

Electroanalysis and Coulometric Analysis

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fractionating columns are few. Van Sway (17) has developed a fraction collector for use in vacuum fractionation. A piston pump ejects the collected fractions through a relief valve into suitable storage vessels at atmospheric pressure. Williams (19) has described an all-glass fraction cutter with a self-lubricated valve. This unit is suitable for vacuum operation at temperatures as high as 300° C.

Little has been added during the past two years to the fund of knowledge dealing with analytical distillation; not only has distillation equipment been of minor interest, but operating procedures and improved techniques have been scarcely considered. Pichler and Fetterer (13) have confirmed earlier findings on the consonance between continuous and intermittent withdrawal of distillate from a fractionating column.

Barker, Jenson, and Rustin (1) developed equations for predicting the rate of approach to equilibrium of a batch distillation column. The equations were solved by an analog computer. Accuracy of the equations was tested with a methylcyclohexane-toluene test mixture in a 4.5-inch diameter bubble tray column. For the column studied, condenser holdup was the most important variable affecting the rate of

approach to equilibrium. In most packed analytical columns, condenser holdup is generally very slight, and should therefore have only a slight effect on rate of equilibration.

Haring and Knol (7) discuss the influence of reflux ratio on the separating effect in a fractionating column. They distinguish between separating performance as functioning at partial reflux and separating power as functioning under total reflux. Elliev *et al.* (4) developed equations to establish a similar relationship.

Finally, a somewhat optimistic role is predicted for distillation by Wilcox (18). He devised special equations to establish conditions for preparing ultra-pure materials. These equations are simpler than those for the usual batch distillation, since the quantity of the second component is assumed to be very small. This approach may be helpful also for the ultimate recovery in purest form of compounds separated by preparative GLC where some contamination by eluted fixed phase from the GLC column has occurred.

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THIS PAPER surveys the literature and developments during 1964 and through December 1965, although papers published before 1964 which have not appeared in previous reviews in this series have also been included.

BOOKS AND REVIEW ARTICLES

A number of books dealing with electroanalytical chemistry and electrochemistry have appeared since the last review. Volume 2a of "Comprehensive Analytical Chemistry" (296) deals with electrical methods and contains one chapter on an introduction to electrochemical analysis and another on electrodeposition by A. J. Lindsey. Purdy's book, "Electroanalytical Methods in Biochemistry" (218), contains an elementary discussion of controlled potential coulometry and coulometric titrations, as well as other electroanalytical methods; Table 6 in this book lists a number of coulometric titrations that have been performed, the limits of concentration for the determinations, and their accuracy; and

Table 7 gives the supporting electrolytes for many coulometric titrations.

The new edition of "Polarographic Techniques" by Meites (179) contains sections on controlled potential electrolysis and coulometry and coulometric titrations. The description of the techniques involved in controlled potential electrolysis measurements and the discussion of perturbing effects in coulometry are of special interest. An introductory book on electroanalytical methods has also appeared (161).

Other books dealing with electrochemistry which may be of interest to workers in the field include "The Encyclopedia of Electrochemistry" (105), Conway's "Electrode Processes" (53), Delahay's "Double Layer and Electrode Kinetics" (62), and Zuman's "Organic Polarographic Analysis" (310), which discuss the fundamental principles and electrode reactions which form the basis of electroanalytical techniques. The recent book, "Amperometric Titrations," by Stock (259) contains numerous examples of this end point

detection technique, so valuable in coulometric titrations. An English translation of the book of Abresch and Claassen on "Coulometric Analysis" (1) has appeared, as well as a new book on this subject by Patriarche (207).

Several review articles on electroanalysis have been published. Szabadvary's (264) paper gives brief biographies for many of the pioneers and research workers in the field of electroanalysis. Foreign language reviews of electroanalysis (191, 198) (Japanese), electrogravimetric analysis (31) (Dutch), coulometric analysis (3, 182) (Russian), and controlled potential coulometry (237) (French) have also appeared.

NEW TECHNIQUES

Flow Electrolytic Methods. Interest has been revived in techniques based on electrolysis of flowing streams of solutions for analysis or separations. Sporadic reports in the past have been concerned with attempts at carrying out the electrolysis of a flowing

solution on an electrode contained in a column—a marriage of chromatographic and electrodeposition techniques—but recent interest in this method, described as electrolytic chromatography (84, 85), potentiostatic chromatography (228), or partition chromatography by electrodeposition (24, 25), may signal a more widespread application of the technique.

For an electrodeposition on a mercury electrode, the ratio of the concentration of metal in the mercury, C_m , and in the solution, C_m^{+n} , is governed by the usual type of partition or distribution (Equation 1):

$$\frac{C_m}{C_m^{+n}} = D = \exp \left[\frac{-nF}{RT} (E - E^{\circ'}) \right] \quad (1)$$

except that the distribution coefficient, D , is a function of potential, and, if electrochemical equilibrium is attained, can be calculated by the Nernst equation, as shown in Equation 1. For depositions on a solid electrode, a similar equation usually holds in which C_m may be taken as 1 for amounts of C_m greater than a monolayer. Usually D can be made sufficiently large by adjustment of the potential that a successful separation can be made with a single batch operation. For separation of substances with similar formal potentials (E° 's), a multiple extraction or column technique may prove useful, although shifts in potentials by complexation or pH variation can also be used. Other advantages of a column technique include the possibility of selective stripping of deposited metals from the column, the concentration of trace quantities of metal ions, and the continuous purification of electrolyte solutions. Techniques and cells for carrying out the process vary. Blaedel and Strohl (24, 25) and Roe (228) attempted to minimize the iR drop through the column to obtain a uniform potential. Fujinaga and co-workers (84, 85) purposely introduced an iR drop so that a graded potential down the column was established.

Packing materials for the columns have included graphite (24), amalgamated nickel (228) or platinum (25), and silver (85) powders or wires. Successful separations of Cu, Pb, Cd, and Zn (24) and Cu, Pb, and Cd (84, 85) have been reported. Under some conditions, operation as a true chromatographic technique with the measurement of retention times and elution curves can be accomplished (25).

When the electrode reactions during the flow through the column proceed with 100% current efficiency and with 100% conversion, coulometric measurements are possible. The concentration of the electroactive substance, C ,

in the flowing solution can then be calculated by equating the current, i , with the rate of flow of solution into the column, G , yielding

$$C = \frac{i}{nFG} \quad (2)$$

where n is the number of electrons transferred in the electrode reaction and F is the faraday.

Eckfeldt and Shaffer (75) used this technique to determine oxygen (and suggested the term "constant potential derivative coulometry" for the method), employing a flow cell with silver spheres as the working electrode. The obvious advantage of this method of analysis compared to galvanic analyzers with smaller electrodes is that calibration is unnecessary (no unknown calibration terms appear in Equation 2) and the current is independent of changes in temperature, electrode surface, solution viscosity, etc. Oxygen at the 1-p.p.m. level was determined by this technique with a relative error within 1%; at the 0.01-p.p.m. level, the error was -10%.

Shropshire (245) used a fritted glass sparger coated with silver or platinum black as the electrode in the flow cell, and showed that satisfactory results could be obtained for the reduction of permanganate ion in 3.7M H₂SO₄. Novak (195) proposed an analysis of SO₂ at low concentrations in gas streams based on the reaction of the SO₂ with a solution stream of H₂SO₄ or Na₂SO₄ containing excess I₂. The I⁻ produced as a result of the reaction is oxidized at a platinum anode at a constant potential with 100% current efficiency; the current for this oxidation is a measure of SO₂ concentration as given in Equation 2. An internal electrolysis technique, employing a platinum-K₂Cr₂O₇ cathode, was used to maintain the anode potential constant. Although this method is reminiscent of continuous coulometric titration with an electrogenerated titrant, it is different in that it is a controlled potential, rather than a controlled current, technique, and does not require separate indicator electrodes nor the usual feedback loop for controlling the current. On the other hand, reagent must be added to the sample stream and the flow conditions and conversion efficiency may be more stringent. Novak suggests the name potentiostatic coulometric analysis for the method.

Interest in fuel cell technology had led to application of these methods to analysis. For example, H₂ in inert gas mixtures can be determined by measuring the current resulting from its oxidation under fuel cell-type conditions at a porous graphite-platinum black electrode (18). The accuracy for 0.1 to 100% H₂ is better than ±0.2%. Similarly, Langer and Haldeman (158)

showed that O₂ can be separated from air and other gas mixtures using catalytic porous oxygen electrodes and the electrolytes and membranes usually employed in fuel cells.

Thin Layer Electrolysis. Anson and co-workers (46, 47, 113, 114) introduced the technique of electrolyses carried out in thin layers (0.02 to 0.1 mm.) of solution. Christensen and Anson (46) showed that for electrolysis at a constant current, i , at an electrode of area A , and a cell thickness, l , the following equation holds:

$$\tau = \frac{nFAIC^{\circ}}{i} - \frac{l^2}{3D} \quad (3)$$

for $l^2 < \tau D$, where D is the diffusion coefficient of electroactive species, C° is its concentration, and τ is the transition time. Under conditions where the term $l^2/3D$ is negligible, Equation 3 becomes

$$Q = nFAIC^{\circ} \quad (4)$$

the usual coulometric analysis equation, which holds for both constant current or constant potential analysis. The advantage of this technique, as with other electrolytic techniques involving large electrode area-solution volume ratios—e.g., flow electrolysis and high speed coulometry—is rapid analysis with calculations based only on Faraday's law. Although the early electrodes used in thin layer methods, accidentally or purposefully imperfect platinum-in-glass seals, were rather inconvenient to use, improved electrodes (113, 200) make the method easier to apply. Recently, Reilly and co-workers have presented a cell design for use with a mercury-coated platinum electrode (200) and discussed the coulometric determination of a mixture of Cu(II), Pb(II), Cd(II), and Zn(II) and a mixture of Cl⁻, Br⁻, and I⁻ at a concentration level of 5 to 10mM (199). The average errors in these determinations was rather large (about 10%), mainly because of difficulty in obtaining an accurately known l and the large background current due to diffusion to the edges at the electrode. The technique has also been used to study adsorption of electroactive substances (114) and the kinetics of solution reactions of electrogenerated substances (47).

ELECTROSEPARATIONS

Electrolytic Sample Dissolution and Preparation Methods. Several recent reports have appeared on anodization of metallic samples as a method of dissolution and separation. Barabas and Lea (10) used anodic dissolution of a Cu sample at a high current for a short time in an automated colorimetric analysis of P in Cu. Anodic dissolution techniques have also been reported for the analysis of oxide inclusions in

steel (44). The steel sample, connected as an anode, is dissolved into an ammonium citrate electrolyte at a current density of 100 ma. for several hours. A residue of the oxides and other impurities collects in the cell and is separated and analyzed by a bromination procedure.

The determination of beryllides in a steel sample following anodic dissolution into a NH_4F -citric acid-HCl electrolyte has also been reported (306). Several electrolytic methods of sample prepara-

tion before analysis have been described. Dobzhaeva (66) employed electrolytic deposition of Au on a C anode as a means of concentrating the Au (present at a 0.03 gram per ton level) before spectrographic analysis. Deposition of Au on a Cu disk electrode prior to x-ray spectrographic analysis has also been described (183).

Mark and Berlandi (170) found that controlled potential electrodeposition of metals on a pyrolytic graphite electrode is a useful method of sample

preparation before neutron activation analysis. The use of pyrolytic graphite as an electrode material is of importance in this application because it is available in a highly pure state, has a low neutron cross section, and gives a low background count. The method combines the selectivity of controlled potential procedures with the sensitivity of neutron activation analysis; determinations of Ag in concentrations as small as $10^{-7}M$ have been accomplished. Deposition of Au, Ag, Cu, and Co on a pyrolytic graphite electrode under carefully controlled conditions has also been shown to be useful in the preparation of standards (289).

Dryburgh (68) described a cell for preparation of sample of radioactive samples by small scale electrodeposition; the preparation of a 14.4-k.e.v. γ -ray source of cobalt-57 was given. The separation and determination of tantalum-182 and niobium-95 by electrolytic procedures have been investigated (100). Parker and Baumgartner (205) describe a method of preparation of samples for electron microscopy based on electrolysis on a specimen support grid covered with a thin layer of mercury. After electrolysis the mercury is removed and the deposited material on the specimen grid is ready for observation.

Electrophoretic Deposition. Deposition of charged particles moving as a result of an applied electric field has been used for sample preparation in radioactivity measurements in several recent papers and in the past. Donnan and Dukes (67) deposited microgram quantities of Pu, Np, Am, and Cm, employing U as a carrier and an $\text{NH}_4\text{Cl-NH}_3$ electrolyte and Pt electrode. The mode of deposition involves hydrous oxide formation in the higher pH region near the cathode, followed by deposition. Essentially quantitative recovery of the actinides is obtained in the presence of the carrier.

Use of a U carrier was also recommended by Smith and Barnett (251) in the deposition of Pa at a stainless steel cathode employing a fluoride or oxalate medium. Deposition of Pa on a platinum cathode from a formate medium has also been described (241). Other studies of this type include the deposition of Th, U, rare-earth elements (under the title of molecular plating) (206), and Ac (116). The general theory and mechanism of electrophoretic deposition, particularly with metal powders and other inorganic suspensions, have been reviewed recently by Brown and Salt (32). Electrodeposition of organic substances, which has been widely used as a technological method of forming organic coatings [see for example (94)], may be of interest in the future as an analytical separation technique.

Table I. Electroseparations

Separation of	From	Method	Reference
As, Sb	Fission products	Formation of AsH_3 and SbH_3 by flash electrolysis	(277)
As		Formation of AsH_3 at Pt electrode	(6)
Bi	Co	Electrodeposition of Bi at Hg cathode	(157)
Bi	Pb, Fe, Cd, In, Ga, Zn	Selective oxidation of mixed metal amalgams	(93)
Bi, Cu	Pb	Electrodeposition of Cu and Bi at Pt electrode	(144)
Bi, Cu	Ni	Electrodeposition at Pt electrode using internal electrolysis with Pb anode	(159)
Cd	Ni	Electrodeposition of Cd in media containing various complexing agents	(99)
Cd, Cu, As	In	Electrodeposition of Cd, Cu, and As prior to polarographic determination of In	(148)
Cu	As	Electrodeposition of Cu, followed by deposition of As and evolution of AsH_3 by controlled potential	(147)
Cu	As, Cd, In, Zn	Electrodeposition of Cu	(190)
Cu, Zn, Ag		Deposition of Pt electrode using internal electrolysis with Cu, Zn, or Mg anode	(243)
Eu	Fission products	Reduction with electrolytically prepared Li amalgam	(35)
In	Fe, Zn	Electrodeposition of In at controlled potential	(145)
In	Ga, Ge	Electrodeposition of In at controlled potential	(140)
Mo, Ni		Electrodeposition at Pt electrode as $\text{Mo}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and Ni	(217)
Mo, Re		Electrodeposition as $\text{Mo}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and Re	(89)
Ni	Fe, Pb, Zn, Cr, Cu	Oxidative internal electrolysis with PbO_2 , Pb cathode	(164)
Ni	Th	Electrolytic reduction of Ni	(285)
Ni		Electrodeposition of Ni under various conditions	(216)
Pb	Sn	Electrodeposition on Cu-clad Pb or Pt microelectrodes	(146, 194)
Pb	Co	Electrodeposition of Pb at Hg cathode	(156)
Pb	U	Electrodeposition of Pb at solid cathode	(149)
Pm	Lanthanons	Reduction at Li amalgam cathode in citrate medium	(201)
Rh	Ir	Electrodeposition of Rh under various conditions	(168)
Se	Cu, other metals	Electrodeposition of Se and Cu; dissoln. of Cu in dilute HNO_3	(307)
Sm	Pr, Nd	Reduction of Hg cathode in tartrate medium	(246)
Sn	W	Electrodeposition of Sn in oxalic acid medium	(141)
Sn	Ge	Electrodeposition of Sn at controlled potential	(139)
W	TiC	Anodic oxidation of W in sample in NaOH medium	(174)
Yb	Y, Er	Deposition at Hg electrode from acetate-citrate medium	(261)
Stepwise Deposition of Metals by Controlled Potential Electrolysis			
Au, Cd, Cu, Hg, Pd, Pb, Sb, Se, Sn		Pt electrode in oxalate medium	(273)
As, Cr, Fe, Mn, Pd, Se, Te		Pt electrode in various media	(274)
Bi, Cu, Pb	Ge, Th	Various media	(40)
Cu, Cd, Co, Ni, Zn		Cu or Pt electrodes	(43)

Other Separations. Electrochemical methods for concentrating trace elements by electrolysis in the analysis of metal samples have been reviewed (92, 143, 150). Collén (51, 52) studied the electrolytic separation of Li isotopes at a streaming mercury electrode in LiCl and LiOH solutions. The oxidation of cobalt(II) in the presence of EDTA using an internal electrolytic technique with a PbO₂ cathode prior to the photometric determination of Co has been investigated (154). Fong (81) has studied the electrolysis of rare earth ions in CaF₂, SrCl₂, and BaBr₂ in the solid state at temperatures of 300–700° C., at W or Au electrodes. Although the purpose of this work was not analytical, the concept of solid state electrolysis is an interesting one, particularly in light of recent interest in solid state reactions in analytical chemistry (291). Table I summarizes other work in electroseparations.

ELECTROGRAVIMETRY

Further developments in the use of electrodeposition methods involving radioactive tracers for measuring rates of exchange reactions have been reported (16). Carman and Markham (41) described the electrodeposition of Pb as PbO₂ on a Pt electrode; the electrode and deposit were immersed in distilled water during the final weighing. This technique has the advantage of not requiring drying the electrode, and yet does not necessitate measuring the density of the deposition medium. Even with the necessary buoyancy corrections, an average error of only ±0.2 mg. for 40-mg. quantities of Pb was reported. This method seems particularly attractive for deposits which might undergo unknown changes on heating. Rosanda (230) observed that occlusions of organic material which sometimes occur during the electrodeposition of Cu by a constant current method do not occur when deposition is carried out by a controlled potential method. Other work on electrogravimetric methods is summarized in Table II.

CONTROLLED POTENTIAL COULOMETRY

Determinations. The latest value of the faraday is 96,487.0 coulombs per equivalent based on a carbon-12 scale and an atomic weight of silver 107.870 (104). Several variants of controlled potential coulometry have been described. Rechnitz and Srinivasan (224) described a differential coulometric technique and its application to the reduction of dichromate to chromium(III). In this technique, a cell containing a standard amount of substance to be determined is connected

Table II. Electrogravimetric Determinations

Determination of	Method	Reference
Ag	Controlled potential deposition in 0.1N HNO ₃ and ammoniacal EDTA media	(268, 283)
Au	Controlled potential deposition in oxalate and NaOH media	(273)
Cd	Controlled potential deposition in oxalate and NaOH media	(273)
	Effect of solution conditions on structure of electrodeposited Cd	(95)
	Rapid electrodeposition on Winkler electrodes	(125)
Cu	Deposition at controlled potential	(60, 98, 268, 273)
	Deposition at vibrating and Winkler electrodes	(79, 125)
	Constant current depositions; determination in Al alloys, copper naphthenate, and other	(17, 110, 284)
	Internal electrolysis, using Zn anode	(2)
Co	Cathodic deposition from various complexing media	(15)
	Deposition at rotating Pt cathode; interference of various ions studied	(247)
Fe	Deposition at controlled potential in oxalate and NaOH media	(273)
Hg	Deposition at controlled potential in oxalate and NaOH media	(273)
In	Deposition at Cu-clad Pt cathode at controlled potential in oxalate-HCl medium	(140)
Mo	Deposition as Mo ₂ O ₃ ·3H ₂ O at controlled potential at Ni-plated electrode	(88)
Ni	Cathodic deposition from various complexing media	(185)
Pb	Deposition as PbO ₂ at Pt anode	(41)
	Depositions as Pb	(39, 149, 239, 273)
Pd	Controlled potential deposition of Pd in various media	(60, 274, 282, 283)
Pt	Constant current deposition at Pt electrode	(87)
Sn	Controlled potential electrodeposition at Cu-clad Pt electrode from various oxalate media	(138, 139)
	Rapid deposition on Winkler electrodes	(125)
Te	Controlled potential deposition from various media	(274)
U	Deposition at UO ₂ ·2H ₂ O on Pt electrode by internal electrolysis using Cd or Zn anode	(160)
Zn	Controlled potential deposition in oxalate and NaOH media	(273)
	Deposition by internal electrolysis using Al anode	(2)

in series with an identical cell containing the sample at a slightly higher concentration. Controlled potential coulometry is carried out in the standard until the current decays to background, and then in the sample cell, integrating the current for the remainder of the electrolysis in the usual way. The amount of electroactive substance in the sample is equal to that in the standard plus the amount determined by the additional electrolysis. The major advantage of this technique appears to be an automatic cancellation of the residual current during the major part of the electrolysis, if it is assumed that the standard and sample cell conditions are almost identical. Errors below 0.1% in the determination of 0.4-mg. amounts of Cr were obtained when similar amounts of standard and sample were employed. King and Bard (133) pointed out the advantages of measuring the amounts of gas evolved during a coulometric electrolysis. One application of this technique is in elucidating the mechanism of electrode reactions and was employed in studying the electrochemistry of the methylhydrazines (134). The method may also be of value in making corrections for electrolysis of the solvent for electrode reactions occurring at potentials where

appreciable solvent reduction or oxidation occurs.

Goode and Herrington (96) used a modification of the previously reviewed high-speed coulometry technique, involving a cell with a large electrode area-solution volume ratio, and carried out the electrolytic reduction of Fe(III) and oxidation of Pu(III) with electrolysis times less than two minutes. Johanson (121) also described an efficient electrolysis cell composed of rotating platinum gauze disks in a small solution volume, and used it to monitor the effluent of chromatographic columns. At flow rates below 1 ml. per minute, less than 0.5% of the effluent material—e.g., copper ion—was unreduced. Takata and Muto (270) also used a coulometric cell containing a Cu gauze electrode for monitoring the effluent of a cation exchange chromatographic column. The separation, detection, and estimation of Au(III), Cu(II), and Fe(III), were described.

The examination of boron carbide electrodes for controlled potential coulometry was reported; results of this initial study do not appear promising (187). Modifications of the Karl Fischer titration method for the determination of water, previously used as a coulometric titration technique, for

use in controlled potential coulometry have been described. In Lindbeck and Freund's method (162), the Karl Fischer electrolyte, 0.15M SO₂, 0.6M pyridine, 0.1M NaI in methanol, is added to the cell and a known quantity of iodine is generated. The sample is added and allowed to react, and the excess iodine is determined by controlled potential coulometric reduction. A blank correction for the amount of iodine lost in the absence of sample is necessary. Water in methanol and dimethyl sulfoxide in 10- to 80- μ g. amounts was determined with standard deviations of 0.2 to 0.3 μ g. In the method of Rechnitz and Srinivasan (225), all of the iodide in the Karl Fischer reagent is oxidized to iodine, and the iodide produced as a result of reaction of the water was determined by controlled potential oxidation. Errors of 1 to 5% were reported for 1- to 2-mg. amounts of water. Other controlled potential coulometric determinations are summarized in Table III.

Electrode Mechanisms. Meites (178) showed that in the coulometric electrolysis of a substance undergoing a totally irreversible electrode reaction, complete reduction or oxidation occurs at any potential where appreciable current flows—i.e., at potentials on the rising part of the polarographic wave; the reduction of hydrogen ion on mercury was used to demonstrate this case. An evaluation of the rate constants for various competitive and competing reactions in controlled potential coulometry has been described (90).

The technique of reversal coulometry has been introduced to study reactions following the electron transfer reaction (11). The technique involves carrying out a coulometric reduction (or oxidation) for a known time, followed by a change of potential—for example, to cause oxidation (or reduction) of the electrogenerated species. From the difference in the amount of electricity consumed in the forward and reverse

direction, an estimate of the rate constant of reactions consuming the species electrogenerated during the first electrolysis can be made. The technique was checked by investigating one of the favorite reactions of electrochemists, the hydrolysis of benzoquinone imine, electrogenerated by the electrooxidation of *p*-aminophenol. Rechnitz and McClure (223) discussed the application of controlled potential coulometry to the study of reactions in which the electroactive species is regenerated by a chemical reaction following the electrode reaction (a catalytic reaction). When reactions like this occur, a steady state current significantly higher than the background current occurs, and by a study of the variation of the steady state current with steady state concentrations, the order and rate of the catalytic reaction can be determined. The reaction between IrCl₆⁻² and ClO₃⁻ was studied using this technique (221).

Controlled potential coulometry was used in the study of a number of inorganic electrode reactions. The reduction of Be(H₂O)₄⁺² was shown to occur in a two-electron reaction to Be(OH)₂, H₂, and water in a 0.5M LiCl medium (244). Ward and Wright (294) showed that the oxidation of azide ion produces nitrogen in a one-electron reaction. Desideri (65) investigated the reduction of permanganate at various concentrations of mineral acids. At concentrations of H₂SO₄ below 2M, the apparent number of electrons involved in the reaction (*n*) was five. At higher H₂SO₄ concentrations, *n* decreases, becoming two in 18M H₂SO₄. The reduction of titanium tetrachloride in acetonitrile was shown by Kolthoff and Thomas (142) to occur in two one-electron steps to Ti(III) and Ti(II).

Jones and Anson (124) used coulometry to study ligand bridging by chloride and iodide ion in the oxidation of Cr(II) at a mercury electrode. The reduction of Mo(VI) in acidic chloride media was studied by Wittick and Rechnitz (301). Israel and Meites (115) studied the oxidation and reduction of various vanadium species at a mercury electrode in sulfate media and described several possible analytical applications of the electrode reactions. The reduction of Re(VII) in H₂SO₄ was shown to occur by a three-electron reaction when the reduction was carried out under the usual electrolytic conditions (245). When the electrolysis is carried out under high speed electrolytic conditions, however, *n* values of about 1.4 were obtained. This was ascribed to the reduction of Re(VII) to the VI state, followed by a slow disproportionation of the Re(VI) to the VII and IV states.

VanLoon and Page (288) investigated the reduction of Rh(III) by coulometry

Table III. Controlled Potential Coulometric Determinations

Substance determined	Method	Reference
Ag	Trace amounts in U (nuclear fuel)	(271)
Am	Reduction of Am(VI) → Am(V) at Pt electrode in 2M (NH ₄) ₂ SO ₄ -0.2M H ₂ SO ₄	(137)
Co	Reduction of cobalt-60(II) at microelectrode	(242)
Cr	Cr(VI) → Cr(III) at Pt electrode	(224)
	Cr(III) → Cr(II) in fused KCl-LiCl	(42)
Cu	Cu(II) → Cu(0) in microgram amounts using I-Q recorder	(106)
	Cu(II) → Cu(0) in fused KCl-LiCl	(42)
Eu	Eu(III) → Eu(II) at Hg electrode or Eu(II) → Eu(III) at Pt electrode in 0.1M HClO ₄	(56)
	Eu(III) → Eu(II) at Hg electrode in acetonitrile medium	(297)
Fe	Fe(III) → Fe(II) at Pt electrode	(96, 123)
Ni	Ni(II) → Ni(IV)-dimethylglyoxime complex at Pt electrode	(61)
Pb	Pb(II) → Pb in microgram amounts	(106, 304)
Pd	Pd(II) → Pd(0) at Au or Hg electrode	(269)
Pt	Pt(II) → Pt(0) in fused KCl-LiCl	(42)
Pu	Pu(III) → Pu(IV) at Pt electrode	(96)
Rh	Rh(III) → Rh(0) at Hg electrode	(288)
Sm	Sm(III) → Sm(II) at Hg electrode in acetonitrile	(297)
Sn	Sn amalgam → Sn(II), following reduction of Sn(IV) in bromide medium	(300)
U	Review of methods	(275)
	U(VI) → U(IV) in presence of various metals	(97, 123, 188, 235, 236)
V	V(III) → V(IV) in fused KCl-LiCl	(42)
	Reductions and oxidations of various V species in 1M H ₂ SO ₄ -3M KHSO ₄	(115)
	Trace amounts of U (nuclear fuel)	(271)
Organic Substances		
Substituted hydroquinones	Oxidation (<i>n</i> = 2) at Pt electrode in 1M H ₂ SO ₄	(234)
<i>p</i> -Phenetidine	Oxidation (<i>n</i> = 2) at Pt electrode in 1M H ₂ SO ₄	(233)
<i>N</i> -Substituted phenothiazines	Oxidation (2e) to sulfoxide; oxidation (1e) to radical at Pt electrode; or reduction (2e) of sulfoxide at Hg electrode	(180)
Azo-dyes	Reduction at Hg electrode	(45)
Others		
Fluoride ion	Controlled potential generation of Ce(IV) in null point potentiometry	(197)
Hydrogen, in Fe	Integration of current-potential curves for slow potential scan	(82)
H ₂ O	Methods based on Karl Fischer titration (see text)	(162, 225)
Nitrate ion	Catalytic reduction in presence of U(III) as a catalyst at Hg cathode	(73)

and polarography in a chloride medium. Page and Zinser (203) have reinvestigated the reduction of Ir(IV) in a perchlorate medium, and find results different from those of Rechnitz and McClure (222). The latter authors explained n values larger than one by a reaction between Ir(III) and perchlorate ion, leading to steady state currents larger than background. Page and Zinser failed to find limiting currents larger than background and explain the high n values as some iridium being in an oxidation state higher than IV.

Coulometric methods have also been used in the study of electrode reactions of organic substances. Spritzer and co-workers (255) found that the reduction of pyridinium ion in a pyridine solution containing 0.1M LiClO₄ occurs in a one-electron reaction. Struck and Elving (262) investigated the behavior of the alloxan-alloxantin-dialuric acid system using polarography, coulometry and product analysis; the reduction of alloxan in an aqueous buffer at pH = 4 occurred with $n = 2$, and yielded diauric acid. The reduction of vitamin B12a (aquocobalamin) at a mercury electrode in aqueous buffers was studied by Hill *et al.* (112). At pH's of 1 or 8 the reduction yields vitamin B12r ($n = 1$); at pH 8 and more negative potentials, vitamin B12s ($n = 2$) is produced.

Gelb and Meites (91) studied the reduction of α -furdioxime using polarography and controlled potential electrolysis. Evidence was presented for a chemical reaction following the initial electrode reaction producing another electroactive species (an ECE reaction), and an analysis of the current-time curves during the controlled potential electrolysis was employed to determine rate constants. Controlled potential electroreduction and coulometry were employed by Bréant and Merlin (29) to study the mechanism of reduction of 1,2-dinitrobenzene in acidic, aqueous solutions. Reduction at potentials corresponding to the second polarographic wave was shown to yield *o*-benzoquinone diimine ($n = 10$), which can undergo further coupling or hydrolysis reactions.

Coulometric methods were also used to study the reduction of diazoacetophenone in aqueous buffers at various pH's (54). Solon and Bard (252) showed that the stable radical diphenylpicrylhydrazyl (DPPH) is reduced and oxidized in acetonitrile solutions in one-electron reactions to DPPH⁻ and DPPH⁺, respectively. These authors also studied the reaction of DPPH and bromide ion by an analysis of coulometric data based on previously reviewed theoretical work and proposed a mechanism for the reaction (253).

The oxidation of tetraphenylborate ion at a pyrolytic graphite electrode in

aqueous solution was studied by Turner and Elving (286); although the results were somewhat complicated by film formation on the electrode, they were in general agreement with previous studies at platinum electrode in nonaqueous solvents. Gardiner and Collat (86) demonstrated that the oxidation of borohydride ion in alkaline aqueous solutions at a mercury electrode occurs with $n = 8$.

The electroreduction of tetraphenylstibonium ion at a mercury electrode in 0.1M KCl was shown to occur in two steps by Morris and co-workers (186). Reduction at the first step occurs with $n = 1$ and yields diphenylmercury and triphenylstibine; for the second step, $n = 2$, and triphenylstibine and benzene are formed. King and Bard (134) studied the oxidation of several methylhydrazines at a platinum electrode in H₂SO₄ solution. Methylhydrazine is oxidized in a four-electron reaction, just as hydrazine itself is; the mode of oxidation of the dimethylhydrazines is somewhat more complicated and was elucidated using gas volume and chronopotentiometric measurements during the course of the coulometric oxidation.

Valenta and Koryta (287) used a small auxiliary mercury electrode to record current potential curves on an oscilloscope during the electrolysis. The analysis of solutions during a controlled potential electrolysis by electrochemical, spectrophotometric, or chromatographic methods is a powerful tool in elucidating the course of a complex electrode reaction.

CONTROLLED CURRENT COULOMETRY—COULOMETRIC TITRATIONS

Determinations. Eckfeldt and Shaffer (76) have reemphasized the proposal that the coulomb be established as the standard for volumetric work. These authors demonstrated that precise results can be obtained in the titration of acids with commercially available equipment. Several new applications of the Karl Fischer coulometric titration have been described (214, 290). Two papers have appeared using coulometric titrations of the combustion products of organic substances in carbon and hydrogen determinations. In one method (103) the organic compound is converted to CO₂ and water by treatment with Co₃O₄. The water is determined by electrolysis in an electrolytic hygrometer (a cell for electrolyzing water composed of Rh electrodes and P₂O₅). The CO₂ is passed through a LiOH converter where an equivalent amount of water is produced, which is analyzed as before. The standard deviations by this method were $\pm 0.3\%$ for carbon and $\pm 0.03\%$ for hydrogen for 2- to 10-mg. samples.

In the second method (172), the CO₂ is determined by passing it into a Ba-

(ClO₄)₂ solution and titrating with electrolytically generated base. The water is reacted with PCl₅; the HCl produced in this reaction is reacted with NaHCO₃; and the CO₂ which is produced is determined as before. The determination of carbon and hydrogen in a 5-mg. picric acid sample was reported with average errors of ± 0.3 and $\pm 0.2\%$, respectively.

Badoz-Lambling and Stojkovic (8) described a coulometric titration of phenothiazine in an acetonitrile solution. The oxidation of phenothiazine, *P*, to the radical *R*, occurs first. When the current efficiency of this process drops below 100%, the reaction which occurs is the oxidation of *R* in another one-electron step to *S*. Because any generated *S* will react with *P* to produce *R* in the bulk solution, the overall current efficiency for the process *P* \rightarrow *R* remains 100%. Several different potentiometric and amperometric end point detection techniques were described.

Aikens and Carlita (4) have proposed the novel concept of coulometric generation of a titrant from a thermodynamically unstable species and demonstrated that the electrogeneration of Cr(II) in acidic solutions could be accomplished with a high current efficiency. Because the reduction of Cr(H₂O)₆⁺³ occurs at about -0.65 volt *vs.* N.H.E. and is kinetically controlled, a good current efficiency for the generation of Cr(II) cannot be obtained in strongly acidic solutions. However Cr(H₂O)₅Br⁺², an unstable but substitution inert coordination compound, reduces at -0.105 volt *vs.* N.H.E. [an underpotential of 0.30 volt relative to the thermodynamic reduction potential of Cr(H₂O)₆⁺³, the stable equilibrium species], so that Cr(II) can be generated successfully from this species. The authors point out that this general behavior can be expected for electrode reactions where the reactant is a thermodynamically unstable but substitution inert coordination compound and the product of the electrode reaction is substitution labile. Durand and Tremillon (74) reinvestigated the oxidation of mercury in acetic acid-acetic anhydride media and propose that the previously described coulometric titrations of acetate in acetic anhydride [for example, (175)] are precipitation titrations involving the precipitation of mercury(II) acetate, rather than acidimetric ones.

Bishop and co-workers (21, 22) demonstrated that controlled current two-electrode potentiometry (differential electrolytic potentiometry) is a sensitive end point detection technique in coulometric titrations. The authors describe a microcell with a solution volume of about 0.01 μ l. for titrations of $2 \times 10^{-3}M$ chloride or bromide ion in 0.01M HNO₃-80% methanol (22). Both macro and micro amounts of acids have

been determined using this end point detection technique with antimony electrodes (22). A method of end point location based on using the generator electrode as a potentiometric indicator electrode, during periods when the current is not flowing, has also been proposed (5).

Several new applications of coulometric detectors in gas chromatography have been described. Coulson (58) found that mercury-coated platinum was a better electrode than silver for the microcoulometric titration of chloride in column effluents. Martin and Grant (173) detected sulfur effluents by combustion to SO₂ and titration with electrogenerated iodine. A titration of mercaptans with electrogenerated silver using an acetic acid solution has also been described (83). Among other reported applications, Mead *et al.* (177) used electrogeneration of silver ion to study the formation of amine complexes in acetone. Christian (49) found coulometric titration to be a convenient method of calibrating micropipets. The use of glass coated with tin oxide, "conducting glass," as indicator electrodes and as generator electrodes in coulometry has been described (71). Bréant and Robin (30) have included coulometric and other electrochemical methods in a training program.

Measurements of Reaction Rates. Several new applications of coulometric titrations to the measurement of the rate constant, *k*, of homogeneous chemical reactions have been reported. These methods have the advantage of providing convenient addition of the reactant, particularly unstable ones such as bromine, and, being ideally suited to low concentrations, are capable of use in the measurement of rapid reaction rates. Dubois (69) proposed a method of continuous coulometric generation of a reactant, maintaining the concentration of the reactant at a low constant value. Using this technique, Dubois studied the bromination of several amines, and measured *k*'s of 10⁸ to 10⁹ liters/mole-second. In a later study (70), the reactant (bromine) was generated with a constant current and the rate of consumption of the bromine upon addition of a reactant was followed amperometrically.

Other workers using this technique included Riccoboni and Oleari (226), who measured the rates of iodination of (CH₃)₄Pb, (C₂H₅)₄Pb, and Sn₂(C₂H₅)₆ by generation of iodine, and Janata and Zyka (117), who determined the rate of bromination of diphenyl sulfide. O'Dom and Fernando (196) employed a modification of the amperometric technique to follow the course of a reaction. In this method, bromine is generated with a constant current in the presence of a reactant, and the current at the

indicator electrode is monitored. For slow reactions, the amperometric current increases continually because the bromine concentration continually increases, while for fast reactions the amperometric current remains small until all of the reactant is consumed. For intermediate reaction rates, a plateau is obtained in the amperometric current time curve; for reactions giving this response the rate constant can be determined by noting that at this steady state condition, the rate of reaction = rate of bromine addition = $i/2F$.

Continuous Coulometric Titrations. Takahashi and Sakurai (266) reviewed applications of automatic recording equipment for continuous coulometric titrations of As(III) and Fe(II) with bromine and permanganate and dichromate ions and chlorine with Fe(II). Barendrecht (12) described a cell and instrumentation for a continuous Karl Fischer titration. Buck and Eldridge (36) described the continuous titration of unsymmetrical dimethylhydrazine in p.p.m. amounts with electrogenerated bromine. Titration systems for monitoring a minor constituent in a gas stream—e.g., boranes in air—based on a coulometric titration (181) and for determining chlorine in gases (254) have been described. Other continuous coulometric titrations reported include the determination of iron in water (232) and ozone (59).

A patent has been granted for a cell in which the generator and counter electrodes are separated by ion exchange resin (135). Kesler and co-workers (132, 295) have described the application of coulometric titrations to determinations in pulping liquors.

Galvanic Analyzers. Interest remains high in galvanic oxygen analyzers based on the reduction of oxygen at a silver or gold electrode, usually covered with a thin membrane of polyethylene, Teflon, or polyvinyl chloride, in a cell employing a consumable anode, usually of lead or cadmium (9, 13, 122, 165, 215, 227, 292, 303). The use of the galvanic oxygen analyzer for the determination of oxygen in gas chromatography has been investigated (211). Applications of the water analyzers based on the electrolysis of water at platinum electrodes covered with P₂O₅ (the electrolytic hygrometer or Keidel cell) have been described (209, 293).

In the determination of water in liquid hydrocarbon streams, the water was chromatographically separated before it passed on to the detector (209). Hibbs and Nation (111) proposed a method for the determination of p.p.m. amounts PbO based on reduction of the PbO with hydrogen and determination of the water with a water analyzer. Guthke (102) developed analyzers for

determining hydrogen and chlorine in HCl gas streams based on fuel cell principles. Hersch and co-workers (109) recommend electrolytic generation of gases for the calibration of gas analyzers. Methods for direct generation of O₂, H₂, D₂, N₂, Cl₂, CO₂, NO, C₂H₆, O₃, AsH₃, and SbH₃ and indirect production of CH₄, C₂H₂, and H₂S are given.

Stripping Methods. Determinations of the thickness of deposited metals, such as Ni on brass, Cd on Cu or steel, Cu on brass, and Zn on Cu, brass, or steel, have been reviewed (192). Tribalat and Mofidi (278) showed that the anodic oxidation of Re occurs with 100% current efficiency and suggested the coulometric determination of Re films and alloys. A method for the investigation of Ag-Cu alloys based on observation of the potential-time curve during a constant current anodization has been described (176). Recording of the potential-time curve was also employed by Rao and Udupa (220) in the determination of oxygen in solid PbO₂.

APPARATUS

Lott (167) has reviewed instrumentation for coulometry and electrodeposition. Applications of operational amplifiers to electroanalytical studies have been reviewed (118). Booman and Holbrook (28) have discussed the design of optimum stabilization networks for use in potentiostatic circuits. Although this study is primarily concerned with polarographic instrumentation, many of the considerations—e.g., optimization of rise time and effect of uncompensated resistance—apply to potentiostats for macroscale electrolysis as well. In a later paper (238), the simplified use of transfer functions for cells and circuits is described and applied. The papers by Osterwald (202) and Pepersack *et al.* (210) on factors affecting the behavior of potentiostatic circuits are also of interest. The descriptions of two cells for controlled potential electrolysis have been published (55, 208).

Coulometric Titration Apparatus. Patents for two coulometric reagent-generating cells have been reported (14, 136). A transistorized stabilized constant current source has been described (153). Two titrators based on potentiometric end point detection have been designed. Johansson's (120) apparatus is based on solid state operational amplifiers and was used for acid-base titrations with automatic reduction of the current in the vicinity of the end point to prevent over-titration. The instrument of Steed and Fransman (256) can be used for either manual or coulometric titrations. Two potentials are set on the instrument. When the first potential is reached,

pulsed addition of reagent, in pulses of variable duration, occurs. The titration terminates at the second potential. Apparatus for the automatic coulometric titration of bases in concentrations as low as 5 μg . per ml. (240) and for carbon and sulfur in metals (37) have been described. Eckfeldt and Shaffer (77) have designed a semiautomatic precision pipet capable of delivering milliliter size samples with a standard deviation of $\pm 0.02\%$ and said to be especially suitable for use in coulometric titrations.

Potentiostats. Brown (33) described the design of a potentiostat used in the dissolution of nuclear reactor fuel elements; an equivalent circuit for the electrolytic cell used to test the circuit is given. In a later report (34) he suggested that a study of the noise generated at a bubbling electrode may be of use in the design of potentiostats. Rogers (229) discussed a transistorized differential amplifier for use as a potentiostat with an extremely wide output current range (1 μa . to 10 amperes) at up to 20 volts with a response time of 1 msec. and a maximum input current of 3 nanao. A solid state potentiostat based on a silicon-controlled rectifier and a unijunction transistor circuit have been described by Lindstrom and Davis (163); the instrument can supply up to 5 amperes and 10 volts, with a response time of 40 msec. Potentiostats for continuous and discontinuous electrolysis have been described (78).

Of particular interest to Russian electrochemists are the potentiostat of Pamfilov and Skakun (204), designed primarily for kinetic investigations, that of Marshakov and Zakutskii (171), based on a servo-mechanism device, and one (166) based on operational amplifier-type circuitry with a high input impedance (3.3×10^8 ohms) and a maximum output current of 50 ma. and 100 volts. Two descriptions of the Tacussel potentiostat have been given (189, 265). Wood (302) described an all-transistorized potentiostat with an output of 1 ampere and 50 volts and with provision for automatic scanning of potential.

In addition to the many commercial potentiostats now available, a number of commercial highly regulated power supplies employ feedback circuitry which can be converted with little difficulty to potentiostatic operation. For example, Birman (20) discusses modification of a modern programmable power supply to this application.

The use of an integrator circuit incorporating a French operational amplifier in coulometry has been proposed (108). A microcoulometer based on radioactivity measurements of deposits of silver-110 has been described (38).

Table IV. Electrogenerated Titrants and Substances Determined by Coulometric Titration

Electro-generated titrant	Substance determined		Reference
	Oxidants		
Chlorine	Methionine		(128)
	Phenylbutazone		(126)
Bromine	Bismuth [by precipitation of $\text{BiCr}(\text{SCN})_6$; titration of SCN^-]		(64)
	Anthranilic acid, Cu anthranilate		(107)
	Cu, Zn, Co, Ni, anthranilates		(63)
	Furan		(308)
	Dihydralazine		(127)
	Phenylbutazone		(126)
	Cyclic β -diketones		(129, 193)
	Methionine		(128)
	Vinyl acetate, styrene, α -methyl styrene		(101)
	1,3,5-Trihydroxybenzene		(152)
	Dihydric phenols		(249)
	Tetramethyllead		(212)
	Tetraethyllead		
Iodine	Total arsenic and arsenic(III) in glasses		(298)
	Total antimony and antimony(III) in glasses		(299)
	Arsenic(III)		(23)
	Antimony(III)		
	Hydrogen peroxide (by iodometry; titration of excess thiosulfate)		(48)
	H_2S		(218)
	2,3-Dimercaptopropanol		(131)
	Xanthates		(130)
	1,3,5-Trihydroxybenzene		(152)
	Aminoxy-group		(151)
Iron(III)	Titanium(III)		(250)
Platinum(II)	Titanium(II) in LiCl-KCl melt		(72)
Reductants			
Iron(II)	Chlorine		(267)
	Vanadium(V)		(219)
Titanium(III)	Iridium(IV)		(258)
	Uranium(VI)		(272)
	Molybdenum(VI)		(19)
	Phosphate [by precipitation of molybdate, titration of molybdenum(VI)]		(155)
	Selenium(IV)		(280, 281)
Copper(I)	Iridium(IV)		(257)
Vandium(III)	Iron(III), vanadium(V), chromium(VI), manganese(VII)		(279)
Molybdenum(V)	Chromium(VI)		(80)
Chromium(II)	<i>p</i> -Nitrophenol, <i>p</i> -nitroaniline, nitrobenzoic acids		(4)
Precipitating and Complexing Agents			
Silver(I)	Methyl bromide (converted to bromide ion)		(72)
	Halides, cyanide in LiNO_3 - KNO_3 melt		(27)
	Halides in NaNO_3 - KNO_3 melt		(263)
	Halides		(21, 231)
EGTA ^a	Calcium(II)		(50)
	Cadmium(II)		(248)
	Nickel(II)		(276)
Acids and Bases			
Base	Organic acids in benzene-methanol or <i>t</i> -butanol-methanol		(57)
	Organic acids in isopropanol media		(119)
	Organic acids in acetone		(260)
	Boron (converted to boric acid)		(184, 305)
	CO_2 in gases		(309)
Oxide ion	Zinc(II), cadmium(II) in KNO_3 - NaNO_3 melt		(26)

^a Ethylene glycol bis(β -aminoethyl ether)-*N,N'*-tetraacetic acid.

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