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## AMPEROMETRIC TITRATIONS

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TITRATIONS based on the measurement of polarographic diffusion currents were first performed by Heyrovský and Berežický (9), who used the term "polarographic titration" for the new technique. Majer (41) simplified the technique by measuring diffusion currents at a constant applied e.m.f. rather than by recording a series of polarograms, and proposed the name "polarometric titration." Kolthoff and Pan (26) suggested the name "amperometric titration" as more consistent with the terminology applied to other electrometric titrations—viz., potentiometric and conductometric. While the name "amperometric" may be criticized on the basis that it emphasizes the unit of measurement rather than the quantity measured, it is a more descriptive name and is widely used.

In a strict sense, the term amperometric should be applied only to titrations in which a diffusion-controlled limiting current is measured, to differentiate it from methods such as the "dead-stop" end point of Foulk and Bawden (7), or the "galvanometric" titration of Salomon (47) in which the end point is detected by the sudden polarization or depolarization of electrode systems.

The principles of this method have been described by several investigators (11, 16, 21, 54); hence in the present review the emphasis is placed on the advantages and limitations of the method as well as on a critical evaluation of recent applications.

### TITRATIONS WITH DROPPING MERCURY ELECTRODE

The dropping mercury electrode in principle can be applied to a wide variety of titrations, because any polarographic electrode reaction potentially can serve as the indicator electrode reaction. Considering the fact that only one of the two reactants in the titration needs to yield a polarographic diffusion current, the scope of possible titration reactions includes those which can serve for indirect polarographic analyses. For example, sulfate

ion yields no polarographic diffusion current, but the addition of a known excess of lead ion renders possible the indirect determination of sulfate, while the detection of the lead diffusion current after the end point serves as the basis of an amperometric titration (27, 41).

Comparing the amperometric titration with direct or indirect polarographic determination, the titration procedure possesses certain advantages. It is unnecessary to maintain close temperature control in titrations, as long as the temperature does not vary appreciably during the titration. Comparisons can be made directly on titrations carried out with any capillary without calibration. In cases involving precipitates of moderate solubility, the extrapolation of a titration curve removes the uncertainty of the contribution of the precipitate to the measured current. Titrations can often be carried out with greater accuracy than direct measurements, especially in dealing with moderately concentrated solutions which would have to be diluted for polarographic measurements. The apparatus may be simplified greatly for routine work (6, 54). A simple voltage divider to provide 0.1-volt increments of applied e.m.f. and a sensitive galvanometer with a suitable shunt are sufficient. The use of an externally applied e.m.f. can often be avoided entirely by preparing a reference electrode of suitable potential, and short-circuiting the reference electrode-dropping electrode system through a shunted galvanometer (15). A microammeter is suitable for current measurements if a condenser circuit is included for damping the oscillation of the current (40, 46, 53). Titration cells are described by Langer (36) and by Stock (5, 52, 54).

In comparison with other electrometric titrations, the amperometric titration potentially possesses wider scope. Many substances which are not potential-determining in solution yield irreversible polarographic waves with well-defined diffusion current regions. This is especially true of organic substances such as aldehydes and ketones, peroxides, and nitro compounds,

as well as many inorganic materials. The high hydrogen overvoltage of mercury permits its application at very negative potentials. The formation of amalgams permits the deposition of certain metals—e.g., alkali metals—on mercury in cases where they would be unstable in the presence of water. Applications in the region of positive potentials are limited by the electro-oxidation of mercury.

Amperometric titrations are especially suited for the titration of dilute solutions. A concentration range of 0.01 to 0.001 *N* is ideal.

The main theoretical disadvantage of the amperometric titration is that the presence of large amounts of materials (electrolytes or nonelectrolytes), yielding polarographic diffusion currents at lower potentials than that used for the titration, must be avoided. By changing the potential at which the titration is performed, it is sometimes possible to avoid interferences. For example, the titration of lead with dichromate (26) at a potential of  $-1.0$  volt (vs. the saturated calomel electrode) gives a V-shaped curve because both lead and dichromate ions are reducible at this potential. By performing the titration at zero potential, an inverted L-shaped curve results because lead ions are not reducible at the applied potential. Either titration yields satisfactory results, but by using the lower potential, the interference of substances of intermediate reduction potential is avoided. Thus dissolved oxygen interferes in the first case, but not the second.

A practical disadvantage is that in most cases dissolved oxygen must be avoided or removed. Some investigators prefer to use air-free reagents, to use inert gases to remove air from the sample, and to stir the solution between measurements. Most titrations are carried out by passing nitrogen through the cell for a few minutes after each addition, and then shutting off the gas stream during the measurement. In this connection, the apparatus designs of Wise (58) and of Laitinen, Higuchi, and Czuha (29) are of interest in permitting the continuous passage of gas during measurements.

Often a practical limitation is the rate at which reaction equilibrium is reached during the titration. This is especially true of titrations involving organic reagents. In situations where several minutes of waiting are necessary before equilibrium is reached even with an excess of reagent, an indirect polarographic determination of the excess reagent is to be preferred.

In precipitation reaction, a limiting concentration is reached when the precipitate, owing to its solubility, produces a diffusion current which is the same order of magnitude as that given by a moderate excess of reagent. Langer and Stevenson (37) have described a graphical method of locating the end point which is valid, providing that solubility equilibrium is reached at each titration point in the vicinity of the end point. Kolthoff and Laitinen (17) have calculated the location of the minimum in V-shaped titration curves in relation to the equivalence point.

#### TITRATIONS WITH ROTATING PLATINUM ELECTRODES

The advantages to be sought in applying the rotating platinum electrode rather than the dropping mercury electrode are increased sensitivity and greater simplicity and convenience.

Increased sensitivity is brought about by increasing the rate of diffusion by stirring. A hundredfold or greater increase in diffusion current over the dropping mercury electrode can be achieved in favorable cases. The absence of a "condenser current" decreases very markedly the residual current, thus permitting the use of sensitive current-reading instruments.

The fact that the diffusion current is steady rather than fluctuating is an obvious advantage in simplicity of measurement. Because of the inertness of platinum anodes, a much wider range of positive potentials can be used. Thus many titrations can be carried out in the region of potentials at which dissolved oxygen does not interfere. Such titrations can be carried out in open beakers rather than in closed systems.

However, the possible scope of amperometric titrations with

the rotating platinum electrode is much narrower than with the dropping mercury electrode. First, many potential determining systems yield highly irreversible current-voltage curves at rotating electrodes. For example, dichromate does not yield a cathodic diffusion current (22). Secondly, the low hydrogen overvoltage of platinum is a limitation in the range of negative electrode potentials. This disadvantage might be overcome by plating with a suitable high overvoltage metal. Thirdly, the difficult technique of titration in oxygen-free systems using a rotating electrode has limited the practical applications to cases in which oxygen does not interfere. Fourthly, the electrode surface is not renewed continually during operation. Hence the behavior of a solid electrode may depend somewhat upon its previous history. The use of surfaces other than platinum may require cumbersome operations between titrations.

In spite of these limitations, it may be said in general that if a given titration can be performed with both the dropping mercury electrode and the rotating platinum electrode, the latter is preferable for routine work.

#### APPLICATIONS OF DROPPING MERCURY ELECTRODE

The volumetric determination of sulfate is a problem of considerable practical importance. Barium would be the ideal precipitant on the basis of solubility, but the lack of suitable indicator electrodes has prevented the development of a satisfactory potentiometric method. The conductometric titration is not applicable in the presence of high concentrations of foreign electrolytes. Consequently, the amperometric determination has aroused considerable interest. The early work of Heyrovský and Berežický (9) was based on precipitation with barium ion, but the method is subject to severe limitations because of interference by substances of lower half-wave potential than the barium ion. The lead ion is ideal as a precipitant from the viewpoint of polarographic convenience, the main disadvantage being the appreciable solubility of lead sulfate. Majer (41) described a graphical method of locating the end point. This method was criticized by Kolthoff and Pan (27), who pointed out that a knowledge of the solubility of lead sulfate in the titration medium would be required, and that the method is of limited practical utility because of the great variation of solubility with ionic strength. They emphasized the advantage of the extrapolation method of locating end points, and made a systematic study of the accuracy of the titration. In 0.01 *M* solution, sulfate can be titrated with a precision and accuracy of 0.2%.

Spalenka (50) suggested the addition of alcohol to suppress the solubility of lead sulfate. Kolthoff and Pan (27) recommended 20 to 30% ethanol as a titration medium, and reported an accuracy of  $\pm 0.3\%$  for 0.001 *M* sulfate in 30% ethanol. High results (1 to 2%) were observed in the presence of 0.01 to 0.05 *M* potassium nitrate. The error was attributed to coprecipitation of lead nitrate. High concentrations of potassium ion lead to low results owing to the formation of a double salt,  $\text{PbSO}_4 \cdot \text{K}_2\text{SO}_4$ . Applications of the method to the determination of sulfur in coke (1) and of sulfate in precipitated alumina (4) have been described.

Lead ion has been studied as a precipitant for a number of other anions. Kolthoff and Pan (27) described the titration of oxalate and ferrocyanide with lead. Oxalate was titrated without the addition of alcohol with an accuracy of 0.2% in 0.01 *M* solution and 0.5% in 0.001 *M* solution. Ferrocyanide gave an end point corresponding to the formation of lead ferrocyanide. The titration of chloride with lead in alcohol-water medium (28) appears to have no advantage over silver or mercurous ion as precipitants. The titration of molybdate with lead was suggested by Thanheiser and Willems (56) as a method for the determination of molybdenum in steels. A prior separation of iron and of tungsten is necessary. The titration was carried out under conditions such that the lead ion gave a diffusion current whereas the molybdate was not reduced.

The titration of lead ion with dichromate has been thoroughly

investigated by Kolthoff and Pan (26), who obtained excellent results in acid solution using a potential of  $-1.0$  volt (*vs.* the saturated calomel electrode) where both reagents yield diffusion currents. An accuracy of  $0.2\%$  was achieved in the titration of  $0.01 M$  lead solution. To avoid the interference of reducible materials such as oxygen and to simplify the apparatus, titrations were also carried out at a potential of  $0.0$  volt (*vs.* the saturated calomel electrode) by short-circuiting the titration cell through a shunted galvanometer. Under these conditions, the diffusion current of lead was not observed, and an "inverted L" type of curve resulted. Again, excellent results were observed in acid solution, even for  $0.001 M$  lead. In neutral solution, low results due to the formation of basic salts were observed. An attempt was made to determine both lead and barium in a single titration. Serious coprecipitation of barium chromate with lead chromate prevented titration in neutral solution. In acid solution, barium chromate is soluble and does not interfere with the determination of lead.

Kolthoff and Gregor (14) studied the titration of barium with chromate at an applied potential of  $-1.4$  volts. In aqueous medium, the formation of supersaturated solutions caused a very slow attainment of equilibrium in dilute ( $0.001 M$ ) solution. Titrations in 20 to 50% ethanol were successful in that solubility equilibrium was rapidly reached, but the results were 2.4 to 5% low. The error was attributed to coprecipitation of barium salts with barium chromate or possibly the formation of basic barium chromate.

The titration of fluoride with thorium or lanthanum nitrate was studied by Langer (34), who stated that the current passing after the end point at a potential of  $-1.7$  volts (*vs.* S.C.E.) is caused by the reduction of nitrate in the presence of thorium or lanthanum. Kolthoff and Lingane (21) criticized the interpretation of the cause of the current and suggested the need for further investigation. Langer reported satisfactory results with fluoride concentrations as low as  $2 \times 10^{-4}$  molar. The same interferences were noted as in the usual sodium alizarin sulfonate titration, and therefore a prior distillation is necessary. A careful adjustment of pH to a value between 6 and 8 was recommended. The results suggest that the current may be due to hydrogen ion produced by hydrolysis of thorium or lanthanum ions, and that some attention should be paid to the buffer capacity of the solution. The effect of alcohol is peculiar in shifting the end point to considerably higher values. In its present state of development, the amperometric fluoride titration appears to possess little advantage over the indicator method.

Spalenka (50) titrated ferrocyanide with zinc at a potential of  $-1.2$  volts, measuring the diffusion current of zinc. The best results were obtained in  $0.2 N$  hydrochloric acid solution. A noticeable slowness of precipitation of  $K_2Zn_3[Fe(CN)_6]_2$  was reported at room temperature; at  $50^\circ C.$  the precipitate formed more rapidly, but the accuracy was not affected. In ammoniacal medium the solubility was repressed, but reproducible results could not be achieved.

Neuberger (45, 46) titrated phosphate with bismuth oxyperchlorate, determining the bismuth diffusion current. The method is of limited utility because it is applicable only to relatively concentrated phosphate solutions (above  $0.035 M$ ) and because all anions except perchlorate must be absent because they form complexes with bismethyl ion (13). Kolthoff and Cohn (13) described a titration of phosphate with uranyl acetate in the presence of potassium chloride to form  $UO_2KPO_4$ , detecting the end point by the diffusion current of uranyl ion in acetic acid medium. They recommend the destruction of organic anions by ignition or by oxidation with sulfuric and nitric acids to prevent interference caused by the formation of uranyl complexes. Adjustment of the acidity is important in regulating the speed of formation of the precipitate.

The titration is carried out in 20% ethanol, and the concentra-

tion of phosphate is limited to less than  $0.01 M$ . Moderate amounts of magnesium, barium, and calcium cause no interference. The precipitation of calcium sulfate in the 20% ethanol medium caused an error due to coprecipitation of phosphate. Hence the concentration of calcium and sulfate in the final solution should not exceed  $0.02 M$  and  $0.01 M$ , respectively. With the recommended procedure, an accuracy of 1% or better was obtained in solutions  $0.01$  to  $0.0003 M$  in phosphate. Alkaline earth phosphates can be titrated by the standard procedure. Iron interferes, but it can be removed by the addition of cupferron followed by ether extraction. Indirect polarographic determinations of phosphate based upon the determination of excess molybdate have been described by Uhl (57) and by Stern (51).

Amperometric titration of chloride with mercurous ion (21) and with silver (20, 42), and of iodide with mercuric ion (21) using the dropping mercury electrode have been described. As halide titrations can be more conveniently carried out with a rotating platinum electrode, no details are given here.

Titrations of titanous chloride with several oxidizing agents were described in the early work of Strubl (55) and Spalenka (50). In the presence of tartrate or citrate, the titanous-titanic system yields a smooth composite anodic-cathodic wave. Using an oxidizing agent such as ferric iron, ferricyanide, chromate, bromate, or iodate, the anodic current of the titanous titanium decreases to zero and changes sign upon addition of excess oxidizing agent. Although Spalenka (50) stated that the titration points in the vicinity of the end point lie on the same straight line, Kolthoff and Lingane (21) point out that this could not be generally true.

An interesting type of amperometric titration is that based upon compensation of the anodic current of one substance by the cathodic current of another, even though a direct reaction between the two substances may not be involved. Thus Kolthoff and Miller (24) titrated oxygen, which yields a cathodic wave (25), with sulfide ion which yields an anodic diffusion current due to the formation of mercuric sulfide at the dropping electrode. No simple stoichiometric ratio of the two substances exists at the end point, but rather the quantity  $nCD^{1/2}$  becomes equal, where  $n$  is the number of electrons involved per molecule in the electrode reaction,  $C$  is the concentration, and  $D$  is the diffusion coefficient.

Another example of an amperometric titration involving the compensation of current is the titration of stannous tartrate, which yields an anodic diffusion current at a potential of  $-0.2$  volt (*vs.* S.C.E.), with cupric ions, which gives a cathodic current at the same potential. Lingane (39) showed that no direct reaction occurs in the bulk of the solution.

Organic reagents have successfully been used in several amperometric titrations. Advantages to be sought are high selectivity and high sensitivity. Many organic analytical reagents have polarographically reducible functional groups and potentially are useful for the determination of substances that cannot be directly determined by polarographic means.

Kolthoff and Langer (18) have titrated nickel in ammoniacal solution with dimethylglyoxime at a potential of  $-1.85$  volts (*vs.* S.C.E.) when both nickel and reagent show diffusion currents. An accuracy and precision of  $0.4\%$  in  $0.01$  to  $0.001 M$  solution was achieved. At a concentration of  $0.0001 M$ , the results were still accurate to within 2%. Cobalt was found to interfere because of the formation of a soluble and reducible complex. A prior separation of cobalt as potassium cobaltinitrite was recommended in cases where the cobalt content was more than 5% of the nickel content.

The titration of cobalt, copper, and palladium with  $\alpha$ -nitroso- $\beta$ -naphthol was studied by Kolthoff and Langer (19). At potentials more negative than  $-0.6$  volt, the reagent yields a diffusion current both in acid and in ammoniacal medium. For cobalt, an acetate buffer was recommended, using an applied potential of

−0.6 volt. Under these conditions, the cobalt derivative is stable toward air oxidation, and only the reagent gives a diffusion current. Copper and palladium can be titrated in the same way but here the metal ion also yields its diffusion current. One cobalt ion combines with four molecules of reagent, whereas one copper or palladium ion combines with two molecules. Zinc, aluminum, and manganese were found not to interfere. Results were high in the presence of nickel. Further work is needed to establish the scope of the reagent and to investigate interferences in more detail.

Langer (35) showed that  $\alpha$ -benzoin oxime can be used for the titration of copper. At applied potentials between −0.8 and −1.4 volts, using an ammoniacal medium, the reagent was not reducible and L-shaped titration curves were observed. At −1.7 volts, a V-shaped curve was observed, because both reactants are reducible. The solubility of the precipitate increases with increasing ammonia concentration. For 0.001 *M* copper solution in 0.02 *M* ammonium hydroxide solution, the results were accurate to about  $\pm 1\%$ . Nickel was found to interfere badly. Iron, lead, and zinc showed smaller interferences. A more detailed study of the effect of foreign ions should be made.

Neuberger (45) proposed the determination of copper with salicylaldehyde. An excess of reagent was added and titrated with a standard copper solution, and the appearance of the copper diffusion current was noted.

Stock (54) investigated the reaction between quinaldic acid and copper in acetate buffers, and showed that equilibrium is reached more rapidly if the copper solution is added to the quinaldic acid solution than if the procedure is reversed. Accordingly, the recommended procedure is to add an excess of quinaldic acid and back-titrate with copper.

Bismuth has been titrated with 8-hydroxyquinoline (8), using a tartrate solution with an acetate buffer added. At an applied e.m.f. of 0.85 volt, both reactants yield diffusion currents. The same reagent has been used for zinc, copper, and aluminum (59), in a buffered acetate medium. Magnesium was determined in an ammoniacal medium containing ammonium chloride (59).

The titration of potassium with dipicrylamine in cooled solutions was mentioned by Langer and Stevenson (37), but no details were given.

Cohn and Kolthoff (2) devised an indirect amperometric determination of calcium, based upon precipitation with picrolonic acid and back-titration of the excess reagent with methylene blue. The end point was detected by measurement of the diffusion current corresponding to the reduction of methylene blue to leuco-methylene blue.

Another titration involving two organic substances was described by Conn (3). Various diamidines were titrated with sodium alizarin sulfonate to give insoluble alizarin sulfonates, the excess reagent yielding a diffusion current. The results in general were reproducible and accurate within  $\pm 0.5\%$ .

The amperometric titration of  $\alpha$ -tocopherol with auric chloride was studied by Smith, Kolthoff, and Spillane (49). In a benzoate buffer, at a potential of −0.075 volt (*vs.* S.C.E.), only the reagent gave a diffusion current. In a concentration range between  $1 \times 10^{-3}$  and  $3 \times 10^{-4}$  *M*, an accuracy of 0.3% was achieved.

Recently cupferron as a titration reagent has been studied by Kolthoff and Liberti (38). Accurate results were obtained in the titration of copper in neutral or slightly acid media. Equilibrium was rapidly reached. Using citrate or tartrate buffers of pH between 1 and 3, ferric iron was successfully titrated. A serious disadvantage of cupferron is its instability, which makes necessary frequent standardizations.

Kolthoff and Johnson (10) have recently studied *n*-nitrophenylarsonic acid as a reagent for uranyl, thorium, zirconium, titanium (IV), and tin (IV). Under carefully controlled conditions, satisfactory results were obtained for uranyl and thorium ions, with rapid establishment of equilibrium. Zirconium

yielded a precipitate of somewhat variable composition. Tin (IV) gave a slow reaction. Titanium (IV) did not give a precipitate of stoichiometric composition. Tetraphenylarsonium chloride proved to be an excellent reagent for tin (IV) as chlorostannate in media of high acidity and high chloride ion concentration. Other titrations with the reagent are being investigated.

#### APPLICATIONS OF ROTATING PLATINUM ELECTRODE

In the early work of Nernst and Merriam (44) it was shown that distinct diffusion currents could be observed with a rotating platinum microelectrode for solutions of iodine, bromine, chlorine, silver ions, and permanganate ions in the presence of an excess of indifferent electrolyte. Although such diffusion currents are seldom useful for direct measurements of concentration except under carefully controlled conditions (33), they form the basis of several amperometric titrations.

The titration of arsenite with bromate was studied by Laitinen and Kolthoff (33). In an acid solution containing bromide, the end point was detected by measuring the diffusion current of bromine which was formed after the end point. Rapid and accurate titrations were carried out in an open beaker with an applied potential of +0.2 volt (*vs.* S.C.E.), where oxygen does not interfere. Solutions 0.001 *N* in arsenite were titrated with an accuracy of 0.1%, and 0.0001 *N* solution yielded results accurate to 0.3%. Myers and Swift (43) used the diffusion current of bromine to detect the coulometric end point of the same titration reaction. By using a larger electrode in a stirred solution, the sensitivity was increased considerably. A diffusion current of 1.0 microampere per  $10^{-7}$  mole of bromine per liter was reported. In a titration volume of 50 ml., an average absolute error of 0.5 microgram of arsenic was observed regardless of the amount of arsenic being determined. The same end point was used by Sease, Niemann, and Swift (48) in the determination of thiodiglycol by means of electrolytically generated bromine, and by Kolthoff and Bovey (12) in the amperometric titration of styrene with potassium bromate. In the latter titration, using a solvent of 75% methanol and a temperature of 10° C. to minimize loss due to volatilization of styrene, slightly low but satisfactory results were obtained.

Chloride, bromide, and iodide were titrated with silver nitrate by Laitinen, Jennings, and Parks (30). For the titration of chloride, acetone was added to decrease the solubility, and gelatin was added to prevent depolarization by colloidal silver chloride. The titrations could be carried out rapidly and conveniently. Although accurate in 0.1 *N* solution, the titration showed a tendency toward low results at high dilution. Standardization in a similar concentration range is recommended. The successive titration of all three halides (31) in one solution proved to be simple, rapid, and convenient. Ammonia was added for the iodide titration, excess nitric acid for the bromide titration, and gelatin for the chloride titration. The three titrations could be carried out within 10 minutes.

Silver nitrate was used as the reagent for amperometric titrations of mercaptans (thiols) in alcoholic ammoniacal medium by Kolthoff and Harris (15). Amounts of mercaptan sulfur as small as 0.2 mg. in 100 ml. could be determined with an accuracy of 1 to 2%. Amounts greater than 2 mg. per 100 ml. were determined with a precision and accuracy of at least 0.3%. The mercaptan titration has been used in the determination of disulfides (23).

The titration of cyanide with silver (32) proved to be as accurate as the potentiometric or visual indicator methods in 0.2 *N* to 0.002 *N* solution, and applicable at much higher dilution. Even in  $4 \times 10^{-6}$  *N* cyanide, a distinct amperometric end point could be observed.

Dichromate has been titrated in acid solution with ferrous iron (22) using the anodic diffusion current of ferrous iron to determine

the end point. Dichromate gives no cathodic current. Excellent results were found in solutions as dilute as  $10^{-4}$  M in dichromate.

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# ELECTROANALYSIS

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ALTHOUGH 20 years ago a foreign worker in the field of electroanalysis concluded that it "now belongs to the museum class" (20), the past pentad has seen a stir of activity that presages a renaissance. This worker might have been warned by the conclusion in 1883 that the work on electroanalysis was finished with the publication of Classen's classical treatise (60). However, the volume of current papers appearing in the field of electroanalysis is a very poor indication of the potential value of work in this field. The development of new techniques in the field of instrumentation and the re-examination of poorly founded conclusions provide opportunity for fruitful investigation.

Recent years have recorded the passing of Henry J. S. Sand (55), a pioneer in the development of electroanalysis, at a time when his most important work on electrodeposition with controlled cathode potential is just coming to be generally appreciated and used. In fact, the application and extension of these principles are probably the most important phase of current activities in electroanalysis.

Most developments of theoretical interest to electroanalysis are at present occurring in the field of polarographic analysis, which is treated in a separate review.

## BOOKS

After 24 years a completely revised third edition of the classical Fischer-Schleicher "Elektroanalytische Schnellmethoden" has

made its appearance (56). The length of the book has been halved from the previous edition, probably because of material shortages, but much new material relating to internal electrolysis has been introduced. This feature is likewise a reflection of war economy, as the use of internal electrolytic methods permits the substitution of base metals for platinum anodes. Material omitted from this edition of the book includes detailed description of specific procedures for the analysis of commercial alloys completely by electroanalytical methods, and the historical section included in earlier editions. Diehl has contributed another welcome book in the field of electroanalysis, a monograph on the use of the graded cathode potential control (15). Although the book is concerned largely with its author's own automatic apparatus for this type of analysis, other equipment is described by reference, the theory of the method is discussed, and a number of interesting and suggestive examples are presented for the practical use of this method. The only other books to appear during the years covered by this review are by Jilek (29), which appears to be in the possession of only a single library in the United States, and by Tamburrini (66) not located here at all. Neither was available to this reviewer.

## REVIEW ARTICLES

In the present review there is no discussion of microelectrolysis, largely because there is no sharp differentiation of technique, de-