Electroanalysis and Coulometric Analysis

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THIS review mainly surveys the literature during 1960 and 1961, and is patterned closely after previous reviews in this series. Papers published before 1960 which have not appeared in previous reviews have also been included. Research has increasingly been concerned with a study of the fundamental electrochemical principles upon which electroanalytical procedures are based. The discussion of these theoretical electrochemical developments has been limited to areas which have the most direct bearing on electroanalysis. As a general trend of the past two years, coulometry continues to enjoy increasing development and application, while classical electrogravimetry has mainly been concerned with extension of previously developed methods.

BOOKS AND REVIEW ARTICLES

The book of Charlot, Badoz-Lambling, and Tremillon (*33*) discusses electrochemistry from the viewpoint of the analytical chemist. Extensive use is made of current-potential curves for explaining the basis of the various techniques. Chapters on coulometry, potentiometry, amperometry, and nonaqueous solvents, as well as an extensive bibliography, are included. Reinmuth has written a chapter on the theory of electrode processes for the new series "Advances in Analytical Chemistry and Instrumentation" (*160*). The text of Laitinen (*107*) includes a chapter on electrolytic separations and electrolysis, which gives a brief, but particularly lucid, discussion of the fundamental principles of electrolysis. Controlled potential electrolysis, as applied to organic chemistry, has been reviewed by Meites (*131*). Vetter has given a modern treatment of electrochemical kinetics in his recent book (*207*). A welcome addition to the growing list of chemical journals is the Journal of Electroanalytical Chemistry. This journal contains an abstract section, which provides up-to-date, extensive, abstracts on many phases of electroanalytical and electrochemistry.

A number of recent review articles have dealt with coulometry. Reilley (*159*) emphasized the importance of the appreciation of thermodynamic and kinetic features of electrode processes in the development of coulometric meth-

ods. The application of coulometric (and other electrochemical) methods to analytical problems in atomic energy work has been reviewed (*135*). The reviews by Barendrecht (*14*) (66 references) and Morris (*137*) (161 references) on coulometry, as well as one by Meites (*130*) on the application of controlled potential electrolysis to electrogravimetry, coulometry, and synthesis, deserve mention. Other reviews on various phases of coulometry have also appeared (*32, 110, 146, 183*).

ELECTROCHEMICAL THEORY

Platinum Oxide Films. A topic which continues to enjoy attention is the effect of oxide films on electrode reactions occurring at platinum electrodes. Previous work concerned with the evidence for oxide films on platinum electrodes has been reviewed by Laitinen and Enke (*108*). These authors also present new experimental work on the oxide films and offer possible mechanisms for their formation. While the existence of oxide films is undisputed, the effect of these films on electrode reactions remains controversial. Davis (*40*) studied the variation of the rate constant, k, and the transfer coefficient, α, of reactions occurring at a platinum electrode, with the extent of electrode oxidation. He concluded that a heavy layer of oxide suppresses the rate of an electrode reaction, but a film about 1 monolayer thick increased the rate of such electrode reactions as the oxidation of arsenic(III) or the reduction of vanadium(V), vanadium(VI), oxygen, and iodate ion. Anson previously had shown that iodate reduction proceeded more reversibly at oxidized electrodes (*5*). Lingane demonstrated that an oxide film hinders the oxidation of oxalate ion (*112*), but is necessary for the reduction of oxygen (*113*). No chronopotentiometric reduction wave for dissolved oxygen was found at a platinum electrode which was immersed several days in an oxygen-saturated sulfuric acid solution. This was ascribed to the dissolution of platinum oxide in the acidic solution. Sawyer and Interrante (*170*) concur that the reduction of oxygen occurred with less overpotential at a freshly oxidized platinum electrode, but assign increas-

ing irreversibility with time to "aging" of the oxide film. Both papers (*113, 170*) assume that the reduction of oxygen proceeds via a direct chemical reaction between oxygen and platinum, followed by electrochemical reduction of the platinum oxide(s). Apparently the rate or extent of the platinum-oxygen reaction in an acidic solution is sufficiently small that a prereduced electrode in an oxygen-saturated solution will maintain the characteristics of a reduced surface.

Anson has recently found that the reversibility of both the reduction of iron(III) and the oxidation of iron(II) is markedly decreased by the presence of an oxide film on the electrode (*4*). He further showed that some effects heretofore ascribed to the presence of an oxide film are actually caused by a film of platinized platinum formed when an oxidized electrode is reduced. It is this platinized platinum (rather than platinum oxide) which increases the reversibility of many electrode reactions. Contrary to some reports, Anson believes, as a general rule, that oxidation of a platinum electrode produces a decrease in the reversibility of oxidations occurring at the electrode. The nature of the electrode surface also affects rates of organic electrode reactions (*22*).

Other factors may certainly affect the behavior of platinum electrodes, and the absence of these effects must be assured before oxide film effects are invoked. Adsorption of surface active agents on an electrode is known to affect the rate of some polarographic reactions (*160*), and similar effects on platinum electrodes must be expected. Formation of metal hydrous oxide films when an electrode is cathodized may affect electrode behavior. Even the orientation of the electrode cystallites can affect the rate of electrode reactions. Nikulin (*142*) recently showed that the rate of oxygen reduction on a single crystal of silver depended on the crystallographic face upon which the reaction occurred.

EPR Spectroscopy. The past two years have witnessed a very rapid growth in the use of electron paramagnetic resonance (EPR) [also called electron spin resonance (ESR)] spectroscopy as a means of identifying free radical intermediates of electrode

processes. A knowledge of the electrode reaction mechanism is fundamental to the application of electroanalytical techniques such as controlled potential coulometry to organic determinations. Many, if not most, organic electrode reactions involve the addition or abstraction of a single electron as a primary step, causing the formation of a free radical. The presence of an unpaired electron on this radical suggested the use of EPR as a means of identifying extremely low concentrations (10^{-8} to $10^{-9}M$) of intermediate radicals, which usually continue to react in various secondary reactions. The first applications of the electrogeneration of radicals inside the cavity of an EPR spectrometer were made by Maki and Geske (118), who presented evidence for the production of $\cdot ClO_4$ radical during the electro-oxidation of lithium perchlorate in acetonitrile. In a subsequent paper (56) they described the electrogeneration and EPR spectra of the nitrobenzene anion radical, a fairly stable radical, and resolved the spectrum into the full 54 hyperfine components expected. The EPR spectra of radicals generated from a number of substituted nitrobenzenes have subsequently been described by Geske and Maki (56, 119, 120). Other electrogenerated radicals observed by EPR include the p-phenylenediamine positive ion radical (132), tetracyanoethylene derivatives (162), N-alkylpyridine radicals (173), and aliphatic nitro-negative ion radicals (154). Most work on the electrogeneration of radicals was performed in nonaqueous solvents, such as acetonitrile, dimethylformamide, or 1,2-dimethoxyethane (glyme) (86), mainly to avoid the large dielectric losses of water and other polar solvents in the EPR cavity. By using a specially constructed sample cell (now commercially available) and 100 kc. per second field modulation, Piette, Ludwig, and Adams were able to obtain spectra in aqueous solutions (153, 154), which aided in the elucidation of several electrode mechanisms. Recently Bard and Mayell used EPR spectroscopy to confirm a free radical intermediate in the electroreduction of quaternary ammonium compounds (13). Various diffusion and kinetic considerations in the EPR spectroscopic detection of electrogenerated free radicals were discussed by Geske (55). Continued interest in the mechanism of organic electrode reactions will lead to further application of EPR (and also visible and ultraviolet) spectroscopy to the detection and identification of free radical intermediates. It is possible that electroanalytical techniques for the determination of trace quantities of organic substances by EPR spectroscopic observation of electrogenerated radicals may be devised.

ELECTROSEPARATIONS

Electrolytic separation of radioactive isotopes by deposition on mercury or solid electrodes continues to enjoy application. Polonium was separated from other metals on a platinum or tantalum cathode (1). An internal electrolysis method for separation of polonium has also been described (204). A study of the effect of current density and various solution conditions on the electrodeposition of tracer quantities of the actinide elements from an NH_4Cl-HCl system was made by Mitchell (136). A similar study was performed by Samartseva (168). Plutonium was separated by deposition on a tantalum disk cathode (214). The separation of radium and barium at a mercury cathode by a constant current technique has also been described (102).

Further investigations of the electrolytic separations of the rare earth elements have also been made. Lanthanum-140 of 99.9% purity was prepared by constant current electrolysis of a Ba^{140}-La^{140} mixture in a perchlorate ion medium at a platinum cathode (64). More frequently separations are made at mercury or amalgam cathodes. The effects of current density and solution conditions in the separation of Ce^{144}, Pr^{144}, and Ho^{166} were investigated (167). The electroseparation of europium has also been described (181). Onstott has continued his investigation of the separation of the lanthanons at amalgam cathodes; especially by reduction at lithium amalgam cathodes in a citrate medium (148). In general, lanthanons showing a II oxidation state (Eu, Sm, Yb) are easily separated from those that show only a III state; so that separation of Yb from Tm at pH 6 allows preparation of 99.98% pure Yb (149). The more difficult separation of a pair showing only a III oxidation state, Nd and Pr, has also been made (147).

Sayun and Tsyb (171) deposited In, Zn, Cd, and Tl with a constant current at a mercury electrode. The resulting amalgam was removed, and the elements, stripped into $1M$ H_2SO_4 with a constant current, were determined titrimetrically or polarographically. The potential of the mercury pool was monitored and the stripping was halted at various potentials to obtain separations of the metals. Obviously a potentiostatic stripping procedure would be simpler. The controlled potential electrolytic removal of interferences prior to a determination of Mo was studied (150). The separation of small amounts of Ag, Cu, Bi, and Hg in biological materials by an internal electrolysis technique has been described (43). Other separations reported include the separation of Cu in bronze analysis (82); the separation of Fe from Zn

(189); the separation of In from Fe (172); the separation of Co, Ni, and Cu from Pu (16); and the separation of Sb and Sn from large amounts of Zn (9).

An interesting method for the determination of gases in metals is based upon the liberation of a gas upon anodic dissolution of the metal (100). The determination of hydrogen in steel is described. The method was also considered applicable to the determination of nitrogen, but oxygen determinations would probably require dissolution in a nonaqueous medium.

ELECTROGRAVIMETRY

Reinmuth (161) has shown that a three-dimensional representation of the reversible deposition of a metal on a solid electrode (plotting potential, current, and percentage deposited) is useful in teaching the theory of electrodeposition.

Controlled Potential Methods. The Japanese investigators continue to work on electrolytic analysis in the presence of chelating agents. Tanaka (198) studied the deposition behavior of Au, Ag, Hg, Cu, Bi, Sb, Pb, Cd, Sn, Ni, Co, and Zn at several pH's from solutions of ammonium nitrate, chloride, or acetate and varying amounts of (ethylenedinitrilo)tetraacetic acid (EDTA). Although all of the metals, except Ni, Co, and Zn, were deposited at the cathode, only Cu, Cd, and Ag were deposited quantitatively. Furthermore, the deposited metals were found to contain considerable amounts of EDTA, leading to positive errors. Nakagawa (140) investigated the application of diethylenetriaminepentaacetic acid (DTPA) to the determination of Cu in the presence of Bi, Sb, and As. The recommended procedure involves electrolysis at 70° to 80° C. at a potential of about -0.50 volt vs. S.C.E. from a solution containing DTPA, citrate or tartrate, and hydrazine. A procedure for the determination of Zn in the presence of Ni in an EDTA medium is also described (140).

The determination of Cu (139), as well as Zn (199) and Pb and Sn (155), in copper alloys by rather conventional methods has been reported. Alfonsi (3) has continued his investigations of electrogravimetric determinations of nonferrous alloys by describing methods for the determination of Cu, Pb, Sn, and Sb in Pb- and Sn-based alloys. Kovalenko stressed the importance of potential control in the electrogravimetric determination of Bi (103). The stability of the potential of a saturated calomel electrode when employed as an anode in controlled potential electrolysis was investigated by Hayakawa (69).

Controlled Current Methods. Interest in controlled current (or "con-

stant current") electrogravimetric methods in the presence of EDTA continues. Nakagawa (140) determined Cd in the presence of Zn from an EDTA solution, containing gelatin as a brightener, maintained at a pH of 3.5 to 4.0 with a citrate buffer. Zinc could be determined by then making the solution strongly alkaline, converting the Zn–EDTA complex to ZnO_2^{-2}, which is electrolytically deposited. Hayakawa (68) was able to deposit Bi quantitatively at a platinum cathode from EDTA solutions of pH 3.5 to 5.5. Lead could also be determined under similar conditions, at pH of 6 to 7. These results appear to disagree with the conclusions reached by Tanaka (198) concerning depositions from EDTA solutions (see above). Hayakawa determined Ag and Hg (on a silver-plated platinum cathode) from EDTA solutions (70).

Vernon (206) also determined Hg, in organomercury compounds, after dissolution of the compound in an ethyl alcohol–sodium sulfide mixture. Foster and Williams (51), in agreement with previous workers, found that cathodic deposition of Co leads to high results because of simultaneous deposition of some cobalt oxides. Yokosuka and Morikawa (218) reported similar findings, but showed that the determination of Co was accurate when deposition was made from a $Na_4P_2O_7$–NH_4OH or $(NH_4)CO_3$–NH_4OH medium. The duration of electrolysis under these conditions was about 20 hours. Kobal (101) reported that the determination of Cu is inaccurate in the presence of large amounts of Fe. The application of Winkler electrodes to several electrogravimetric determinations has been described (84, 85).

Internal Electrolysis. Lipchinski and Iordanov (115) determined Mn by anodic deposition of $MnO_2 \cdot H_2O$ on a platinum anode from an acetate buffer, pH 4.5, at 80° C. The cathode was graphite immersed in a PbO_2–Na_2SO_4 paste contained in a cellulose Soxhlet thimble coated with collodion. Cadmium and Bi were plated on a platinum cathode using a Zn- or Fe-plated platinum anode separated from the catholyte by a sintered-glass disk (219).

COULOMETRY

Attention is directed to the suggestions of Delahay, Charlot, and Laitinen (41) concerning the classification and nomenclature of electroanalytical methods. In particular they suggest that the term "coulometric titration" be reserved for controlled current coulometry, or, in general, to processes involving the electrogeneration of a titrant. The practice of some authors to use this term for what is more precisely "controlled potential cou-

lometry" should be discouraged. Craig et al. (38), at the National Bureau of Standards, have redetermined the value of the faraday as $96,490.0 \pm 2.4$ coulombs per equivalent (chemical scale) by measuring the weight loss of a silver anode during electrolysis in a perchloric acid medium. This value is in very good agreement with the one previously determined by electrolytic oxidation of sodium oxalate. Several different electrode materials which have been used for electrolysis might find application to coulometric methods. These include boron carbide (138), silicon (46), and germanium (54) electrodes.

Controlled Potential Coulometry. This technique continues to find application for the determination of the actinide elements, especially in nuclear fuels. Modifications of previously described methods for the determination of uranium (26, 78, 186, 220), plutonium (66, 174, 180), and neptunium (185, 187) have been published.

Davis determined iron(III) and cerium(IV) by reduction at a platinum cathode in $1M$ sulfuric acid (39). The solution containing Fe and Ce was first oxidized at a potential of 1.5 volts vs. S.C.E. A new platinum electrode, pretreated by immersion in a $0.01M$ ceric ion solution, was introduced and ceric ion was reduced at 0.80 volt, followed by ferric ion at 0.20 volt. A new, pretreated, electrode was necessary so that reproducible corrections could be made for the reduction of the platinum oxide(s) which occurs simultaneously with ferric ion reduction. The determination of 0.15 to 0.8 meq. of Fe and Ce was carried out with an average error of ±0.3%. The controlled potential coulometric determination of tin(IV) has been reported by Bard (11). Reduction occurred in two steps in a $3M$ NaBr–$0.3M$ HCl medium, first to tin(II) (−0.40 volt vs. S.C.E.), and then to tin amalgam (−0.70 volt) at a mercury pool cathode. Determinations of 20 to 50 mg. of tin based on the second reduction step were performed with an average error of about 0.3%. Wise and Cokal determined europium(III) and ytterbium (III) by reduction to the divalent ions at a mercury cathode (215). Because the divalent ions of Eu and Yb tend to react with water, causing an apparent current efficiency of less than 100%, the determination was carried out in absolute methanol, employing $0.1M$ tetrabutylammonium bromide as a supporting electrolyte. Only the sum of Eu and Yb can be determined by this procedure, but Eu itself can be determined in aqueous solution by a previously described reoxidation procedure. The use of such nonaqueous solvents as acetonitrile and dimethylformamide

for the controlled potential coulometric determinations of metals seems promising, and should be especially useful in cases where the product of the electrode reaction reacts with water. Máthé, Csáthy, and Richter (123) determined chromium(III) by oxidation to CrO_4^{-2} in $5M$ NaOH at 0.35 volt vs. S.C.E. From 1 to 17 mg. of Cr could be determined with an average error of 1%.

Duncan has reported the determination of nitrate ion at a mercury cathode at −1.0 volt vs. S.C.E. (44). The reduction proceeds quantitatively to nitrogen gas in the presence of uranium (III), which acts as a catalyst. Only zinc and substances which complex uranium are said to interfere, and 0.1 to 0.5 mg. of nitrate can be determined with a standard deviation of ±0.5%. Kulandaivelu and Nair (106) have determined ferricyanide ion by precipitation with silver ion formed by controlled potential oxidation of a silver anode at 0.32 volt vs. S.C.E. in an acetate buffer, pH 5. Analysis of 35 to 70 mg. of ferricyanide can be performed with an average error of ±0.6%, in the absence of chloride and other ions which precipitate with silver ion. This same reaction has been used for a constant current coulometric titration of ferricyanide (152) (see below). Foresti described an improved apparatus for the coulometric determination of hydrogen (50).

Controlled potential coulometry continues to find application to the analysis of organic compounds. Ascorbic acid was oxidized in a 2-electron process at a platinum anode in a potassium acid phthalate buffer, pH 6, at 1.09 volt vs. S.C.E. by Santhanam and Krishnan (169). This reaction was made the basis of a coulometric determination, and 15 to 100 mg. of ascorbic acid were determined with an average error of ±0.7 mg. Citric, succinic, and tartaric acids do not interfere with the determination. Takiura, Masui, and Sayo determined α-hydroxyamino derivatives of several fatty acids by reduction at a mercury electrode at pH 2 (197). The electrode reaction is the 4-electron reduction of the $=$N—OH group to —NH_2, to form the corresponding amino acid.

Several papers have appeared which describe coulometric analysis employing internal electrolysis for potential control. This method seems attractive, since a potentiostat is not needed, and analysis can be performed by shortcircuiting the electrolysis cell through a necessarily low-resistance coulometer. Niwa and Musha (143) determined Ag by depositing it on a gold electrode, using a Bi amalgam anode. These authors also determined Bi, in the presence of large amounts of Pb or Cd, by depositing it on an amalgamated Cu electrode, employing a Pb amalgam

anode. Average errors in both determinations were about ±3%. The total amount of electricity required for the depositions was determined by integration of recorded current-time curves. Both Lipchinski (114) and Kis and Sheitanov (97) describe oxidation of iodide by an internal electrolysis procedure. The latter authors, employing a platinum gauze anode and a PbO_2-H_2SO_4 paste catholyte, determined 30 to 100 μg. of iodide with an average error of ±3%. The coulometric determination of hydrogen by oxidation at a platinum anode, employing a potassium peroxydisulfate solution as a catholyte has also been reported (178).

The application of controlled potential coulometry to the study of mechanisms of electrode reactions has been discussed by Bard (12). Mechanisms involving secondary electrode reactions following the primary electrode reactions are common in organic electrode reactions, especially when the primary reaction involves the formation of a free radical. An example of a reaction of this type is the electroreduction of quaternary ammonium salts discussed by Bard and Mayell (13). Rechnitz and Laitinen studied the reaction of molybdenum(V) with perchlorate ion by performing the electroreduction of molybdenum(VI) at a mercury electrode in the presence of ClO_4^-, an example of a catalytic reaction (158). Several unpublished applications of this method have also been mentioned in a recent review article (130).

Badoz-Lambling discussed the origin of the residual current in controlled potential coulometry with reference to the oxidation of bromide ion (8). Mašek advocated the use of a separate reference electrode in millicoulometric determinations (122).

Several modifications of controlled potential coulometry have been proposed. A technique described as "voltage scanning coulometry," which involves the slow variation of the potential through the region at which a substance is reduced or oxidized, is said to give more reproducible residual current readings, and therefore is more useful for determining very low concentrations of substances (175). By this technique, reduction of iron(III) samples of 0.025 to 5 μg. was analyzed with a deviation of ±0.02 μg. It is difficult to see why this method should give more precise or accurate determinations that constant potential coulometric techniques. Meites has determined 0.07 to 10 μg. of Zn, and by employing careful background current corrections obtained an accuracy of about 0.007 μg., using conventional constant potential procedures (129). Moreover the voltage-scanning technique involves more complex instrumentation, and

requires the determination of a calibration curve, since current, rather than coulombs, is the quantity actually measured. Shults has described a coulometric titration of plutonium(VI) with iron(II) formed at constant potential in $1M$ sulfuric acid (179). In this technique, a platinum electrode is maintained at 0.27 volt vs. S.C.E., and the Pu and Fe are reduced to the III and II oxidation states, respectively [an excess of iron(II) is necessary to complete the reduction of plutonium(VI)]. Uranium(VI) is not reduced at this potential. The potential is increased to 0.66 volt, whereupon oxidation to iron(III) and plutonium(IV) occurs. The net result of this reduction and oxidation procedure is the reduction of plutonium(VI) to the IV state. This method will be useful only when one couple [in this case plutonium(VI)-plutonium(IV)] is electrolyzed irreversibly. In many cases an auspicious choice of a dual intermediate system will allow the determination to be performed by a constant current coulometric titration. The reported accuracy for the determination of Pu was only about 2%, probably because of some oxidation of the platinum electrode itself during the reoxidation step.

Ružička has presented an interesting combination of isotope dilution measurement and electroanalysis (165, 166). To determine Ag, the unknown amount of silver(I) in the sample is mixed with a known amount of radioactive Ag. The Ag is deposited on a platinum electrode in a cell connected in series with one which contains only the radioactive silver. Since equal total amounts of Ag are plated on the cathodes of both cells, the ratio of radioactivities of the cathodes is a measure of the Ag content of the unknown. The cell containing the known amount of radioactive Ag functions essentially as a "radioactivity coulometer" (165). This method is especially useful for the determination of very small amounts of metals, since plating need not be quantitative, and loss of sample by adsorption onto the cell walls does not affect the accuracy of the analysis, as long as it affects both the stable and radioactive isotope to the same extent. Using this technique, amounts of silver of 1 to 100 μg. were determined with errors of 0.8 to 2.3%.

Controlled Current Coulometry-Coulometric Titrations. Although applications of coulometric titrations continue to increase, only cyanide ion (6) and sulfhydryl compounds [thioglycolic acid (133) and monothioethylene glycol (134)] may be listed as new coulometric titrants. The classification of coulometric titrations given below is based upon the electrogenerated titrant employed.

BROMINE. Bishop described the titration of microamounts of hydrazine (21). Using two-electrode potentiometric end point detection, and cell volumes of 50 to 500 μl., 5×10^{-10} to 10^{-6} mole of hydrazine was determined with errors of ±5 to ±0.1%. Olson also titrated hydrazine and substituted hydrazines, employing an acetic acid-methanol mixture, and mercuric acetate as a catalyst (145). Although most monosubstituted hydrazines consumed four equivalents of bromine, asymmetrically disubstituted hydrazines consumed six equivalents. Employing two-electrode amperometric end point detection, milligram amounts of the hydrazines were determined with a standard deviation of ±1%. The determination of several substances of pharmaceutical interest, including antipyrene (190), thymol (88), thiopental sodium, and rivanol (191) have reported. Additional applications of bromine to the determination of olefin compounds (211, 212) have also been made. Iodide, which previously has been titrated to the I state in strongly acidic solution, was oxidized to iodate at pH's of 2.8 to 4.5 by Berraz and Delgado (18). These same authors also describe titration of metallic 8-quinolates by a modification of a previous procedure (17). Although the titration of iron(II) with bromine has been reported (196), the errors of the determination are so large (5 to 7%) that the titration with chlorine (47, 94) appears preferable (see below).

CHLORINE. Two titrations of iron (II) have been reported. The method of Khakimova and Agasyan (94) employed potentiometric end point detection for the determination of microgram amounts of Fe. Farrington, Schaefer, and Dunham (47) found that copper(II) is a catalyst for the iron(II)-chlorine reaction, and determined 500 μg. of Fe in 50 ml. of solution with an average error of ±0.1% employing one-electrode amperometric end point indication. Titrations of thallium(I) (93), cyclohexal, and hexobarbitone (89) with chlorine have also been described.

IODINE. Braman and coworkers (27) described a coulometric borane monitor. The boranes are titrated with iodine until the two-electrode amperometric detecting system indicates a preset iodine level has been reached. Incremental generation of iodine prevented coupling between the generating and indicating electrodes. Determinations of parts per million amounts of boranes agree with colorimetric determinations to within 0.02 p.p.m. Sulfur analyzers based on combustion of the sulfur-containing compounds and titration of the resulting SO_2 with iodine (74) have been reported (49, 58). Titrations of tin(II) (30) and thiamine hydrochloride (90) have also been described.

CERIC ION. Takahashi and Sakurai determined a number of organic compounds, including 2-naphthylamine, aniline, phenol, oxalic acid, D-mannitol, and D-sorbitol by generating an excess of ceric ion, and back-titrating with electrogenerated ferrous ion (195). The rate of oxidation of quinol and p-aminophenol by ceric ion was so rapid that they could be titrated directly, but the reported titration efficiency was only 90 to 95% (194). A modification of the uranium(IV) titration, employing urea to eliminate interference of nitrate ion, has been reported (52).

MANGANESE(III). Although incontrovertible evidence has been presented that manganese(II) is oxidized to manganese(III) under the usual conditions of coulometric titrations (176), some authors still persist in describing these as titrations with electrogenerated "permanganate ion." Fenton and Furman (48) independently studied the oxidation of manganous ion in sulfuric acid–phosphoric acid media at both gold and platinum electrodes, and reached conclusions similar to those of Selim and Lingane (176). Tutundžić and Paunović described the titration of hydrogen peroxide (201), iodide, and ferrocyanide (202) with electrogenerated manganese(III) employing potentiometric end point detection.

FERRICYANIDE. Titration of chromic ion to CrO_4^{-2} in a $5M$ NaOH, 0.1 to $0.2M$ $K_3Fe(CN)_6$ medium, employing 2-electrode amperometric end point detection, allowed the determination of milligram amounts of Cr with an error of 1% (123).

REDUCTANTS. Kies and Buyk titrated periodate with electrogenerated ferrous ion (96). In solutions containing 0.1 to $0.2M$ sulfuric acid, periodate is reduced to iodate, so that iodate itself, even in very large amounts, does not interfere in the titration. Apparatus has been devised for continuously and automatically measuring the chlorine concentration in bleach solutions, containing between 20 p.p.m. and 3% chlorine, by continuous coulometric titration with ferrous ion (45). The magnitude of the current, which is a measure of the chlorine concentration, is continuously adjusted to maintain the potential of an indicator electrode near the equivalence point potential of the iron(II)-chlorine reaction. Electrogenerated stannous ion has been employed in the titration of platinum(IV) (10). The titration reaction involves reduction of platinum(IV) only to the II state probably because of the slow rate of reaction between tin(II) and platninum(II). Using potentiometric and spectrophotometric end point detection, milligram amounts of Pt could be determined with an error of ±0.5%. Chromous ion has been used to titrate oxygen in a KCl-

$Cr_2(SO_4)_3$ medium at pH 3 to 4 (83). Although the current efficiency for the electrogeneration of chromous ion was not investigated, the titration efficiency for the determination of 4 to 40 µg. of oxygen, employing potentiometric end point detection, was close to 100%. An application of the previously described titration of ferric ion with electrogenerated titanous ion to the determination of Fe in silicate rocks has been reported (34).

PRECIPITATION AND COMPLEXATION. Miller and Hume have introduced electrogenerated sulfhydryl compounds to the list of coulometric titrants (133, 134). Both thioglycolic acid and monothioethylene glycol are generated at a mercury cathode by reduction of the corresponding mercury(II) complex. The compounds behave as both complexing agents for metals and strong reducing agents. Using a mercury indicator electrode, the determination of Hg, Au, Cu, and ferricyanide by thioglycolic acid (133), and Hg, Au, Cu, Pt, and Pd with monothioethylene glycol (134) has been described. Another report of a titration of Zn with electrogenerated ferrocyanide has been given (2).

Electrogenerated argentous ion has been used for several titrations. Paunović (152) described the titration of ferricyanide, employing two silver electrodes for amperometric end point detection. Coulometric titrations of bromural and cabromal, compounds of pharmaceutical interest, have also been described (87). A device for the automatic determination of Cl in organic compounds, based on the automatic combustion of the sample and titration with argentous ion, has been reported (37). Kies has expanded his titration of thiourea with electrogenerated mercuric ion to a number of N-substituted thioureas (95).

Electrogenerated cyanide ion, reported by Anson, Pool, and Wright (6), is a welcome addition to the ranks of coulometric titrants. Cyanide ion was generated by reduction of Ag-$(CN)_2^-$ at a platinum cathode in a solution containing $0.01M$ NaOH and $0.25M$ $K_2Ag(CN)_2$. The determination of milligram amounts of silver(I), nickel(II), and gold(III), using two silver electrodes for potentiometric end point detection, has been described.

ACIDS AND BASES. Several papers describe the determination of boron by formation of boric acid, and titration with electrogenerated base in the presence of mannitol (81, 151, 217). Small quantities of CO_2 were determined by adsorption onto filter paper impregnated with barium hydroxide and phenolphthalein and held between two silver electrodes (156). The time required for the disappearance of the red phenolphthalein color while current is passing

through the paper is a measure of the CO_2 concentration. To ascertain the ultimate practical precision of coulometric titrations, Taylor and Smith (200) titrated several acids in a cell designed to eliminate interchamber transfer, using a quartz crystal controlled time-interval meter and accurate measurement of current. These authors give an excellent discussion of the errors and precision of measurements in coulometric titrations. In general, the standard deviations and errors of the titrations were within 0.003%. It should be noted that for most coulometric titrants, the deviation of the current or titration efficiency from 100% will be the most serious limitation to very high accuracy.

NONAQUEOUS SOLVENTS. Interest in coulometric acid-base titrations in nonaqueous solvents continues. Mather and Anson (124) have titrated fluoride ion, in acetic anhydride containing a small amount of acetic acid, with hydrogen ion generated at a mercury anode. The end point was determined potentiometrically with either a glass or amalgamated gold indicator electrode, and a mercury-mercurous acetate reference electrode. From 8 to 88 µeq. of fluoride ion were determined with an accuracy of 2 to 3%. The mechanism of the electrode reaction, and the cause of the lack of success when a platinum generator electrode was used, was also investigated (125). Interest also continues in coulometric acid-base titrations in acetonitrile (20, 205).

Nonaqueous solvents also seem promising as media for oxidation-reduction titrations. Although no comparable coulometric titrations have been described to this writer's knowledge, several recently reported methods, involving iodimetry (42) and cerimetry (157) in acetonitrile, and titrations with titanous and chromous ions in dimethylformamide (76), should be adaptable to coulometric titrations. Liu has described the coulometric titration of copper(I) with palladium(II) generated at a palladium anode in a Li_2SO_4-K_2SO_4 fused salt eutectic (116). Two modifications of the coulometric Karl Fischer titration have been described (15, 144).

MISCELLANEOUS. Hanselman and Rogers have published their previously reported method of "generating" reagents by passage through ion exchange membranes (67). In this technique a solution containing the ion that one wishes to generate is contained in a cell separated from the titration chamber by an ion exchange membrane. The production of anions—e.g., OH^-—at the cathode will force solution anions through the membrane and into the titration cell. The auxiliary electrode may be contained in the titration cell, or in a separate, third, chamber. Generally, considerable deviation from

100% "current efficiency" results from interdiffusion, incomplete selectivity of the membranes, etc., and the accuracy is only fair. The technique should be useful in certain special cases. A similar technique has been reported in a recent patent (61).

Some interest continues in the use of coulometric titration detectors in gas chromatography. Using variations of the technique described by Liberti (111), coulometric detection of halide ions with electrogenerated argentous ions and SO_2 with bromine, from halogen- or sulfur-containing compounds has been described (28, 29, 36, 98). Several coulometric (or amperometric) oxygen gas analyzers, based on reduction of adsorbed oxygen on a Ag cathode, using Pb or Cd anodes have been reported (73, 91, 104).

Stripping Methods. Several additional methods for the determination of thin metal deposits by constant current anodic stripping have been reported. These include methods for Sn on an Fe base (105), Cr on steel (126), Ni on Cu base (128), and Ag on various substrates (127). Robson and Kuwana found that boron, deposited on platinum, could be determined by a similar technique (163). Boron was oxidized in a 3-electron step to borate ion. Narayanan, Sundararajan, and Kasabekar (141) found an alternating current impedance change (rather than the usual direct current potential change) could be used to indicate complete stripping of metals. Coulometric reduction of oxide films (24, 164) and sulfide films (77) on copper has also been described.

Voorhies and Davis (208) described a technique for the coulometric determination of substances adsorbed on powdered carbon black. The carbon black was made an electrode, and the substances were stripped at a constant current, completion of desorption or reaction being indicated by a potential change. The technique suffers from desorption of the substances into the electrolyte and shows rather large deviations, but it should be useful in some analyses.

APPARATUS

Galvanostats and Coulometric Titrators. A constant current source using a 24-volt power supply and transistor stabilization, capable of producing currents of up to 3 amperes (213), and a simple transistorized galvanostat for student use (121) have been reported. A constant current supply using a photoresistor as a control element, for currents of up to 100 μa. and load resistances of up to 1000 megohms (62), may be useful in nonaqueous solution coulometry. Vorstenburg and Löffler (209) suggested that a crystal

oscillator and counter as a timing source for coulometric titrations is free of start-stop errors and is capable of high accuracy. Maekawa and Okazaki (117) have described a counter being used essentially as a coulometer, which indicated the quantity of electricity consumed irrespective of the current level. A silver coulometer has been recommended for a similar purpose in student work (203). Several automatic coulometric titrators, based on previously described principles, have also been reported (7, 109, 193, 216).

Potentiostats. Descriptions of new potential control devices, most of which offer few advantages over previously described ones, continue. These include electromechanical types (23, 72, 79, 192), operational amplifier types (35, 92, 184, 210), and others (59, 99). One which deserves notice, however, is the simple apparatus devised by Hickling (75). Hickling, who constructed one of the first potentiostats, presents a three-tube device capable of delivering up to 300 volts at 0.3 ampere, and capable of controlling to ±10 mv. with a response time of 10 milliseconds. The control device is a beam tetrode, the grid of which is controlled by a Schmitt trigger circuit. The cost is said to be below $100. Two papers dealing with factors controlling the design of potentiostats for the study of the kinetics of electrode reactions stress the interaction of the experimental system and the potentiostat (19, 53).

Coulometers. Two titration coulometers, one using coulometric titration (182), have been described (188). Colorimetric coulometers, based on optically measuring the changes in concentration of iodine (60) and copper(II) (31), have been devised. Bourgault and Conway (25) devised an automatic recording variation of a gas coulometer. Hanamura (65) attempted to improve the characteristics of a low inertia direct current motor integrating unit by adding a tachogenerator correction unit and a synchronous motor operating with the direct current motor through a beveled gear arrangement to increase effective output power. Modification of a direct current motor integrator for low currents and input resistance has been reported (177). Use of a direct current motor as an integrator for student experiments has also been suggested (71). Hudson and Dickey (80) describe a low impedance electronic coulometer composed of a servomechanism amplifier, an argon lamp relaxation oscillator, and a counter. Although the input impedance of this coulometer is only 15 ohms, its response time is relatively slow because of the use of a servomechanism-type direct current amplifier. A nonelectronic integrator with figure registration and a linearity of ±0.2% has been reported (63).

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Review of Fundamental Developments in Analysis

Extraction

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WITH the intense emphasis in recent years on instrumental methods of analysis, particularly those techniques involving the measurement of physical properties which eliminate or minimize chemical manipulation, it might be expected that the more classical chemical techniques would be neglected. This is certainly not so in the case of solvent extraction, where each year sees a substantial increase in its application to a large variety of analytical problems. A review of the literature reveals the valuable assistance of this simple separations technique to many fields of analysis, but especially in radiochemistry, colorimetry, and for preconcentration in conjunction with

many of the more sophisticated instrumental techniques.

This review follows the scheme of classification of extraction systems as set forth by the authors in their book (*335*) and in their previous reviews (*334*). The emphasis is on the separation of inorganic materials, with particular attention to its use in analysis. This review surveys the literature from late 1959 to late 1961 and follows without duplication the material presented in the previous review.

REVIEWS AND BOOKS

A few general reviews of extraction in analytical chemistry have appeared (*502, 540*), as well as a discussion of the

role of extraction in ferrous analysis (*30, 80*). An extensive tabulation of extractions for the separation of the elements has also been prepared by Morrison, Freiser, and Cosgrove (*336*). Two reviews of interest in organic analysis include one on the determination of functional groups (*386*) and another on countercurrent distribution methods (*165*). Irving has written a chapter on extraction in the Treatise of Analytical Chemistry (*192*). Two treatments of the subject of liquid-liquid extraction in inorganic chemistry have also been published (*98, 303*).

Of particular importance to radiochemistry has been the publication of a series of monographs on the radio-