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Electroanalysis and Coulometric Analysis

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THIS PAPER surveys the literature and developments during 1962 and through December 1963, although papers published before 1962 which have not appeared in previous reviews in this series have also been included.

BOOKS AND REVIEW ARTICLES

Several books dealing wholly or partly with electroanalytical methods have appeared. A welcome English translation of the book by Charlot, Badoz-Lambling, and Tremillon (46) has been published. The book is written mainly for analytical chemists and uses current-potential curves and graphical methods to treat a variety of electroanalytical techniques. Numerous applications are given and the book is highly recommended as an introduction to this field for the practicing analyst. Volume 4 of Part I of the treatise by Kolthoff and Elving (121) is largely devoted to electrical methods of analysis. Chapters on the fundamentals of electrode processes, electrodeposition, and coulometric analysis are included. Rechnitz's monograph, "Controlled Potential Analysis," (209) has just appeared and is a valuable addition to the literature of electroanalytical chemistry. The theory and apparatus of both electrogravimetric and coulometric controlled potential methods are discussed extensively, and an element-by-element survey of applications, in most cases including de-

tails about the experimental conditions, is included. A book on coulometric methods by Abresch and Claassen (3) has also appeared.

An extensive review on the analytical applications of mercury electrodes to electrodepositions, separations, and coulometric methods has appeared (202). This review contains tables listing the elements determined and separated on mercury electrodes and the experimental conditions employed in the methods. The literature between 1948 and 1960 is surveyed, and 423 references are given. Application of electrolytic methods to trace analysis has also been reviewed (137, 169). A general review of electroanalytical methods appeared in the annual report of the Chemical Society (London), (44). A number of review articles on coulometric methods have appeared. Of special interest to English-speaking chemists is the review by Kies (115), with 267 references, on coulometry. A brief review of applications of controlled potential coulometry to metal analysis has appeared (65) as well as other, foreign language, reviews on coulometric methods (1, 2, 178, 230, 234, 244, 301).

ELECTROCHEMICAL THEORY

Many of the fundamental electrochemical studies most directly applicable to electroanalysis have been

concerned with the effect of surface oxidation, activation, and adsorption on the rates of electrode reactions.

Oxide Films and Surface Effects.

The nature of the surface films on solid electrodes continues to enjoy attention. The mechanism of the formation and reduction of the oxide film on platinum was discussed by Feldberg, Enke, and Bricker (76). The authors used various cyclic techniques to study oxide film effects and concluded that the formation occurs in two, one-electron, steps, involving the slow formation of $\text{Pt}(\text{OH})_2$, followed by a rapid step yielding $\text{Pt}(\text{O})_2$. On reduction, the reverse steps occur; reduction of $\text{Pt}(\text{O})_2$ to $\text{Pt}(\text{OH})_2$ is rapid, and of $\text{Pt}(\text{OH})_2$ to platinum is slow. The mechanism of surface oxidation of platinum has also recently been discussed by Gilman (89).

Evidence for a series of platinum oxides on the electrode surface has been presented (133, 168). Mayell and Langer (168), by oxidizing platinum potentiostatically or with a constant current in acidic solutions, removing any gaseous oxygen and electrolytically reducing the surface oxides, showed that the number of coulombs involved in the reduction of the surface depended upon the potential to which the electrode was oxidized. Increasing the potential of preoxidation increased the extent of oxygen coverage up to a potential of about 1.8 volts vs. N.H.E. Above this poten-

tial the number of coulombs decreased to a constant value. The authors propose a series of platinum-oxygen couples, ending with a "tight" platinum oxide at potentials higher than 1.8 volts. Kozawa (133) found humps on current-potential scans for a platinum electrode in strongly alkaline solutions and ascribed these to various platinum oxide and hydroxide couples.

Some previous experiments on platinum oxide formation have been repeated and reinterpreted. Previous results indicating preferential oxide formation at grain boundaries have been questioned (181). Breiter (33) has re-examined the chemical stripping of surface oxides in chloride media and concluded that the stripping of the oxide occurs by an electrochemical mechanism rather than by a direct chemical reaction, and that the experiment does not demonstrate a true oxide film as opposed to chemisorbed oxygen. Peters and Lingane (203) examined film formation in chloride media at several pH's and concluded that platinum chloride and oxychloride films containing both platinum(II) and platinum(IV) form.

Work continues to accumulate on the effect of surface oxides on the rates of electrode reactions. General evidence appears to support the conclusion that oxide films hinder most electrode reactions, both oxidations and reductions, and that an electrode can be activated by forming a film of finely divided metal on its surface by oxidation of the electrode followed by reduction. Kabanova (111) showed that the oxidation of iron(II) occurs less reversibly on an oxidized platinum electrode. In general, the overpotential for ferrous ion oxidation at a rotating disk electrode increased by up to 200 mv., depending upon the duration of oxidation of its surface and the magnitude of the potential at which the oxide film is formed.

Anson and King (11) similarly demonstrated that the increased reversibility of reduction of iodate and vanadium(V) previously ascribed to the presence of a thin oxide layer, is caused by activation of the electrode by a layer of finely divided platinum. Oxidation of the electrode surface was also shown to hinder the reduction of peroxydisulfate ion (160) and the oxidation of hydroxylamine (60) at a platinum electrode.

Similarly a.c. impedance measurements demonstrated that both the chloride-chlorine (151) and the bromide-bromine (150) systems are made less reversible by the oxidation of the electrode. The oxidation of hydrazine was first reported to be made more reversible by oxide film formation (112), but later work indicated that here too a freshly formed layer of finely divided platinum, rather than the oxide, was

responsible for an increase in reversibility of the electrode reaction (18).

Evidence that a fresh layer of finely divided platinum increases the rate of an electrode reaction has been obtained in other studies. Shibata (237) examined the effect of preoxidation and reduction of the electrode on the overpotential for hydrogen ion reduction and concluded that the beneficial effect of this anodization-cathodization procedure is not due to impurity desorption, but rather to "a freshly electrodeposited platinum... layer which has high activity associated with a small crystallization rate." Similar evidence for active centers on a platinized electrode has been presented (61, 190). The electroreduction of oxygen at platinum has been investigated further (180, 227) and additional evidence is presented for the reduction of oxygen with less overpotential at a freshly oxidized electrode.

The oxidation and reduction of H_2O_2 at a platinum electrode have been studied (146) and both reactions directly involve participation of the electrode surface. The H_2O_2 also undergoes a catalytic decomposition at the platinized electrode (146) [and also at iridium and palladium electrodes (31)]. The oxidation of hydrogen at platinum electrodes was studied by Sawyer and Seo (228) and was shown to involve reduction of the oxide film and platinization of the surface. Breiter (37) has indicated that the reaction between the oxide film and hydrogen occurs by an electrochemical mechanism. It has also been shown that formation of oxide on the active centers of a platinum surface inhibits the hydrogen oxidation reaction (4, 36).

Surface oxide effects on other metals have also been observed, and generally these effects parallel the behavior found with platinum. Kabanova (110) found that the rate of oxidation of ferrocyanide at a rotating gold electrode is decreased by an order of magnitude by oxidation of the electrode. The reduction of oxygen at gold electrodes was studied by Evans and Lingane (74). The course of the reaction was found to be very dependent upon the electrode pretreatment and the nature of the electrode surface. At an electrode which was recently oxidized and reduced, reduction of oxygen in an alkaline medium occurred in essentially a single wave, corresponding to reduction first to H_2O_2 (or HO_2^-) followed by catalytic decomposition of the peroxide at the active electrode surface. At an aged electrode, where the catalytic decomposition occurs more slowly, two waves, corresponding to the reduction of oxygen and the intermediate H_2O_2 , occur.

Rozental and Veselovskii (218) also studied the reduction of oxygen at active (treated with hot concentrated

H_2SO_4 and washed) and passive (heated in oxygen at 850° , forming a stable oxide coating) electrodes and found that the rate of reduction at an active electrode was about double that at a passive one. These authors also found that hydrogen oxidation occurs at active electrodes but not at passive ones. These results are in disagreement with those of Sawyer and Seo (228) who found no evidence for hydrogen oxidation at gold electrodes. The reduction of oxygen at palladium electrodes was studied by Blackburn and Lingane (32). The behavior here was similar to that found for the reduction of oxygen at gold electrodes. Evidence for two palladium oxides at the electrode surface was presented.

Adsorption Effects. The adsorption of various components from the solution, including the electroactive species itself or the products of the electrode reaction, can also affect the rate of electrode reactions. Well known methods, such as electrocapilarity measurements and analysis of polarographic pre- and postwaves have been used for some time to study adsorption at mercury electrodes. Some recent work on the measurement and effect of adsorption on solid electrodes is reviewed. For a review of previous work on adsorption at solid electrodes and its effect on electrode reactions, especially on the hydrogen-hydrogen ion system, the recent chapter by Frumkin (83) should be consulted.

The extent of adsorption of a species from solution on an electrode can be measured using radioactive tracer methods, involving such isotopes as carbon-14 and sulfur-35 (57, 58, 91, 297) and ultraviolet spectrophotometric techniques (26). Adsorption of electroactive species and products has been studied using chronopotentiometric (16, 101, 199) and linear scan voltammetric (87, 88, 200) techniques. Evidence for adsorption of substances which interfere with electrode reactions by blocking of active sites, preventing adsorption of the electroactive substance, or promoting recrystallization of the electrode surface, has been presented. Anson and Schultz (12) showed that adsorption of chloride and thiocyanate ions and amyl alcohol inhibited the adsorption and subsequent oxidation of oxalic acid at a platinum electrode. Balaschova (14) studied the effect of electrode pretreatment on the extent and kinetics of adsorption of ions, and demonstrated that adsorbed ions can retard oxygen adsorption (or oxide film formation). This retardation of oxide film formation can have the effect of increasing the rate of an electrode reaction. For example, addition of bromide ion increases the ease of oxidation of the cobalt(II)-EDTA (10). Part of this effect is ascribed to pre-

vention of formation of the oxide film by preferential adsorption of bromide ion, although electron bridging by bromide ion or prevention of adsorption of the electroactive species itself may also be involved.

In many cases, however, adsorption of nonelectroactive substances hinders the electrode reaction (or "poisons" the electrode). Iodide ion has been shown to retard the reduction of oxygen at platinum electrodes in acidic or neutral media (303), inhibit the oxidation of hydrazine (18), and cause the reduction of iodate ion to occur less reversibly (11). Similarly adsorption of sulfide ion decreases the reversibility of the bromine-bromide ion couple (150). Klyanina and Shlygin (120) investigated the effect of Hg, As, and CN^- on the electroreduction of SO_2 at a platinum electrode. Only cyanide was found to inhibit the electrode reaction, and formation of platinum cyanides at the electrode surface was suggested. Adsorption effects have also been observed during the oxidation of hydrogen at a platinum electrode (4, 83) and for the reduction of aromatic nitro compounds (105).

These studies have various applications to electroanalytical methods. Solid electrode pretreatment procedures generally involving repeated oxidation and reduction of the electrode surface will often prove beneficial. Similarly elimination of adsorbable ions and substances may be necessary in some cases. Harrar (95), for example, noted that a rigorous pretreatment procedure was necessary for the successful coulometric determination of H_2O_2 at a platinum electrode. Addition of halide ions in this case also appeared to have a retarding effect on the electrolysis. Preferential surface effects may be useful in certain cases. For example, the presence of a film of tin hydrous oxide on a platinum electrode, formed by cathodizing the electrode in a solution containing tin(IV), has been found to increase the hydrogen overpotential at the electrode and allow the generation of stannous ion at close to 100% current efficiency for coulometric titrations (19).

ELECTROSEPARATIONS

Herringshaw and Kassir (102) studied the effect of electrode area, current density, and applied stirring on the rate of electrolysis at a mercury electrode. They found that the rate of deposition of Cu, Cd, Zn, and Fe from 0.3N H_2SO_4 is higher under constant current conditions when the applied current is greater than the limiting current for deposition of the metal, than under controlled potential conditions. The higher rate under constant current conditions is ascribed to the simultaneous rapid evolution of hydrogen gas at the electrode surface, effective in

increasing the rate of mass transfer of the metal ions to the electrode. Of course the selectivity of an electrolysis carried out under these conditions is not so high as that of a controlled potential separation using vigorous applied stirring.

Electrolytic separations in radiochemical procedures continue to be used. Millard (172) described the separation of lead-212 and polonium-210. Electro-separation before neutron activation analysis was described by Lux (152). During the determination of traces of Ag in a mixture containing Cd, the reaction $\text{Cd}^{110}(n, p)\text{Ag}^{110}$ forms silver and causes interference. Silver was separated from up to 10^4 times more Cd by electrolysis at a rotating cathode with a 99% yield. Samartseva (224) described the separation of americium-241 and curium-242 from HNO_3 solutions adjusted to a pH of about 3 at a platinum cathode (probably as hydrous oxides). Molnar (132) has devised a glass column packed with rings of platinum wire acting as a cathode for continuous electrolytic separation of carrier-free radioisotopes.

Electrolytic separation of the lanthanide elements also continues (107). Use of amalgam cathodes and a methanolic medium containing LiCl has been reviewed, and the separation of small amounts of Tm in Lu studied (197). Studies of Lu and Ho enrichment in boiling methanol have also been made (196). Separation of Pm and Sm from other elements in the group at a mercury cathode has been described (143).

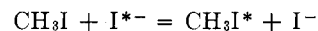
Kovalenko described a series of electrolytic separations of metals, including separation of Bi from Cd, using an amalgamated copper electrode (128); Pb from Cd, as PbO_2 (130) and on an aluminum cathode (124); Bi from Ni (125); Cu from Ti (126); Cu and Bi from Zn (127); and Bi from several metals (129). Tsyb and Sayun have studied the separation of In from Zn and Fe (285) and from Cu (286) by electrolysis at a mercury cathode. Other separations reported include the separation of vanadium compounds in aqueous solutions (90); the separation of β -titanium (304); and the separation of hydrogen in steel by a previously reviewed method (119).

Internal electrolytic procedures have been applied by Lipchinski and co-workers to the separation and determination of several substances. In all cases the electrolytic procedures employed platinum anodes and PbO_2 cathodes and were used to adjust the oxidation state of the element, which was then determined by a photometric method. Procedures for the oxidation of chromium(III) to chromate (147), arsenic to the V state (148), and manganese to the III state in the presence of

diaminocyclohexanetetraacetic acid (149), are given.

ELECTROGRAVIMETRY

Beronius (28) has presented an electrodeposition method involving radioactive tracers for measuring the rates of moderately rapid exchange reactions. For example, to measure the rate of the exchange reaction



first only radioactive iodide (I^{*-}) is added to a cell. (The asterisk denotes radioactivity.) Iodide is deposited for a known time (about 300 seconds) at a silver anode, and the activity of the electrode is noted. Then CH_3I is added and iodide is again deposited, presumably under identical electrolysis conditions, for the same time, and the activity is measured again. Since some of the I^{*-} is now exchanged, the activity measured the second time will be lower, and from this change in activity, the rate of the reaction can be determined.

Controlled Potential Methods.

Electrodeposition of metals in the presence of EDTA continues to be of interest and methods for the controlled potential electrodeposition of Ag, Cu, and Hg have been developed (84, 284). Tanka continued his studies of the controlled potential deposition of a number of metals in various media. The deposition of Ag, Hg, Au, Bi, Cu, Pb, Te, Se, Pd, Cd, Co, Fe, Ni, and Zn in pyrophosphate media of pH 7 and 10 (273), alkaline triethanolamine media (274), formic acid-formate buffer at pH 4.1 (275), and an acetic acid-acetate buffer at pH 5.3 (276) was investigated. Potentials and electrolysis conditions for the deposition of the metals at a platinum cathode are given and many successful determinations are described.

Alfonsi (5) described procedures for the electrodeposition of Sb, Pb, Cu, and Sn in lead- or tin-based alloys, and of Bi, Pb, Sb, and Sn, in bismuth-based alloys. Lanese and Jaselskis (140) determined Te by electrodeposition at a copper cathode from a supporting electrolyte consisting of 2M H_2SO_4 , 0.4M $(\text{NH}_4)_2\text{SO}_4$, 0.1M sodium tartrate, and 0.06M NaNO_3 at a potential of -0.6 volts vs. a saturated mercurous sulfate electrode and showed that the average error was less than 1%. A statistical study of the controlled potential deposition of Cu from various aqueous solutions has been made (300), and the authors conclude that the method is most precise and accurate from a HNO_3 or tartaric acid supporting electrolyte.

Controlled Current Methods. Tantalum and platinum-clad tantalum electrodes have been used successfully

for the electrodeposition of Cu and Ag (194). The determination of Cu in high manganese brassy was found to be successful when organic reducing agents, such as methanol or formaldehyde, were added to the electrolysis medium (47). A procedure for determining Ni and Mo has been described (208). The deposition of Re at a platinum gauze cathode from a 2N H₂SO₄ solution at 70° yielded results within 1% for 10 to 30 mg. amounts of Re (233).

Internal Electrolysis. Deschamps and Bonnaire (66) have investigated the application of various anodes to the deposition and determination of Au, Bi, and Sb at a platinum cathode. Procedures based upon the use of a Pb, Zn, or Mn anode and various anolyte and catholyte compositions are given and metals in 1 to 3 mg. amounts were determined to within a few per cent. An internal electrolytic procedure for the determination of Se by precipitation of Cu₂Se was found useful for determining about 5 mg. of Se with an absolute error of about 0.3% (232). Shiobara (238) described an internal electrolytic method for the determination of Ag, Cu, and Zn. Methods for the determination of Cu, Zn, Tl, and Mn have also been reviewed (302). An analysis of ores for Bi based on an internal electrolytic procedure has been described (219). Facsko and Radoi (75) discussed internal electrolysis with vibrating electrodes, and demonstrated the utility of their method in the determination of Cu.

CONTROLLED POTENTIAL COULOMETRY

Some new techniques involving controlled potential coulometric determinations have been described. Hanamura (94) continued his study of the *I-Q* recorder. In this recorder the synchronous motor ordinarily used to drive the *X*- or time-axis is replaced by Hanamura's integrating motor, a low inertia direct current motor equipped with a tachogenerator correction unit and a beveled gear differential to increase the output power, so that the *X*-axis is now a function of *Q*, the total coulombs passed during the electrolysis. Since *Q* is directly proportional to *I*, the electrolysis current, during the usual constant potential determination, a linear plot is obtained on the *I-Q* recorder, and the initial linear portion can be extrapolated to find the final *Q*. This technique was successfully used for the determination of Cu, Pb, and Cd in mixtures with an error of about 2% at the 10 μg. level.

A technique called constant current potential limit coulometry has been devised (153). This technique is based on the application of a constant current to a cell until the electrode potential reaches a preset limit, at which point

the current is halved and the electrolysis continued; the current is halved each time the electrode potential reaches the limit. As originally designed, with a single constant current, the technique had the advantage of not requiring a coulometer. In the present case, however, a fairly complex device which halves a timing pulse frequency counted by an electronic scaler is needed. Since the electrolysis must take longer by this technique than by conventional controlled potential coulometry, and the apparatus is no simpler, it is hard to see the advantage of this technique. The determination of Cd, Cu, and U in a citrate medium with errors of about 0.3% was described.

Bard (17) devised an apparatus consisting of a fast potentiostat and coulometer and a cell using a larger electrode area-solution volume ratio and ultrasonic stirring, and showed that electrolysis times of the order of one to two minutes could be obtained under these conditions. The application of this apparatus to electrode mechanism studies was also described. Van Norman (289) demonstrated that the technique of controlled potential coulometry could be successfully applied to analysis in fused salt media. Determinations of Zn, Cd, Ni, and U in a LiCl-KCl eutectic at 450° are described. Because of a considerable cathodic background current, the most accurate procedure involved plating the metals and then coulometrically stripping them. During the past two years the atomic weight table was changed to one based on carbon-12 as a reference so that the new value for the faraday is 96,487.2 coulombs per equivalent.

Metals. Application of this technique to the determination of the actinide elements continues (174). Methods for the determination of U, including the use of a Ag cathode (177) and solvent extraction procedures before electrolysis (33, 242, 243), determination of mixtures of U in different oxidation states in a triphosphosphate medium (305) and in the presence of nitrate ion (240), as well as other techniques (287) have been described. Methods for the determination of Pu (64, 176, 239, 241) and Np (85, 174) have also been published.

The reduction of iridium(IV) has been studied. Page (201) showed that the one-electron reduction could be accomplished successfully in an HCl medium. Rechnitz and McClure (211) showed that the indications of a reduction of iridium(IV) involving more than one electron in a HClO₄ medium were caused by the secondary reaction of iridium(III) and perchlorate ion, regenerating iridium(IV). Rechnitz (210) also showed that ruthenium(IV) could be reduced coulometrically to the III state at a mercury cathode in a chloride

medium. The coulometric determination of Hg at a mercury-plated platinum electrode has been described (7). Harrar and Stephens (96) determined Au by reduction of gold(III) at a gold-plated platinum electrode in an HCl medium. The background correction was very low in this determination and errors of less than 0.1% were obtained for milligram amounts of Au.

Reduction of iron(III) to the II state and its subsequent re-oxidation formed the basis of a determination by Milner and Edwards (175). The coulometric determination of Fe based on the internal electrolytic oxidation of iron(II) has also been described (235, 236). Controlled potential coulometric reduction of dichromate at a gold electrode has been used for the preparation of a standard chromium(III) solution (98). The determination of milligram amounts of In, by reduction of indium(III) at a mercury cathode and by re-oxidation of the indium amalgam in a chloride medium, with errors of less than 0.2%, has been described (187).

A previously reviewed method for the determination of Tl by reduction at a mercury electrode has been tested (195). Dunlap and Shults (70) determined Sb in both the III and V state by reduction at a mercury electrode in a tartrate medium. The reduction of pertechnetate ion was shown to occur stepwise, yielding two closely occurring waves of three and one electron each, in H₂SO₄ and chloride (222) and tripolyphosphate (278) media. Although coulometric reduction to technetium(III) at a mercury electrode was possible in all media, the errors were somewhat lower in the tripolyphosphate medium. Cokal and Wise (50) described the determination of Na in an acetonitrile medium. Sodium(I) was reduced at a mercury electrode at -2.3 volts vs. SCE and re-oxidized at -0.10 volt, with an error of less than 2% for 1.31 μmoles of Na. The application of nonaqueous solvents to other similar determinations seems promising. Segatto (232) determined Pb, Cd, and Zn in glasses at the milligram level. Coulometric precipitation analysis of metals has been mentioned in a Russian patent (288).

Other Determinations. The determination of H₂O₂ (95) has already been mentioned as an example of a determination in which the electrode reaction is dependent upon the surface state of the electrode. It is interesting that although this reaction is perturbed by oxide film and adsorption effects and the catalytic decomposition of H₂O₂ at the electrode surface, by using proper pretreatment procedures and high speed electrolysis, Harrar was able to determine milligram amounts of H₂O₂ with relative errors of less than 0.2%. Pretreatment of the electrode was also

necessary in the determination of hydrazine by oxidation at a platinum electrode (35). The mechanism of this reaction has been studied (18, 112) and secondary electrode reactions, surface oxidation and adsorption effects, and catalytic decomposition of hydrazine were shown to occur (see below). In 1M H₂SO₄, 55 to 440 μg. of hydrazine were determined with a relative error of about 0.5% (35).

The determination of thiourea by oxidation at a platinum electrode has been described (226), as well as the coulgravimetric procedure for the determination of mixtures of chloride and thiocyanate ions (138). Yamada and Sakai (299) determined cyanamide by precipitation of the silver salt, with subsequent dissolution in HNO₃ and coulometric determination of silver. Langer and Landi (141) devised a technique called electrogenerative hydrogenation, which could be applied as an internal electrolytic coulometric technique. The anode is the usual hydrogen fuel cell anode and hydrogenation of olefins occurs at the cathode. Application of this technique to the determination of olefins with no more apparatus than a low resistance coulometer appears promising.

Electrode Mechanisms. The use of coulometric methods in the study of the rates and mechanisms of electrode reactions has been extended. The determination of the number of electrons involved in electrode reactions is well known, and many previous studies of metal ion reductions and oxidations of organic substances have been made. A sampling of some recent applications to the determination of the number of electrons involved in reactions include the following. Wilson, Butler, Ingle, and Taylor (295) found that the aminoacridines were reduced at a mercury cathode via a one-electron reduction, except for the 5-aminoacridine, whose reduction apparently involved a direct two-electron transfer. Butler and Martin (43) reported that crystal violet reduced in a one-electron reaction, but that the reduction of another triphenylmethane dye, brilliant green, was more complex. The perylene cation radical was reduced in a trifluoroacetic acid medium to perylene by a one-electron reaction at a mercury electrode (272).

Hoffman (104) found that alloxan is reduced irreversibly at a mercury electrode in neutral media via a one-electron reaction. Eriochrome violet B underwent a four-electron reduction in aqueous solutions of pH 4.6 to 11.2 (79). Masui and Sayo (162) studied the coulometric reduction of 2,2-dinitropropane in various ethanolic buffers. In alkaline solutions a two-electron reduction was found, while in acidic solution four electrons per mole were re-

quired in the overall reaction. Dapo and Mann (59) observed that the coulometric oxidation of triethylamine in dimethylsulfoxide involved transfer of one electron followed by a rapid chemical reaction. The coulometric reduction of pyrimidine and related compounds in aqueous buffers was studied by Smith and Elving (245).

While many of the previous studies showed an integral number of electrons gained or lost in the overall reaction scheme, many coulometric studies, especially those involving organic electrode reactions, show apparent electron changes, n_{app} , which are variable and nonintegral. Recent studies have been concerned with treating these types of coulometric determinations theoretically, and using the variation of n_{app} with experimental conditions to help elucidate the overall reaction mechanism. Bard and Mayell (20) theoretically treated cases where an intermediate formed in the electrode reaction underwent first or second order chemical reactions and then a subsequent electrode reaction. A very similar case for a second order intervening chemical reaction was also treated by Meites (170). Bard and Solon (23) treated reactions in which the electroactive species was produced by a slow chemical reaction or underwent a simultaneous chemical reaction and electrode reaction. Considering the variation of n_{app} and the current-time behavior during the electrolysis, criteria were established for identifying the type of complication occurring during the electrolysis. Using this technique, Mayell and Bard (167) studied the electroreduction of quaternary ammonium compounds.

Karp and Meites (112) studied the oxidation of hydrazine at a platinum electrode and observed that n_{app} decreased from the expected 4.00 (for complete oxidation to N₂) as the hydrazine concentration was increased and the hydrogen ion concentration decreased. A mechanism for this variation, based on an intervening coupling reaction of the product of the first electrode reaction, was proposed by them, and was shown to be consistent with this type of mechanism (20). The complication during the electroreduction of tropolone, as studied by Tanaka and coworkers (277), probably also involves a chemical reaction intervening between two electrode reactions.

Moros and Meites (186) also found a second order intervening chemical reaction during the electroreduction of manganese(II) in a cyanide medium. This reaction involved the reaction of a manganese(I) species with HCN, regenerating manganese(II) and yielding n_{app} -values larger than expected. The rate constant for this reaction, measured during the coulo-

metric experiment, was shown to agree with that determined by spectrophotometry and polarography. Another type of complication occurring during coulometric determinations is the induced reaction, the reduction (or oxidation) of the solvent or supporting electrolyte induced by the simultaneous reduction (or oxidation) of the electroactive substance being determined. Evidence for an induced reaction was found during the electroreduction of manganese(II) (186) and also during the reduction of dimethylglyoxime (248).

Ficker and Meites (78) examined the coulometric reduction of zinc(II) at a mercury electrode and its subsequent stripping, and noted that not all of the zinc was recovered when the plating was carried out in the presence of certain other metals, such as Co. This was ascribed to the occurrence of intermetallic compound formation—e.g., Zn-Co-Hg—a phenomena well known in stripping voltammetry at a hanging mercury drop electrode, and the current-time curves during the stripping were used to study the rates of the stripping reactions and the species involved.

The existence of complicating chemical reactions must be considered when devising coulometric analysis of both organic and inorganic substances. Sometimes strictly mathematical corrections can be made for the complicating reactions, after these reactions have been studied in detail (186), although often this procedure will be sufficiently complicated as to discourage its use in practical analysis. Often a change in the solvent, supporting electrolyte, or temperature will decrease the effect of the complicating reaction (112, 167). Higher rates of electrolysis will also minimize the effects of intervening chemical reactions (17).

CONTROLLED CURRENT COULOMETRY—COULOMETRIC TITRATIONS

Determinations. A summary of determinations using electrogenerated titrants is given in Table I; some specific considerations are discussed below. Marinenko and Taylor (158, 159) continued studies into the precision of coulometric titrations. Potassium dichromate in half-gram samples, was titrated with electrogenerated iron (II) with a standard deviation of 0.003% (159). A discussion of the current efficiency of iron(II) generation based on current-potential curves was also given. By use of similar techniques, four milliequivalent amounts of the halides were titrated with electrogenerated silver ion with a standard deviation of 0.005% (153).

A differential coulometric technique for improving the accuracy and precision of coulometric titrations has been described by Monk and Goode (183).

Two coulometric titration cells are connected in series, one containing a standard amount of the substance to be determined and the other, the sample with slightly more of the constituent of interest. The titration is carried out at a high uncontrolled current until the end point in the standard cell is approached. Then a small known constant current is used to determine the excess of the constituent in the sample cell. Dichromate samples of about 32 mg. were determined by titration with electrogenerated iron(II) with error of about 0.005% using this technique.

A study of the current efficiency for the generation of chromium(II) at a mercury electrode was made by Bard and Petropoulos (21), and a supporting electrolyte composed of 0.1M chromic sulfate and 0.1M potassium chloride was found most suitable. Some studies of coulometric titrations with electrogenerated tin(II) have appeared (221, 268) recommending a chloride supporting electrolyte and a platinum generating cathode. Under these conditions, however, a current efficiency of only 94 to 96% can be obtained, and even this depends upon some special surface effects at a platinum electrode in these media (19); the previously reviewed methods of generating stannous ion, based up on a bromide supporting electrolyte and a gold cathode, seem preferable.

Buck and Crowe (41) made a detailed study of the current efficiency of the electrogeneration of manganese(III) and iron(II) at platinum, carbon, and boron carbide electrodes. Buck (40) also studied the application of various end-point detection techniques in connection with these titrants. Laitinen and Liu (139) recently studied the current efficiency for plating and stripping chloride ion at a silver electrode at various current densities and chloride ion concentrations. At high chloride ion concentrations and low current densities formation of AgCl_2^- occurs, while at low chloride ion concentrations and an applied current density greater than the limiting current for chloride deposition, the current efficiency also fell below 100%. Optimum conditions appeared to be at a 0.01M chloride ion concentration and a current density range of 5.5 to 4100 $\mu\text{a.}$ per sq. cm.

Maricle (157) has introduced the new and potentially important technique of using electrogenerated free radicals in aprotic solvents as coulometric titrants. The generation of biphenyl radical anion in dimethylformamide solutions containing 0.1M biphenyl and 0.1M tetra-*n*-butylammonium bromide at a platinum cathode was described. Water did not constitute a serious interference, and the titrations of several organic compounds, including anthracene, nitromethane, and benzophenone, were suc-

Table I. Electrogenerated Titrants and Substances Determined By Coulometric Titration

Electro-generated titrant	Substance determined	Reference	Electro-generated titrant	Substance determined	Reference
	Oxidants		Cerium(IV)	Hydroxylamine Hydrogen peroxide	(220, 269) (220, 269)
Chlorine	Hydrazine Cyclic β -diketones	(108) (92, 291)	Ferricyanide	Selenious acid	(188)
Bromine	Thallium(I) Aluminum (via 8-hydroxyquinolate) Zinc(II), copper (II) (as thiocyanates)	(81) (122) (29)		Reductants	
	SO ₂ Hexamethylditin Cyclic β -diketones Methyl vinyl ketone Quinine Ascorbic acid Olefins	(25) (260) (92, 291) (306) (258) (113) (6, 27, 161)	Iron(II)	Vanadium Permanganate Chlorine	(179) (271) (71, 262, 271)
	Hydrazine Carboxylic acid hydrazides Aromatic amines <i>N,N'</i> -diphenylphenylenediamine	(108) (135) (63) (154)	Tin(II)	Dichromate Cerium(IV), iodine, bromine Iodine Copper(II)	(159, 271) (221, 268) (254) (21)
Iodine	Phenols Hydrazine Hexaethylplumbane Ascorbic acid Ammonia	(62, 131) (108) (259) (113) (49, 136)	Chromium (II)	Iron(III) <i>p</i> -Quinone dioxime Vanadium, iron	(15) (68) (55)
Hypobromite	Aminoxy group Iron(II), antimony(III), Niobium tin(II) Oxalic Acid	(134) (123) (250) (255)	Uranium(V) Titanium (III)	Reducible organic substances	(157)
Manganese (III)	Nitrite	(40, 41)	Biphenyl radical anion		
Manganese (III)-Iron(II) system				Precipitating and Complexing Agents	
			Silver(I)	Chloride, chlorine in organic compounds Halides Potassium (via the tetraphenylborate) Orthophosphate Organomercurials	(252) (158, 263) (251) (48) (171)
			Thioglycolic acid EDTA	Ca ⁺⁺ , Ni ⁺⁺ , Cu ⁺⁺ , Zn ⁺⁺ , Sr ⁺⁺ , Cd ⁺⁺ , Ba ⁺⁺ , Pb ⁺⁺ , Y ⁺⁺⁺ , Ce ⁺⁺⁺⁺ , Ce ⁺⁺⁺⁺ , Nd ⁺⁺⁺ , Thorium Copper(II)	(184) (283) (264)
			Ferro-cyanide		

cessful. The method should prove useful for other radicals and solvent systems, and may also yield information on the thermodynamic properties of free radicals.

Macero and Janeiro (154) used electrogenerated bromine in a glacial acetic acid medium to form the radical of *N,N'*-diphenylphenylenediamine, and demonstrated that the electrode reaction involved one equivalent per mole of electroactive substance. By using an ethanol medium, Christian, Knoblock, and Purdy (48) were able to titrate orthophosphate by precipitation of the fairly soluble silver salt. Extension of the use of nonaqueous solvents for oxidation-reduction and precipitation titrations will probably prove to be a fruitful field for research.

Interest in acid-base titrations in nonaqueous media and investigations of end-point detection methods for these continue to hold interest. Suzuki (253) considered the titration of aro-

matic acids in an isopropanol-water medium. Pyridine was successfully determined in an aqueous medium using a photometric end point (189). The use of anion and cation exchange membranes for separating the anode and cathode compartments in acid-base titrations was investigated (106). Fairly large errors were obtained in titrations of acids, but the titrations with electrogenerated hydrogen ion were more successful. A detailed discussion of the theoretical and experimental current-potential curves with platinized and polished platinum electrodes has been given (51), and application of those electrodes to coulometric acid-base titrations has been discussed.

Methods for determining carbon and hydrogen in steel based on the coulometric titration of CO₂ by Ba(OH)₂ generated coulometrically from BaCl₂ have been reported. In the determination of carbon (99), oxidation to CO₂ is direct. For the hydrogen deter-

mination (86), the evolved H_2 is oxidized with CuO to water, which is reduced with graphite at $1200^\circ C.$ to H_2 and CO . The CO is finally oxidized to CO_2 by passing through a tube containing silica gel, Na_2CO_3 , and $Mg(ClO_4)_2$ and determined as described. A method based on the direct coulometric determination of the water itself (see below) seems more straightforward.

Determination of water by coulometric methods continues to find new applications. Karl Fischer methods, with various modifications, continue to be of interest (249, 256). A novel coulometric method for the determination of water in liquid ammonia has been presented by Klingelhofer (118). The water is reduced by potassium generated at a platinum cathode, and the end point located by the increase in conductivity associated with the formation of excess potassium dissolved in the ammonia. The method is sensitive to 1 to 100 p.p.m. of water. Several papers were concerned with the determination of water by adsorption on a P_2O_5 film and subsequent electrolysis between platinum electrodes (198, 247). A similar technique was used for the determination of hydrogen in organic compounds (9, 193, 246). By using this technique, 3-mg. samples containing about 3.2% hydrogen could be determined with a standard deviation of between 0.01 and 0.03%.

Miscellaneous Techniques. The further use of pulse generation techniques has been described (77, 131, 132). Voorhies and Davis (292) extended their interesting technique involving coulometry of substances adsorbed on carbon black to the study of electrode processes. The adsorptive properties of the carbon black is so high that reactants, products, and reactive intermediates remain quantitatively adsorbed, and by current reversal techniques the rate of reaction of products and intermediates can be determined. The electro-oxidation of *p*-aminophenol, *p*-toluidine, and aniline were studied using this technique. Cover and Meites (52, 53) described the application of coulometric and automatic titrations involving a constant rate of addition of reagent to the determination of rate constants from the shape of the potentiometric titration curves.

Kozak and Fernando (132) studied the rate of the reaction of bromine and phenetole by electrogeneration of bromine and observation of the rate of decay of the limiting current due to bromine reduction at a rotating platinum electrode. Coulometric addition of reagents was also found useful in other studies. Klein and Fontal (117) used the electro-oxidation of thiocyanate at a platinum electrode to form sulfate ion for studies of the nucleation and precipitation of $BaSO_4$. Evans and Lin-

gane (73, 145) used coulometric oxidation of a gold anode in halide media to study equilibria involving gold(I) and gold(III) in chloride and bromide media. Further applications of coulometric titration procedures for the determination of Cl- and S-containing effluents in gas chromatography have been made (45, 67, 279).

Continuous Coulometric Titrations. Takahashi, Niki, and Sakurai (266, 267) reviewed the fundamentals and working methods for automatic continuous coulometric titrations. Some applications include continuous analysis of acidic and basic components of process gas streams (42) and alkalinity of water (265). Some continuous analyses of metal ions, such as iron in water, using electrogenerated bromine (270), and copper(II) with electrogenerated ferrocyanide ion (264) have also been described. The determination of halide ions with electrogenerated silver(I) (263) and chlorine with iron(II) (71, 262) have been discussed. Barendrecht and Doornekamp (24) described the continuous automatic determination of traces of water by the Karl Fischer method. Takahashi (261) discussed the determination of relatively high concentrations of substances by continuous coulometric methods.

Galvanic Analyzers. Further extensions of galvanic cell analyzers for oxygen have been discussed (185, 216). Recent work has been concerned with investigations of cathode materials for more stable operation of the cell and both gold (192) and silver (156) electrodes have been recommended. Hersch and Deuringer (103) devised a method for the galvanic monitoring of ozone based on the oxidation of bromide ion in a neutral medium. Because the current is related to the rate of supply of ozone to the electrodes by Faraday's constant, temperature changes and cell geometry variations have no effect, and calibration with a standard source is not needed. Czuha, Gardiner, and Sawyer (56) reviewed the behavior of the $Pt-P_2O_5-H_2O$ system in the galvanic water analyzer.

Stripping Methods. Determination of metal coatings by coulometric stripping methods include Al coatings (204), Cd on steel and copper-base metals (165), Cr coatings over copper and brass (164) and nickel (163), and Ni and Cu over brass (163). A stripping method for the analysis of such metal ions as Zn, Cu, and Cd, has been devised, based on the plating of the metals at a current exceeding the limiting current for the elements, and subsequent stripping at a low current density (223). Coulometric stripping methods for the determination of hydrogen in palladium (82) and in catalyst powders (54) have been described.

Lewin (144) has discussed the fundamentals of electroanalysis instrumentation. A cell useful for coulometric and other electrochemical studies of small quantities of gas has been devised (281). Kesler (114) described an electrolysis cell for constant current generation of titrants for use in continuous analyzers.

Coulometric Titration Apparatus. Several general automatic coulometric titrators have been described based on automatic termination of the titration at the end point using amperometric (215), potentiometric (13, 25, 109, 142, 231), or photometric (173) end-point detection methods. Several have been designed specifically for bromine number determinations (161, 173, 293). Hanamura (93) described a recording coulometric titrator. An automatic, on-stream analyzer, designed for the determination of SO_2 in gases by titration with bromine has been discussed (25). An analyzer has been designed to provide results directly in such terms as percentage or molarity (257). Several descriptions of devices for the automatic determination of plating thickness by constant current stripping of the plate and automatic termination of the stripping process have been described (191, 212, 294).

Potentiostats. Bewick and Fleischmann (30) discussed in detail many of the factors involved in the design and performance of potentiostats. Although the discussion is mainly from the viewpoint of potentiostats for measurements of rapid electrode reaction rates, many of the points discussed also apply to the design of electronic potentiostats for coulometric work. Booman and Holbrook (34) applied similar considerations to instruments more closely designed for controlled potential coulometry. Besides describing the application of feed-back theory and stressing the necessity of measuring electrolysis cell parameters in the design of controlled potential instrumentation, these authors give detailed discussions of the electrolysis cells used and of the effect of placement of the counter electrode and reference electrode on the potential distribution over the electrode surface. Continued descriptions of various potentiostats based on operational amplifiers have appeared (39, 166); several stress the application of solid state operational amplifiers (97, 217) or transistorized power amplifiers (97, 205, 207).

The analyst desiring more information about operational amplifiers can find useful discussions in the introductory treatments by Reilley (213) and Malmstadt, Enke, and Toren (155), and in the November 1963 issue of ANALYTICAL CHEMISTRY, which has a section devoted to a symposium on

instruments based on operational amplifiers. A multipurpose electro-analytical apparatus for use in controlled current or controlled potential applications, containing as principal elements a potentiostat, a coulometer, and a pH-meter regulator, has been described (72). Other potentiostats, most designed for corrosion studies, have been designed (69, 80, 116, 225, 298). Dugdale (69) gives a useful comparison of several of the potentiostats currently in use, listing output currents and voltages, sensitivities, and response times.

Probst (206) described an interesting scanning controlled potential coulometer, which scans a potential range and records the coulombs. A novel circuit based upon a silicon diode allows a scan rate which is an inverse function of the electrolysis current. A network to provide compensation for the faradaic (background) current and charging of the double layer is also included. Although it is moderately complex (involving seven stabilized operational amplifiers), it should be very useful for analysis of multicomponent systems. The increase in the availability of commercial potentiostats of various kinds during the past several years should lead to an even greater application of controlled potential coulometric methods.

Coulometers. Several groups simultaneously announced the application of voltage-to-frequency converters to coulometric determinations (7, 8, 22, 296). The basis of this integrator is a commercially available voltage-to-frequency converter which will convert, for example, one volt input to an output signal of 10,000 counts per second. By using this converter to measure the iR -drop over a standard resistor in the electrolysis circuit and feeding the output to a scaler, the current-time integral is obtained. Although, as has been pointed out by Booman and Holbrook (34), the voltage-to-frequency converter is based on an integral operational amplifier, so that the overall accuracy of the apparatus can be no greater than that of an operational amplifier-capacitor integrator, the accuracy of these coulometers is about 0.01%, which is certainly sufficient for most coulometric analyses. An integrator of this type has performed very satisfactorily in the author's laboratory for the past few years.

Schoedler (229) described a new integrator based on a d.c. potentiometric controller which controls an electromagnetic encoder in such a manner that pulses originating in a quartz oscillator are fed to a counter at a rate proportional to the current magnitude. The precision of this integrator is about 0.3% for currents down to one hundredth of the full-scale

current, but the linearity is rather poor at the lower current values. Toren and Driscoll (280) designed a digital read-out device for use with operational amplifier-capacitor integrators. An operational amplifier switching device is used to reset the integrator each time the voltage across the capacitor reaches a preset value, simultaneously tripping a mechanical register. The relative error and standard deviation of the method are said to be within 0.1%. Among the more classical coulometers, Helbig (100) discussed an ultramicrotitration coulometer based on the production of iodine, which is titrated with thiosulfate, and Van Soestbergen (290) considered some aspects of the relationship of gas production and current in the hydrogen-oxygen gas coulometer.

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