of furazan and furoxanes in aqueous ethanolic and DMF solutions at a Hg electrode has been reported (164). Coulometric reduction of quinoxaline, formed by *in situ* reaction of glyoxal and *o*-phenylenediamine, in an alkaline ethanolic solution was shown to proceed by a reversible two-electron reduction; the high precision of the coulometry suggests that a practical analytical procedure based on these reactions is possible (200). Coulometric oxidation at a boron carbide electrode was employed to generate the phenoxyl radicals of 2,4,6-tri-*tert*-butylphenol and 2,6-di-*tert*-butyl-4-phenylphenol (206).

Several coulometric reductions of halogen-containing compounds have been described. Covitz (66) showed that the reduction of α,α' -dibromo-*p*-xylene involves 2 faradays per mole. Controlled potential electrolysis was also employed in a study of the stereochemistry of the electroreduction of cyclopropyl bromides (11). Mooney and Stonehill (197) studied the reduction and reoxidation of all eight of the monohalogenated 9,10-anthraquinones in an alkaline ethanolic medium at a Hg electrode. Coulometric reduction and reoxidation involved 2 faradays per mole for all of the anthraquinones, except for the 1-iodo derivative, in which some dehalogenation occurs. Two studies involving coulometry of the insecticides dieldrin, endrin, and β -chlorodane have been made (60, 61).

The kinetics of the electrochemical oxidative coupling of decahydrocyclo-decaborate (B₁₀H₁₀²⁻) in AN was investigated using coulometric techniques (186). The electroreduction of tris(*p*-nitrophenyl) phosphate in DMF was shown to involve a four-electron reaction, with a cleavage reaction leading to 4,4'-dinitrobiphenyl (256). Geske (84) reported an investigation of the oxidation of picrate ion in AN; the short-lived picryl radical was shown to decay by at least two different reactions.

Haynes and Sawyer (101) studied the reduction of CO₂ in DMSO at Au and

Hg electrodes; the mechanism of the reaction was dependent upon potential and water content and involved CO_2^- and CO_3^{2-} as intermediates, which could undergo disproportionation reactions. The electroreduction of oxygen in DMSO solution was the subject of two studies. Sawyer and Roberts (257) provided coulometric evidence for the reduction of O_2 to O_2^- and O_2^{2-} at Pt and Hg electrodes. Johnson, Pool, and Hamm (122) showed that the potential of the one-electron reduction to O_2^- is shifted in the presence of several metal ions, because of formation of metal-superoxide compounds.

Mason (183) considered controlled potential electrolyses in which the product of the initial electron transfer process is electroactive at these potentials (the ECE-mechanism). He found, contrary to a previous treatment, that in the true mass transport limiting region no appreciable amounts of intermediate appear in the bulk solution and log current-time curves are linear. Ducret and Cornet (71) proposed the use of the thermal convection electrode in coulometric experiments. With this electrode, the mechanical convection usually employed in bulk electrolysis methods is replaced by thermal convection induced by maintaining a temperature gradient between the electrode and the solution. Although successful coulometric determinations of Cu(II) and Fe(II) were carried out at an indirectly heated Pt electrode, this technique will probably prove useful only in very special circumstances.

CONTROLLED CURRENT COULOMETRY— COULOMETRIC TITRATIONS

Determinations. Interest continues in high precision coulometric titration and the establishment of the coulomb as the standard for volumetric work. Marinenko and Taylor (178) presented detailed studies of the current-potential curves for iodide ion oxidation at a Pt electrode in a pH 7 buffer and showed that the current efficiency for iodine generation is greater than 99.9999%. Standard 0.5-gram samples of As_2O_3 were analyzed with a standard deviation of 0.003%. Cooper and Quayle (64) showed that coulometric titrations of 3- to 30-gram samples of pure Na_2CO_3 agree with the best volumetric determinations to within 10 ppm. The high precision titration of dichromate ion with electrogenerated Fe(II) has been suggested for the calibration of microburets (179).

Several novel titrants and coulometric procedures have been proposed. Quinone, electrogenerated from hydroquinone at Pt electrode in an H_2SO_4 medium was used as an oxidant (311). Tutundzic and Stojkovic described the

Table III. Electrogenerated Titrants and

Electrogenerated titrant	Substance determined	Reference
OXIDANTS		
Bromine	Phenols	(152, 232, 260)
	Piperidine	(306)
	Beryllium, after separation from Ga or Al	(143)
	Iron(II)	(145)
	Aluminum(III) (by precipitation with, and titration of, 8-hydroxyquinoline)	(142, 145)
	Sulfite ion	(342)
	Phosphites	(182)
	S compounds	(234)
	S-containing gases in kraft mill emissions	(2)
	SO_2 and H_2S	(19)
	SO_2 , H_2S from gas chromatography column effluents	(1)
	Bromine number determination	(27)
	Arsenic(III)	(58)
	Cyclic β -diketones	(123, 124)
Hexaorgano-ditin compounds	(300)	
Iodine	SO_2 and H_2S	(19)
	S compounds	(234)
	S in iron and steel by conversion to SO_2	(24)
	Hexaorgano-ditin compounds	(300)
Iodine	Arsenic(III)	(178, 337)
	Hypochlorite, by reaction with arsenic(III) and titration of excess	(147)
Hypobromite	Hydrogen peroxide	(77)
	Selenium(IV) and tellurium(IV)	(5)
	Proteins	(56)
Iron(III)	Titanium(III)	(274, 275, 277)
	Chromium(II), vanadium(II), molybdenum(III)	(276)
Cerium(IV)	Uranium(IV), by reaction with iron(III) and titration of iron(II)	(88)
Permanganate ion	Iron(II)	(142, 312, 316)
	Antimony(III) in sulfur and selenium	(142)
Quinone	Titanium(III), vanadium(II)	(311)
REDUCTANTS		
Titanium(III)	Rhenium(VII)	(269)
	Ruthenium(IV)	(285)
	Iridium(IV), ruthenium(IV)	(287)
	Molybdenum(VI)	(336)
	Iron(III)	(278)
	Manganese(III)	(131)
Copper(I)	Iron(III)	(166)
	Iridium(IV)	(286)
	Gold(III)	(313)

generation of Bi(III) (317) and Pb(II) (318) by anodization of the metal electrodes, and the use of these for the precipitometric determination of a number of anions. Blackburn and Greenberg (39) described the generation of hydrogen ions in aqueous or methanol solutions by passage of hydrogen gas through, and oxidation at, palladium membrane electrodes. Sinicki (271) proposed possible coulometric applications in a study of the iodide-iodine system in DMF. A study of the current efficiency of peroxydisulfate ion generation at a Pt electrode (108) suggested that a coulometric titration based on this reaction might be possible. However, preliminary attempts to generate peroxydisulfate as a titrant by Dr. Joe Sadler in the author's laboratory did not show good current or titration efficiencies. Several new applications of

the Karl Fischer coulometric titration have been described (38, 219, 334).

End point detection methods in coulometric titrations have been the subject of several papers. Christian (57, 58) recorded amperometric titration curves and demonstrated that nanogram amounts of substances could be determined by relating the change of the amperometric current level to the rate of change of indicator current with time during electrogeneration of titrant. Ariel and Kirova-Eisner (12, 13, 130) have presented detailed discussions of coulopotentiometric acid-base titrations involving mercury or mercury-coated electrodes. Alexander and Barclay (9) have proposed a new amperometric end point technique, involving two generator electrodes in the sample compartment. The generating current is di-

Substances Determined by Coulometric Titration

Electrogenerated titrant	Substance determined	Reference
Iron(II)	Manganese(III)	(131, 312, 316)
	Chromium(VI)	(59, 179, 316, 337)
	Uranium(VI), by conversion to uranium(IV), reaction with dichromate and titration of excess Molybdenum(VI)	(174)
Molybdenum(V)	Cerium(IV), vanadium(V), chromium(VI), permanganate, peroxydisulfite, iodate, ferricyanide	(7)
Iodide ion	Selenium(IV)	(78, 114, 335)
PRECIPITATING AND COMPLEXING AGENTS		
Silver(I)	Chloride ion, trace amounts in acids	(3, 4)
	Organic chlorides or bromides, by combustion and titration of halide	(194, 195)
	Bromide ion	(112, 128)
	Iodide ion	(50)
	Tetraphenylborate ion	(44)
	Alkaloids and organic base, by precipitation with, and titration of, tetraphenylborate ion	(222)
	Sulfide ion	(223)
Mercury(I)	Hexaorgano-ditin compounds	(51, 52)
	Potassium xanthate	(300)
Lead(II)	Chromate, dichromate, oxalate, molybdate, tungstate, ferrocyanide ions	(125)
	Phosphate ion	(318)
Bismuth(III)	Thorium(IV)	(317)
EDTA ^a	Silver(I)	(89)
Sulfide and thiocyanate ions		(79, 80)
ACIDS AND BASES		
Base	CO ₂ , titration in acetone containing methanol	(330)
	Oxygen in metals, by conversion to CO	(91)
	Copper(II), by titration of H ⁺ liberated at anode during reduction	(193)
	Manganese(II) by titration of H ⁺ liberated during electro-oxidation	(191, 192)
	Salts, by passage through cation exchange resin	(208, 209)
	Organic acids in sugars separated by passage through anion exchange resin	(42)
	5,5-Diethylbarbituric acid	(215)
Acid	Sodium carbonate	(64)
	Standard base	(39)
	Organic nitrogen compounds, conversion to NH ₃ following gas chromatographic separations	(181)

^a Ethylenediaminetetraacetic acid.

vided between the electrodes by adjustment of resistors in series with each so that the voltage difference between the two is maintained constant. The smaller current through one of the electrodes is proportional to the ion being determined and may be employed for end point detection. Radiometric end point detection in coulometric titrations, such as the titration of iodide labeled with iodine-131 with electrogenerated silver ion, has been described (44). A discussion of the accuracy of end point detection methods, including a comparison of coulometric and other titration methods, has been given (322).

Durst and Taylor (72) have employed constant current coulometric generation of silver ion in the reference half cell in a null point potentiometric determination of Ag(I). Coulometric base

generation was employed in a determination of the pK of 5,5-diethylbarbituric acid in aqueous dioxane solutions (215). Coulometric techniques can also be employed in the preparation of solutions of known pH (207). A method of determining carbon based on conversion to CO and automatic coulometric titration has been described (28). Several anodic stripping methods have been proposed.

Manuele (177) described a cell suitable for the determination of tin plate. A KF electrolyte was suggested for the measurement of the thickness of Ag deposits on Cu wires (203). Stupak and Dmitrenko (294) described the procedure and apparatus for determination of coatings of Ni on a Cu base and Cd on an Fe base. Other coulometric titrations are summarized in Table III.

Measurements of Reaction Rates.

The application of coulometric titrations and related techniques to the study of the rates of homogeneous chemical reactions has been developed further. Cover (65) discussed the application of programmed stresses, equivalent to programmed generating currents in coulometric titrations, as opposed to constant ones, to the study of homogeneous chemical reactions. The application of analog computers to the study of reactions involving electrogenerated titrants has been reported (120, 121). By employing the analog computer to simulate the amperometric indicator current during constant current generation of the titrant, rate constants for quite complicated reaction schemes can be determined. The technique was employed to study the kinetics of the reactions of organic sulfides with electrogenerated bromine in an aqueous acetic acid medium. The kinetics of bromination of some 8-quinolines (212) and of iodination of tetra-organo lead compounds (244) have been studied using constant current generation of the halogens. Smith and Downing (279) used the electrogenerated reagent to introduce a competitive reaction. For example, they measured the rate of the reaction of two components, A and B, by generating a substance which reacts with A in a fast reaction. The rate of the A-B reaction is determined from the time required for the disappearance of A with and without B in the solution. The technique was used to study the rate of reaction of methyl bromoacetate with S₂O₃²⁻, using external generation of iodine and amperometric detection. Carr and Meites (55) studied the rate constant of the disproportionation of U(V) by titration of U(VI) with Cr(II) added at a constant rate using amperometric end point detection; the procedure and theoretical treatment involved in this study is the same as that for coulometric generation of the titrant.

Continuous Coulometric Titrations. A continuous coulometric analyzer in which the end point is sensed photometrically is described in a Czechoslovakian patent (70). With it the continuous determination of SO₂ in air was accomplished with electrogenerated iodine, in a solution containing starch as an indicator. The method was said to be more reliable than systems involving electrometric detection methods. An analyzer for continuous determination of HCN in the atmosphere by titration with electrogenerated bromine and employing amperometric detection has been described (290). Two methods for the determination of ammonia vapor or other alkaline materials have been described. In one method the NH₃ is titrated with hydrogen ion generated at a Pt anode, with potentiometric detec-

tion using Sb and calomel electrodes (264). Sambucetti (252) describes a coulometric method in which the reaction of the alkaline component at an Al electrode in an unbuffered Na_2SO_4 solution occurs. Because a large area Al electrode is employed, Faraday's law is obeyed and the current is proportional to the concentration of NH_3 or hydroxyl ion. Automatic coulometric determinations of carbon in steel have also been described (48, 295). Several recent patents are concerned with modifications in cell design in continuous coulometric titrators (117, 161, 291, 292).

Galvanic and Gas Analyzers. The importance of the determination of dissolved and gaseous oxygen has led to a number of patents and papers on electrolytic oxygen analyzers. Most of these retain the basic design of a cathode of Au, Ag, Pt, or other inert material at which oxygen is reduced, and usually an expendable anode, such as Cd, Pb, and Zn. A plastic membrane, permeable to oxygen but not many other solution components, is often applied to the cathode surface. The modifications involve improvements in cell design, efficiency of oxygen reduction, response time, sensitivity, electrolyte composition, anode and cathode materials, and separators and temperature stability (8, 20, 21, 33, 81, 94, 95, 103-105, 109, 116, 118, 129, 135, 136, 140, 162, 168, 169, 176, 204, 228, 245, 247, 280, 282, 309, 310, 323). A high temperature oxygen gas sensor employing a solid Ca-Zr oxide electrolyte and porous metallic electrodes has been designed (289). A solid electrolyte was also used in sensor for the continuous measurement of oxygen in liquid sodium (139). Hillman and Lightwood (110) used an oxygen cell as a detector in gas chromatography, allowing determination of oxygen in the presence of such compounds as organic sulfides which might interfere in the usual cell. A method for determining oxygen based on catalytic conversion to H_2O and electrolytic decomposition of water has been described (83). This method can also be applied to the determination of hydrogen (83, 327).

The coulometric hygrometer, based on electrolysis on a P_2O_5 -Pt system, was employed to determine trace amounts of water in hydrocarbons (235). The electrolytic hygrometer was also used in an instrument designed for the determination of dehydration temperature in solids (217). In this instrument, a solid sample, such as a rock, is heated in a nitrogen stream with an increasing temperature; when the dehydration temperature is reached, water is evolved from the sample and is detected and recorded. Two ozone analyzers based on oxidation of bromide ion to bromine which is then reduced at a Pt electrode have been described (106, 248). A

similar principle is involved in a CO detector in which the iodine generated in the reaction of CO with I_2O_5 is reduced at a Pt electrode (29). Reduction of NO_2 at a Pt electrode has also been used in an analyzer for NO_2 or NO (107). Hyman (115) described a cell used for detecting saturated aliphatic hydrocarbons with up to six carbon atoms, based on the reaction of the hydrocarbons with chlorine generated at a Pt electrode. A detector for oxidizable substances in a gas stream, employing a fuel cell-type anode material bonded to an ion-exchange membrane has been patented (22). Coulometric methods have also been used for calibration of gas analyzers. Electrogenerated iodine was employed in an ozone and SO_2 analyzer (262) and CO_2 , electrogenerated by oxidation of oxalic acid, used in a CO_2 analyzer (238).

APPARATUS

Interest continues in the effects of cell geometry and characteristics and reference electrode placement on the response and behavior of potentiostats and the potential distributions in electrochemical cells. Harrar and Shain (99) discussed how the geometric placement of the working and counter electrodes affects the current and potential distributions through the cell and reviewed methods used for calculating these distributions. They showed, for example, that in the electroreduction of Ir(IV), improper placement of the reference electrode or counterelectrode can cause the potential of the working electrode surface to be more negative at certain places, causing undesirable side reactions. They concluded that consideration of the geometry of the cell may be important in separations or determinations which involve close potential control. As a general rule, the reference electrode should be placed on the line of minimum separation between the counter and working electrodes. Several studies have been concerned with the determination and effects of uncompensated resistance, the resistance between the working electrode and the tip of the reference electrode (46, 159, 205). These uncompensated resistance effects are especially important in electrolysis in nonaqueous solvents and where very high currents are employed. Methods of compensation involving positive feedback to the potentiostat input are rather simple to employ and will probably be used more frequently (46, 159). A paper by Booman and Pence (225) concerned with considerations of potentiostat and cell design for rapid response times is also of interest.

Janata and Mark (119) have described a flow cell which is useful for simultaneous coulometric, polaro-

graphic, and spectrophotometric measurements. The cell employs nitrogen gas to pump the sample solution between three separate subcells. A microcell of 2-ml volume for controlled potential coulometry has been described (127); microgram quantities of Fe, U, and Pu were determined in it. Eckfeldt has received a patent on his previously described continuous coulometric flow cell (74).

Coulometric Titration Apparatus.

Pike and Goode (230) have described a precision constant current source and timer which provides 11 currents, from 250 μA to 200 mA with an accuracy for coulombs delivered of better than 30 ppm. Quayle and Cooper (240) discuss a similar instrument with current capabilities of up to 2 amperes and an accuracy within 25 ppm. Several automatic coulometric titrators, which automatically terminate the titration at the end point, have been described (17, 54, 163, 266, 332). These usually employ amperometric or photometric end point detection, and often include end point anticipation circuits and means of resuming the titrations for slow titration reactions. A completely automatic titrator for determination of free acidity in process solutions has been designed (332). The entire titration, including waste disposal and data presentation, was carried out automatically by use of a sequential timer. The titrant was generated externally and the end point detected photometrically. An automatic coulometric titrator for extremely slow acid-base reactions employing potentiometric end point detection has been described (69). Salzer (251) described a combustion apparatus for C-H analysis which employs coulometry to determine the hydrogen.

Potentiostats. New designs of potentiostats have been concerned mainly with improvements in response time, stability, output current and voltage, and conversion to all solid state components. Several papers were concerned with factors important in the design of potentiostats (36, 225, 239, 297). Several circuit modifications, such as the use of hybrid open-loop, closed-loop techniques (36) or the interposition of a "pre-emphasis" (R-C-diode) network (297), are proposed to reduce response times of the potentiostats. Several new potentiostats have been designed to provide high output currents. Bewick and Brown (35) described two solid state potentiostats, one with an output of 4 amperes at ± 40 volts and the other with 100 amperes at ± 20 volts. The rise time of these instruments was very fast (below a microsecond into reasonable loads) and the stability was good; they seem very well suited to large scale electrochemical studies in organic chemical systems.

Conger and Riggs (63) described a potentiostat with good control precision and long term stability and with an output of -10 to $+5$ amperes at 10 volts and ± 5 amperes at ± 20 volts. A potentiostat incorporating a motor generator and capable of a 12-ampere output has been constructed (246). Grimshaw and Quigg (92) have modified a previously reported servomechanism potentiostat by incorporation of a new balancing circuit and improved gain and linearity in the servoamplifier. Tacusel (296) has listed the characteristics of two potentiostats: one with a 50-ampere-10-volt output involving 12 vacuum tubes connected in parallel in the output stage and the other with a 10-ampere-20-volt output and a transistorized output stage. Insufficient details are given in this paper to allow construction of the potentiostats, however.

Several studies have been concerned with the design of all solid state potentiostats. Goolsby and Sawyer (90) employed Philbrick P-65 A control amplifier and either P-66 A (± 100 mA at ± 10 volts) or 6154 (± 10 mA at ± 100 volt) boosters. Harrar and Behrin (98) discussed a modular unit with a Philbrick P-2A control amplifier and a transistorized booster with output capabilities of ± 400 mA at ± 24 volts; a Zeltex 143 operational amplifier was employed in the integrator module. A transistorized potentiostat with an output of ± 1 ampere at ± 20 volts was also discussed (298). Tackett and Knowles (299) describe a simple, all solid state potentiostat especially well suited for student use. Although the output characteristics are rather modest, 2 amperes at 5 volts, the total cost of parts for the instrument, which includes a VTVM and ammeter, is only \$135. A number of other potentiostats, mostly designed for corrosion or metallurgical studies have also been described (18, 34, 132, 259, 267, 268, 283). Two new current integrators, one based on improvements in the design of a Solion cell (25) and the other for use with high currents for long time periods (49), have been constructed.

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Electrophoresis

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THE LITERATURE MENTIONED in this review has been selected from material appearing in approximately a thousand journals published in every part of the world. Even with an excellent library service it has been impossible to locate significant papers at the time of their publication. It has usually been necessary to await their citation in *Chemical Abstracts*, and often to depend solely upon the abstracts for information about the contents of the articles. This is unfortunate because abstracts are frequently inadequate, and because the long delay before their appearance makes the review less current than it should be. Readers are invited to send reprints of their recent publications relating to electrophoresis to the author at the address appearing beneath the title of this review. It would also be helpful to receive summaries of the important points in the papers; summaries would preferably be in English but arrangements have been made for obtaining translations. If this is done on a sufficiently large scale, it will do much to improve the quality and timeliness of this review. Sending a reprint will not guarantee a place in the bibliography, which is selective, but all reprints received will be given careful attention.

The terminology of electrophoresis is stabilizing and now requires little attention. It seems to be generally accepted that *electrochromatography* should refer only to operations in which both electrophoretic and chromatographic effects are used. The need for a verb denoting the performance of electrophoresis is being filled at this time by a new infinitive, "to electrophorese," a word lacking euphony and employing a suffix that is properly used to form adjectives or nouns of origin (e.g., Japanese); *to electrophorese* is preferable because *-ize* is a verb-forming suffix meaning "to subject to."

This review continues the coverage of the previous one (2329) with most of the citations dating between the latter half of 1965 and the early part of 1967. The *Chemical Abstracts* reference numbers have been appended whenever the article mentioned has appeared in a publication that is not readily accessible.

BOOKS AND REVIEWS

There are several books devoted to general electrophoretic methodology (1716, 2103, 2698); one book attempts, with some success, to cover the whole field of analysis by differential migration methods (965); there is a teaching manual for electrophoresis and chromatography (2273). Three books discuss the clinical value of electrophoresis (596, 1995, 2099). Books on specialized applications include one on cell electrophoresis (70), one on crossing electrophoresis (1693), and one on lacquer deposition (2564). Important chapters on electrophoretic techniques (240, 2331), including mobility measurements (2537), amino acid determinations (263), and the significance of findings in serum protein electrophoresis (1262) appear in books that include other subjects.

Current theories relating to electrophoretic mobility (639) have been reviewed, as have the general aspects of technique (90, 1553), particularly with reference to biochemical applications (1793), immunochemistry (885), and the transportation of substances by plasma proteins (465). The methods for using polyacrylamide gels (1095, 1643, 1762, 1763, 1973), starch gel (179, 1011, 2338), thin layers (510, 1760, 1761), and gels made up in buffers containing urea (1899) have been reviewed. A number of reviews are concerned with clinical applications of electrophoresis to serum proteins (486, 814, 1255, 1256, 1379), immunoglobulins (752), and hemoglo-

bins (47, 2164, 2345); and with biochemical studies of carbohydrates and mucoids (1739), glycoproteins (2218), lipoproteins (218, 2130), amino acids (633, 1830), peptides (436, 1647), proteins and their subunits (1897), eye lens proteins (271), and enzymes (2205), including hemolysins (1890) and lactic dehydrogenases (2132, 2505). There are also reviews concerned with proteins in snake venoms (556), the electrophoretic behavior of cells (71), the components of cells and tissue (883), separation of viruses (1493), the composition of saliva (1453), and transformations of antibiotics in vivo (270). Uses of electrophoresis in radiochemistry (23, 1257), pharmacy (2508), and industry (1614) have been discussed. A list of reviews dealing with the use of electrophoresis for the application of coatings appears in the section on PARTICLE ELECTROPHORESIS.

FUNDAMENTAL DEVELOPMENTS

The synthesis of a mixture of polymeric amino-carboxylic acids having closely spaced isoelectric points over a wide pH range has made possible a new form of electrophoresis which has been named *isoelectric fractionation*. When a solution of the mixed amino-carboxylic acids is placed between electrodes, the solute molecules become classified into stationary zones in the order of increasing pI; proteins dissolved in the solution form immobile zones in the regions corresponding to their isoelectric points. It has been reported that proteins with isoelectric points differing by as little as 0.02 unit can be separated by this technique. A number of publications about this method are reported to be in press, and some are already published (733, 1813, 2507). An article in a commercial publication describes the method in some detail and indicates that it will soon