

DEVELOPMENT OF AMPEROMETRIC TITRATION METHODS

(A REVIEW)

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The following basic lines of approach can be discerned in the development of amperometric (polarometric)* titration: the development of new methods, differing in principle and using new types of titration curves, new apparatus, etc; the further development of this method as applied to various practical problems as well as to "pure" solutions; the application of the amperometric method for various research work and for indicating the end point during coulometric titration.

A number of detailed review articles have been published both in Russian and abroad on amperometric titration [1-4]. In the present article we shall consider mainly work which has appeared during 1955 and 1956.

New Types of Titration Curves and New Techniques

Detailed study of oxidation-reduction reactions on a rotating platinum electrode has led to the introduction to the practice of amperometric titration of two new types of titration curves: "differential" and Γ -form.

An example of a "differential" curve, according to I. P. Alimarin and S. I. Terin [5] is titration of Fe^{2+} and VO^{2+} in each other's presence in acid solution. Fe^{2+} is first titrated by means of an oxidizing agent [Ce(IV) or MnO_4^-] using the anode current during its oxidation at +0.9 volt (with respect to the saturated calomel electrode);** then, by changing the applied voltage by 0.5 volt (saturated calomel electrode) VO^{2+} ions are titrated with the same oxidizing agent. After the end point the reduction current for the ions of the titrant solution appear. It should be pointed out that the term suggested for this method by the authors, namely "differential" titration cannot be regarded as wholly satisfactory;*** this method, in essence, is a "successive" titration of two cations.

An example of a Γ -shape curve which is obtained during reduction on an indicator electrode of the product of a chemical reaction, is titration of V (V) with Mohr's salt in a not too strong acid solution (approximately 1 N H_2SO_4) without applying an external e.m.f. (m.i.e.). Under the conditions indicated, Fe^{3+} is reduced on the electrode, the Fe^{3+} ions appearing in solution during titration being proportional to the Fe^{2+} ions oxidized. Another example of such a reaction is one developed by the author in conjunction with A. P. Voiloshnikova, namely titration of As (V) with potassium iodide in a strong hydrochloric acid solution (10-11 N HCl) at a potential of +0.2 volt (m.i.e.) As titration proceeds free iodine appears in the solution and is reduced on the electrode.

*Ia. Heyrovsky who is regarded as the author of the polarographic method of analysis, and his co-workers, in particular I. I. Smoler and R. Kal'voda, have advanced a very convincing argument against the unfounded substitution of the term "polarometric" — suggested by the Czech school — for the term "amperometric." While it is impossible to deal with this point in greater detail in the present review, we think it necessary to draw the attention of the reader to it.

**From here onwards the abbreviation "s.c.e." will be used for the saturated calomel electrode; and "m.i.e." for the mercuric iodide reference electrode.

***See the editorial note to the article by E. M. Skobets and V. D. Skobets in *Zovodskaja Lab.* 23, 2, 173 (1957).

New variants have also been given for precipitation reactions: thus, Kh. Ia. Levitman and Z. A. Krivchik [6] have obtained a curve with a "break," whereby it is possible to determine copper and nickel separately in each other's presence in solution by means of rubeanic acid. A new type of titration method is the "indicator" method [7] which has been developed by Iu. I. Usatenko and G. E. Beklesheva, who have used it for determining aluminum, beryllium, and zirconium [8]. This method is based on the addition to the solution being titrated — the ions of which do not give an electrode reaction — of an ion which is readily reduced on the electrode, e.g., Fe^{3+} , and which also reacts with the solution being titrated, but only after the "basic" reaction has finished. In other words the "indicator" should form with the titrant a less stable compound than the ion to be determined.

Determination of calcium with oxalic acid in the presence of copper ions [9] is of this type, as well as the trilonometric titration of calcium in the presence of zinc ions [10]. Titration of solutions of ethylenediamine-tetracetic acid with zinc salts can also be used for standardizing trilon solutions [11].

Another new type of titration is the trilonometric titration of two or three components mixtures of various ions [12], using cathodic reduction current on a dropping mercury cathode in combination with the anodic current of oxidation of mercury in the presence of trilon. By altering the pH of the medium and the value of the applied e.m.f. it is possible, in succession, to determine bismuth, lead, and calcium; iron and manganese; copper and calcium; and, probably various other mixtures of cations [12].

A new technique in amperometric titration is the determination of small amounts of material by means of a stationary mercury electrode located on the bottom of the titration vessel and having a surface area of about 2 cm^2 [13]. The large electrode surface ensures the large current necessary to obtain appreciable shifts of the galvanometer needle for low contents of the test material in the solution being titrated; there is, however, the possibility of loss of the test material as a result of electrolysis. As a consequence the circuit is only completed on addition of the reagent; while the solution is stirred, etc., there should be no current in the circuit.

For the determination of small amounts of materials, it has been recommended that long — up to 35 mm — platinum wire electrodes [13a] can be used, as well as vibrating electrodes suggested by Lindsay and described by I. P. Alimarin and Z. A. Gallai [14].

Development of the Method for Application to Various Materials

The high sensitivity of amperometric titration, the possibility of using various combinations of chemical reactions in solution, and of electrode reactions on mercury or platinum electrodes, have been the reasons why this method has been used in recent years for determination of a number of rare metals. In the first place, mention should be made of the interesting work carried out on the determination of elements of the titanium subgroup, as well as of titanium itself, zirconium, and hafnium. All three elements can be determined by means of cupferron, since they form very sparingly soluble cupferronates. V. M. Peshkova and Z. A. Gallai [15], and also Elving and Olson [16] have titrated titanium on a dropping mercury electrode on the basis of the reduction current of cupferron at -0.65 – -0.70 volt (s.c.e.) or on the basis of the V-shaped curve at -0.85 volt (s.c.e.), in a supporting electrolyte of 1 N sulfuric acid. Iu. I. Usatenko and G. E. Bekleshova [17] have also used cupferron for determining titanium; they made use of the fact that cupferron is oxidized on a platinum electrode in a supporting electrolyte of sodium or potassium chloride, and also in a sulfuric acid medium at $+0.8$ volt (s.c.e.). Aluminum, magnesium, and silica do not interfere with the determination of titanium; iron is complexed with Trilon B. The same workers, in conjunction with E. I. Grenberg, M. Ia. Genis, and E. E. Karpushei [18], have suggested a method which they have developed for determination of titanium in ferrotitanium, and have checked the method by using it on standardized samples; they concluded that it completely satisfies GOST requirements. We think that this method could be extended to the determination of zirconium for which Elving and Olson [16, 19] specifically designed the cupferronate method, but in the "cathodic variant," i.e., on the basis of the reduction of cupferron on the dropping mercury electrode. Elving and Olson have emphasized that the cupferronate method permits determination of zirconium in the presence of large amounts of fluoride; this fact is of essential practical importance, since fluorides are often used for getting zirconium into solution.

The same method permits determination of zirconium in objects containing niobium and uranium [19]; zirconium is removed as zirconium phosphate; the precipitate is dispersed in an appropriate supporting electrolyte and is titrated as a suspension with cupferron.

Hafnium is titrated with cupferron under the same conditions as those used for titanium and zirconium [16]. V. M. Vladimirova [20] has used the capacity of zirconium to form a stable complexonate at pH 1-2; after addition of excess trilon the latter is back-titrated (using a dropping mercury electrode) with a solution of a bismuth salt, which also forms a stable complexonate under the same pH conditions. R. Wilson and T. Rhodes [21] have titrated zirconium in an acetate buffer with α -nitroso- β -naphthol which gives a dark brown precipitate with zirconium. For improving the conditions under which the precipitate is formed, potassium chloride is added. Titration is carried out on a dropping mercury electrode using the reduction current of excess reagent. All metals which react with α -nitroso- β -naphthol will be precipitated together with the zirconium; they include copper, cobalt, iron, and palladium; nickel also interferes. The method permits determination of 0.004 to 0.05 millimoles of zirconium, i.e., from 0.36 to 4.5 mg.

Since titanium exhibits variable valence, oxidation-reduction reactions can be used for it beside the reaction with cupferron. Thus, V. M. Peshkova and Z. A. Gallai [15] have oxidized titanium with Fe^{3+} salts; titanium is reduced beforehand in a cadmium reducer to Ti (III) and then titrated with a solution of ferric chloride at -0.4 volt (s.c.e.) in the presence of ammonium sulfate for decreasing the oxidizability of Ti (III) by atmospheric oxygen (titanium is fixed as the sulfate complex).

The technique described above for titration with an "indicator" has been suggested for determination of a number of rare metals: zirconium, [22], beryllium [8], and thorium [23].

According to G. A. Kleibs [24] potassium ferrocyanide, which forms with uranium a sparingly soluble precipitate with the composition $5(\text{UO}_2)_2\text{FeCy}_6 \cdot 3\text{K}_4\text{FeCy}_6$, can be used for the amperometric determination of uranium. Titration can be carried out on the basis of the anodic oxidation of ferrocyanide after the end point.

Amperometric methods are also used for determination of "scattered" elements. Titration with potassium ferrocyanide has been suggested for gallium [25, 26]. For indium a complexonometric method [27] has been suggested which is based on the formation of a very stable compound of indium with a complexon at a pH of about 2. Oxidation reactions have been used mainly for thallium previously. Recently, however, use has been made of oxidation-reduction reactions, e.g., the anodic bromide method [28] which is based on the fact that thallium, reduced beforehand to the trivalent state, is titrated with a solution of potassium bromide at a potential of +1.0 volt (m.i.e.); after the end point has been reached the current for the oxidation of excess bromine ions appears. Hartely and Lingane [29] oxidized thallium coulometrically by means of a solution of ferricyanide, and used an amperometric method for establishing the end point - reduction of excess ferricyanide on a platinum electrode. In all probability this method could be realized purely amperometrically. Nair and Ibrahim [30] for the determination of germanium, precipitated it with gallic acid in the hydrochloric acid medium in the presence of ammonium sulfate. Titration was carried out with a dropping mercury electrode at -0.6 volt (s.c.e.); the error does not exceed 0.3%. Arsenic does not interfere with the determination. The amount of germanium that can be determined is about 4 millimoles/liter, i.e., about 300 mg/liter. This is the first method which has been proposed for the amperometric determination of germanium.

The reactions mainly used for cerium determination are oxidation-reduction reactions. Thus, V. L. Zolotavin and L. K. Ponomareva [31] titrated Ce (IV) with vanadyl sulfate solution, while Z. A. Gallai [32] has used ascorbic acid for this purpose. Leonard, Kelly, and Hume [33] have carried out an interesting titration of Ce (III) with potassium ferricyanide using saturated solutions of potassium carbonate; in such a medium the oxidation potential of the system $\text{Ce}^{4+}/\text{Ce}^{3+}$ is strongly shifted to negative values, as a result of which it becomes possible to oxidize it with potassium ferricyanide. When titration is carried out on a platinum electrode without applying an external emf (s.c.e.), a mixed anode-cathode curve is obtained - first the carbonate complex of cerium is oxidized, while after the equivalence point excess ferricyanide is reduced.

Ascorbic acid was also used by Iu. I. Usatenko and G. E. Bekleshova [8] for reducing iron, and by Z. A. Gallai [32] for titrating V(V). Ascorbic acid is oxidized on a platinum electrode; the region within which a diffusion current is obtained lies in neutral and weakly acid solutions between potentials of +0.85 and +1.2 volt (s.c.e.).

An interesting method for the determination of selenium in the presence of tellurium - also by means of ascorbic acid - has been suggested by Simon and Grim [34]: acid solutions (pH about 1-2), containing selenium and heated to 60° are titrated with ascorbic acid by means of the reduction current for selenium at -0.05 volt (s.c.e.) on a dropping mercury electrode. Both quadri- and sexivalent selenium are determined, since both forms

are reduced by ascorbic acid. Only Fe(III) and copper interfere; accordingly, these elements are complexed by means of potassium fluoride and ferrocyanide, respectively. The method has been checked on synthetic mixtures in the form of powders and on copper selenite. From 5 to 30 mg of selenium can be determined in a volume of 20-30 ml.

In recent years, a method which has been described previously has found new applications, an oxidation-reduction titration in which a solution of Mohr's salt is used as titrant. Thus, Hielt and Kobetz [35] have used such a titration for determining vanadium and chromium in silico-aluminum catalysts used for petroleum cracking. In this connection it is interesting to note that instead of selective oxidation of chromium which is normally used in such determinations, Hielt and Kobetz selectively reduced chromium with sodium azide. Titration is carried out with the aid of a rotating platinum electrode; determination of thousandths of a percent of vanadium in the test sample is possible.

It should be pointed out that a similar method has been used by Rulfs, Lagowski, and Babor [36] for the determination of vanadium in alloys based on titanium, and in alloyed steel; the authors of this paper completely ignored similar work carried out earlier and have made an error in the interpretation of the polarograms they adduce in their paper: they consider that they obtained a wave for the reduction of V(V) in a supporting electrolyte of 1 M sulfuric acid, while vanadium under such conditions does not give a diffusion current [37]. The wave shown in the article of Rulfs et al. is, apparently, the wave for the reduction of dissolved oxygen, since the latter was not removed from solution.

Z. A. Gallai [32] has investigated the possibility of carrying out an amperometric titration of tungsten and molybdenum with solutions of Cr(II) salts, the chromium being oxidized on the platinum electrode. Manganese can be determined by the same reagent; a "differential" titration curve is obtained which can be used for the separate determination of molybdenum and manganese, and also chromium and molybdenum. Z. A. Gallai has emphasized that the method for "determination of molybdenum by means of chromium salts has undoubted advantages over titration of molybdenum with lead salts and with β -naphthoquinoline." While being in complete agreement with Z. A. Gallai, we should like to emphasize that the main advantage of this method over other methods is the absence of a precipitate, but, all the same, the method has its weak points - chromium (II) salts are exceptionally readily oxidized, so that complications arise when working with them.

N. M. Degterev [38] has recommended determination of molybdenum in ferromolybdenum by means of potassium ferrocyanide, and also determination of manganese in ferromanganese. The same author [39] has recommended titration with hydroxyquinoline for determination of tungsten in ferrotungsten. Aylward [40] directly titrated molybdenum with lead nitrate in a supporting electrolyte containing acetic acid, potassium chloride, and sodium acetate; at -0.8 volt (s.c.e.) on a dropping mercury electrode, V-shaped curves are obtained.

In recent years considerable attention has been given to the amperometric titration of the noble metals: silver, gold, and palladium.

The iodide method for determining silver by means of the "anodic" variant [41] permits determination of small amounts (about 0.5 mg Ag in a volume of 20 ml) of silver in black copper and in objects containing iron, zinc, lead, etc. The method is based on anodic oxidation of excess potassium iodide on a platinum electrode at +1.0 volt (m.l.e.).

Determination of gold has been studied by N. A. Ezerskaia [42]; solutions of gold chloride are titrated with thiosulfate or mercaptobenzthiazole on a rotating platinum electrode, on the basis of the current obtained during reduction of gold without applying an external e.m.f. (s.c.e.). In the first case there is formed a complex compound of gold with thiosulfate, while in the second a sparingly soluble precipitate is formed. The first method permits determination of gold in amounts of not less than 0.8 mg in 15 ml of solution, while the second permits determination of down to 0.01 mg in the same volume. Nevertheless, in certain cases the thiosulfate method is to be preferred, since it can be used in the presence of copper, while mercaptobenzthiazole precipitates not only gold but copper as well. The method can be recommended for replacing test tube methods and gives results which are quite comparable to the latter.

Recently L. S. Reishakhrir and N. S. Sukhobokova [43] have suggested titrating gold solutions with hydroquinone at a temperature of 60° in a supporting electrolyte of 2 N sulfuric acid; titration is carried out at 1.0 volt (s.c.e.) on a platinum electrode, the current for oxidation of the hydroquinone being used. Down to 0.2 mg/liter

of gold can be determined with an accuracy ranging from 1 to 10%. Selenium, tellurium, and palladium do not interfere; the method has been checked on ores and electrolytic sludges.

Czech chemists have successfully used various oximes for the determination of palladium; dimethylglyoxime gives particularly good results. R and L. Wilson [44] have studied the conditions for the amperometric determination of palladium by means of 1,2,3-benzotriazole which precipitates palladium quantitatively. From 0.2 to 6 mg of palladium can be determined in 20 ml of solution.

Aluminum can be determined in clays, bauxites, and fire clay and also in bronzes [8, 45] by means of the "indicator" method. When iron has to be determined at the same time as aluminum, the iron is reduced beforehand with metallic copper and then titrated with dichromate (the aluminum is determined in another aliquot of the solution); the iron Fe(III) can also be titrated directly with ascorbic acid, while aluminum can be titrated in the same aliquot by means of sodium fluoride.

E. G. Kondrakhina, L. G. Egorova, and O. A. Songina [46] have determined iron (total and ferrous) in chromites and chrome-magnesite refractory materials. Total iron was determined by titration with dichromate after reduction in a bismuth reducer; for determination of ferrous iron, the sample is broken down by A. B. Shevin's method in the presence of V_2O_5 ; the V_2O_5 which does not react with the ferrous ions is then titrated with a solution of Mohr's salt. Both titrations are anodic and are based on the oxidation of Fe^{2+} on a rotating platinum electrode at +1.0 volt (m.i.e.). Chromium can also be determined amperometrically in the materials indicated by means of Mohr's salt [46].

Potassium in the chloride residues from silicate analysis can be titrated by the anodic ferrocyanide method on a platinum electrode [2], a solution of calcium ferrocyanide in the presence of alcohol — for suppressing the solubility of the precipitate — being used for titrating. The method has been checked at the "Sredazsvetmetrazvedka" laboratory; the workers in this laboratory have developed a rapid and convenient method for preparing calcium ferrocyanide for this titration.

The almost complete insolubility of the compound which potassium forms with tetraphenylborate has been used for potassium determination [47].

Cadmium in various alloys can be determined on a dropping mercury electrode by means of potassium iodide, by titrating solutions containing excess pyrimidone at a pH of from 2 to 5 [48]. The cadmium concentration should not be less than 0.002 M.

Magnesium in limestone can be titrated on a dropping mercury electrode at -0.6 volt (s.c.e.). The method is based on the fact that at pH 11.0 magnesium forms a stable complex with the dye "pantachrome violet SW"; calcium is complexed with ethylenediamine; the dye is titrated with the test solution of magnesium [49].

Titration of its solution with a solution of ferric chloride has been suggested for the determination of fluoride [50]; this method is based on complex formation, and is carried out at pH 5-7 in a solution containing 50% alcohol and saturated with sodium chloride.

For the determination of antimony (III) it has been suggested that it be oxidized with dichromate, excess dichromate being then back-titrated with a solution of Mohr's salt [51].

Methods involving the use of potassium bromate have again been suggested for the determination of arsenic [52]; in addition, however, Laitinen and Woerner [53] have suggested the use of a solution of hypochlorite in the presence of bromide in a bicarbonate medium. This method could also be used for titrating ammonium and thiocyanate ions.

Titration with uranyl acetate on a dropping mercury electrode has again been suggested for determination of phosphate ions [54]. The phosphate ions are first of all isolated by means of ion exchange.

As before, many methods have been developed for the determination of the most important nonferrous metals: copper, zinc, cadmium, lead, and also nickel and cobalt. It should be emphasized that among the reagents recommended for the amperometric (polarometric) titration of these cations, special attention has been given to various organic compounds. Cihalik together with Kudrnovska-Pavlikova and Vorcek [55, 56, 57] have carried out work on the polarographic titration of cadmium, lead, copper, silver, mercury, and bismuth by means of mercapto-benzthiazole, and also of silver, mercury, and tin with mercaptophenylthiodiazolone ("vismuton"). Thanks to

differences in the solubility of the precipitates formed between mercaptobenzthiazole and cadmium and copper, it is possible to titrate these ions separately when they are present simultaneously.

Rubeanic [58] and anthranilic acids have been suggested for determination of copper. Anthranilic acid has also been used for determining zinc, nickel, cobalt [59], and cadmium [60]. All titrations are carried out in the presence of alcohol. For the successive titration of copper and cadmium, A. I. Kostromin and M. I. Aparsheva [60] made use of their different reduction potentials, and changed the pH of the solution after titrating copper from 3.7 to 5.5-6. Successive titration of lead and cadmium is based on this same principle.

Work has been published on the use of α -nitroso- β -naphthol for the determination of iron [61].

As before, considerable attention has been given to various oximes, in particular to "inoxime", the dioxime of cyclohexanedione, for the determination of nickel and cobalt [62].

Work has been carried out involving the use of hydroxyquinoline, in particular for the determination of magnesium and bismuth [63]; thus, A. K. Zhdanov, V. A. Khadeev and G. F. Murtazinova [64] have titrated solutions containing bismuth and hydroxyquinoline with potassium iodide, using 5% sulfuric or hydrochloric acid as the supporting electrolyte. Under these conditions, a very sparingly soluble hydroxyquinoline iodobismuthite is formed, and, by titrating with a dropping mercury electrode, it is possible to use the reduction current of bismuth (the shape of the titration curve in this instance is that of an L) or to use the current for the oxidation of the dropping mercury in the presence of iodide. Finally, the same titration can be carried out by means of a rotating platinum electrode; in this case the curve will have an $\perp$ shape as the result of the oxidation of excess iodide.

In addition, bismuth is readily titrated with pyrogallol in a weakly ammoniacal medium [65]. The method is of interest in view of the fact that it permits determination of bismuth in the presence of overwhelming amounts of lead, which is not precipitated by pyrogallol. Titration is carried out on the basis of the oxidation current of excess pyrogallol on a platinum electrode. Japanese workers have used solutions of triphenyl selenium or triphenyl tellurium for the determination of bismuth in the presence of iodide [66].

Complexons which have recently entered analytical practice belong to the class of organic reagents. Trilon has been used for the determination of cadmium in a supporting electrolyte of potassium nitrate [67]. Papers have been published by R. Prshibil on the titration of thallium and nickel, lead, iron, zinc and cadmium at the various pH's and potentials corresponding to the regions in which a diffusion current is obtained for the given ion on a dropping mercury electrode [68].

For the determination of zinc and cobalt, V. A. Khadeev and A. I. Mirbadaleva [69] have used potassium tetrathiocyanatomercuriate which is reduced on the dropping mercury electrode and also on platinum electrodes.

Kh. Ia. Levitman and Z. A. Krivchik, and Kh. Ia. Levitman and R. N. Reznikova [70], for the determination of copper in alloyed steels and in aluminum alloys, have used solutions of rubeanic acid, which can also be used for the determination of nickel. The authors of this method consider that it can be recommended as an express method, particularly for the analysis of aluminum alloys. Good results are obtained when the iodide method is applied to the determination of micro amounts of copper in various natural objects and industrial solutions [62].

Kao Siao-hsia [71] for the determination of zinc in nickel-coating baths has used a fairly complicated method of separating zinc from solution; the zinc is subsequently titrated with potassium ferrocyanide at +0.7 volt on a rotating platinum electrode.

Without dwelling in detail on the determination of organic materials, which is a special branch of analytical chemistry, it is of interest to note that even in this branch, amperometric methods have been widely used in recent years. A particularly large amount of work has been devoted to the determination of sulphydryl groups and other sulfur-containing organic materials [13, 57, 72], and to the determination of alkaloids and various pharmaceutical preparations [63, 73, 74, 75]; a fair amount of research relates to the analysis of organic compounds: aldehydes [76], pyridine [77], flavonoid compounds [78], hydroxyphenylpropane [79], proteins [80], and diantipyrylmethane [81].

Other Fields of Application of Amperometric Titration

In addition to its purely analytical applications, amperometric titration is being used more and more for various research purposes — for determination of the solubility of various compounds and of the composition of

precipitates, for studying complex formation, etc. G. A. Kleibs [24, 82] has studied the composition of the heavy-metal ferrocyanides, using amperometric titration with a platinum electrode or a dropping mercury electrode and using anodic methods. V. L. Zolotavin and V. K. Kuznetsova [83] have determined the solubility products of vanadyl ferrocyanide on the basis of amperometric titration results. Kolthoff and Stock [84] have made a study of the reduction of suspensions of silver halides on a platinum electrode. Khosla and Gaur [85], like G. A. Kleibs, have studied the composition of ferri- and ferrocyanides. Pecsok and Juvet [86] have studied the composition of copper gluconate. McCune and Arquette [87] have made a study of the precipitation of the phosphates of complex cobalt compounds. A study of the conditions for reduction of molybdate and tungstate in the presence of silver nitrate has been carried out by the author of the present article [22]. R. Holt has made use of amperometric titration for studying the cation exchange capacity of soil [88].

Special mention must be made of the fact that the amperometric method, which possesses a high sensitivity, may find, and already does find, application as an indicator method for carrying out coulometric titrations [89]. As examples one can quote the new work carried out by Lingane and co-workers [90, 91] on the coulometric determination of antimony and cerium by means of a solution of iodine generated from potassium iodide, and the work of Hartley and Lingane [29] on titration of thallium with ferricyanide, and also the work of O. A. Songina, N. G. Kemeleva, and M. T. Kozlovskii [92], in which use has been made of the diffusion current for reduction of permanganate, as an indicator for the end point during coulometric titration of Fe(II) with permanganate. Richter [93] has suggested an automatic setup for coulometric titration with an amperometric indication of the end point.

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