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I. ANALYTICAL ION EXCHANGE SEPARATIONS

II. AN AUTOMATIC RECORDING TITRATOR

by

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PART I. ANALYTICAL ION EXCHANGE SEPARATIONS

INTRODUCTION

The separation of metal ions has long been a subject of major interest both to chemists in general and to industry. For the analytical chemist it is often of prime importance to be able to attain a rapid, complete separation of one metal from another which causes interferences in the analysis for the first. Of equal importance is the separation of multicomponent systems into less complex mixtures. Of the many methods available for metal separations, none show more promise than ion exchange. The recent widespread availability of synthetic ion exchange resins has made their use in chemical separations quite common. Good evidence of the importance of ion exchange resins is shown by the scope of the applications listed in some of the more recent reviews of this subject (8, 10, 44, 45). Of particular importance to analytical chemists is a very comprehensive bibliography by Osborn (59) who has listed over 1000 recent papers pertaining to the analytical applications of ion exchange. A review of the analytical applications of ion exchange has been published by Gompkins (26).

There are, in general, three approaches to the separation of metal ions by ion exchange. The first of these is the chromatographic method. This method is illustrated particularly well by the work of Spedding and associates (76-81, 86, 88, 89) in the separation of the rare earth metals. The process consists essentially of adsorbing all the metals from a solution on the top of a column of cation exchange resin which is initially charged with hydrogen ions. An eluting solution containing a complexing agent at a predetermined pH is then passed through the column. The metal ions then pass down the length of the column, being continuously adsorbed and desorbed during the course of movement down the column. The rate of travel of the component metal ions varies with the strength of the complex formed between any metal ion and the complexing agent contained in the eluting solution. Among ions of equal charge, the metal ion forming the strongest complex moves fastest down the column. If the flow rate of the eluting solution through the column is slow enough to establish equilibrium at all points throughout the column, each metal ion of the original mixture spreads out into a band of uniform composition. Each band is exactly adjacent to the ones preceding and following it. This permits the separation of the major portion of each component in a relatively pure form. However, complete separation of components, as is desirable for analytical work, is not achieved; because there is always a slight overlapping of the head of one band with the tail of the one preceding it. Regardless of this, some difficulty would be experienced in the inability to separate the fractions at the exact boundary of the bands as they come off the column. Some difficulty is also experienced in separating metals where the relative concentrations of the components vary greatly.

The work of Spedding _et al._ involved the use of citrate as the complexing agent in the eluant. Later work by the same authors describes the use of EDTA [(ethylenedinitrilo)-tetraacetic acid] for this purpose (86), and the use of copper instead of hydrogen ion as the retaining ion on the column (87). The quantitative theory of the separation of rare earths by this method is well defined by Spedding _et al._ (82-85). Vickery (96) investigated several complexing agents for use as eluants in the separation of rare earths. Stewart (90) applied this method to the separation of tracer amounts of rare earth elements of the yttrium group using glycolic acid as the eluting agent with columns 1 cm. or less in height and of extremely small diameter. He also investigated several of the variables affecting the quality of the separation.

In spite of the difficulties mentioned above, however, there will still be circumstances where this method can logically be used for analytical work. Radhakrishna (63) has achieved a separation of lanthanum from thorium by this method using techniques almost identical to those of Spedding. Here, however, the two ions have different charges and there is a separation of the bands. Judicious choice of the ion with which the resin is charged, or addition of a carefully chosen ion to the sample mixture could result in the interspersing between the bands of interest with a band containing the added ion. The added ion may be chosen to be more easily separable by another method from the metal ions of interest than they are from each other. This would be primarily useful in the case of a binary mixture. The added metal ion may also be chosen to be non-interfering in the methods of analysis for the ions of interest, thus eliminating the need for further separations.

The second method of separation of metal ions by ion exchange may be most clearly described as the displacement of a single component. In this case the eluting solution, again containing a complexing agent, is chosen so as to affect only one of the ions of the mixture. In general, anion exchange resins serve best for this method of separation. The work of Kraus _et_ _al_. (40-43) best illustrates this method. In this case, all the metal ions of a mixture which will form anionic complexes with the anion of the eluting solution are adsorbed at the top of a column of resin charged with the specified anion from a solution of very high concentration of this anion. Each of the metal ions of the mixture which have been adsorbed is eluted separately by stepwise decrements in the complexing anion concentration of the eluting solution. A solution of a particular, predetermined anion concentration is passed through the column until all of the metal it is designed to elute has been collected. The concentration of the eluting solution is then decreased and passed through the column until all of the second component has been collected. This process is repeated until the desired separation is attained. The composition of the eluting solution and the prospects of success in this method are dependent on knowledge of the qualitative composition of the mixture, and on the behavior of the ions concerned under varying conditions of concentration of the complexing anion of the eluting solution in the anion exchange column. This is done by comparing the variation in apparent distribution coefficient of the metal ion between resin and solution with variation in composition of the eluting solution. Considerable success has been achieved in separating many interesting metal ion combinations by this method. One example of this would be the separation of aluminum from zirconium as described by Freund and Miner (18) using HF-HCl mixtures for eluting solutions.

The third method of accomplishing metal ion separations by the use of ion exchange resins may be designated as the single-pass separation. In this method the separation is achieved by simply passing the appropriately prepared sample through the column. One or more of the components of the sample mixture is removed from the solution by the resin, while the remaining components are unaffected and pass through the column and are rinsed out by passing a small additional amount of the appropriate blank solution through the column. In common with the other two general methods, the single-pass method is also dependent on the use of a complexing agent. It can be applied equally well to operations with cation or anion exchange resins as may be dictated by the particular separation desired. The essential requirement is that it form a complex with only one component of the sample mixture, or that it form complexes of different charge types with the metal ions involved in a binary mixture. An extension of this method to more complex mixtures is well illustrated by the work of Wheelwright and Spedding (97) in the enrichment of crude rare earth ores in certain fractions of the rare earth group of metals with cation exchange resin using EDTA as the complexing agent. Similarly, Gordon _et al._ (27) have concentrated microgram amounts of rare earths in thorium using EDTA at a controlled pH to obtain selectivity of complexing action. Several other separations have been accomplished by this method of pH control with EDTA as the complexing agent. Among these are a separation of barium from lead (93), and of iron and aluminum from beryllium (57). Using tartaric acid as the complexing agent, Usatrenko and Datsenko (95) separated iron and aluminum from calcium and magnesium. The separation of iron from aluminum has been reported by Teicher and Gordon (94) using thiocyanate to form an anionic complex with iron, and an anion exchange column. The column adsorbs the iron complex but does not affect the aluminum, which passes through. This same separation has been reported by Kakihana and Kojima (35) using cation exchange resin and an iodide-chloride mixture as the complexing agent. The separation of palladium from iridium using ammoniacal chloride solution and cation exchange resin has been reported by MacNevin and Crummett (50). The positively charged ammonia complex of palladium is adsorbed by the resin while the negatively charged chloride complex of iridium passes through the column. One of the most interesting applications of this technique is reported by Kakihana (34), who accomplishes the separation of beryllium from aluminum without use of a complexing agent. The column of cation exchange resin is charged with calcium ions, which are displaced by aluminum ions but not by beryllium ions.

The method to be described in this thesis is an expansion on the processes of the single-pass method, and includes a more detailed investigation of the variables which affect this method of separation than has been previously attempted. A representative group of metals has been studied with the aim of introducing the method as one of general applicability rather than an independent method of separating a particular mixture.

There are several distinct advantages to the single-pass method of metal separations as compared to the other two methods described when applied to analytical work. The processes involved are quite simple and rapid in comparison to other types of ion exchange separations. Only a very moderate dilution of the original sample is involved; and, in particular cases, concentration of certain fractions of the sample may be attained along with the desired separation. This is particularly true when separating trace quantities of impurities in the major component of the sample. It is hoped that the wide applicability and versatility of the method will be amply illustrated in the discussions that follow.

BASIS OF THE METHOD

The method to be investigated here will consider the use of EDTA as the complexing agent and the conditions necessary to separate a binary mixture of metal ions by passage of the sample solution through a cation exchange column. If it is desired to separate a mixture of two metals, M_1^{+a} and M_2^{+b}, by the adsorption of only one of these on a cation exchange resin column, it will be necessary to convert the other to an uncharged or negatively charged complex species which is unaffected by the resin. In some cases it will be possible to choose a complexing agent which, under normal conditions, reacts with only one of the ions of the sample. However, if a general method is desired which will be applicable to many problems, it will be necessary to choose a complexing agent that reacts with many of the common ions, and then to control its action by careful selection of conditions. EDTA meets these specifications by being sensitive not only to many metal ions, but also to hydrogen ions so that the reaction:

$$M_1Y^{(a-4)} + 4H^+ \rightleftharpoons M_1^{+a} + H_4Y$$

can be made to proceed in either direction by proper control of pH.

If the separation of M_1^{+a} from M_2^{+b} is desired, the following points must be noted concerning this system:

1. Either or both of the metal ions must form an un-

charged or negatively charged complex species with EDTA in order that at least one of the ions may pass through a cation exchange resin column.

2. If both metal ions react with EDTA to form complex species which satisfy the conditions of point 1, the formation constants of the two species must be sufficiently different that proper pH control will largely dissociate one complex while not affecting the other. For the usual analytical accuracy to be attained, this difference must, in general, be 10^4 or greater.

3. The effect of the resin on the species present in the sample should be recognized. The principles in point 2 are valid as stated when both metals form ions of the same charge (*e.g.* $a = b$). Qualitatively, the resin will have a greater effect on an ion of greater positive charge. Semi-quantitatively, this effect may be discussed in terms of a practical distribution coefficient of the given metal ion between a solution containing the metal ion and cation exchange resin charged with a monovalent cation. For mono-, di-, tri- and tetravalent ions these coefficients are in the approximate order: 1, 10^2, 10^4, and $10^{(6 \text{ to } 8)}$, respectively. Since the resin is a part of the total reacting system, this difference in distribution coefficient for differently charged ions will tend to be a levelling or differentiating effect depending on which ion is adsorbed by the resin.

To illustrate these points, consider the problem of separating a divalent metal ion, M_1^{+2}, from a trivalent metal ion, M_2^{+3}. For purposes of this example, consider the formation constant of the M_1-EDTA complex to be 10^{18}, and that of the M_2-EDTA complex to be 10^{15}. This gives a difference in the two constants of 10^3, or a pK_f difference of 3. As stated in point 2, this difference would be insufficient to accomplish the desired separation with ordinary analytical accuracy, but considering the statements of point 3, the effect of the resin must also be noted here. The total reaction to be considered for each metal is a combination of the two reactions:

$$M_1^{+2} + 2R^- \rightleftharpoons M_1R_2 \qquad K_r \approx D$$

$$M_1^{+2} + Y^{-4} \rightleftharpoons M_1Y^{-2} \qquad K = K_f$$

where K_r is the equilibrium constant for the metal-resin reaction, K_f is the formation constant of the M_1-EDTA complex, R represents the anionic sites on the resin and D is the practical distribution coefficient mentioned above. Since the reaction of the metal ion with the resin is in competition with the reaction of the metal ion with EDTA, the effective constant, K', of the total reaction to form the complex is K_f reduced by K_r. This gives $K_1' \cong 10^{16}$ for the M_1-EDTA complex reaction, and $K_2' \cong 10^{12}$ for the M_2-EDTA complex reaction. Now if a third competing reaction is introduced, that of the protonation of the EDTA, the effective constants, K_1'' and K_2'', for the complex-formation reactions can be reduced to 10^4 and 1, respectively. This is attained by proper control of pH. Now the separation can be accomplished because all of M_1 is still effectively complexed, and the M_2-EDTA complex is sufficiently dissociated that it will be taken up by the resin as it passes down the column. The possibilities of formation of pH-dependent $MHY^{(a-3)}$ or $M(OH)_xY^{(a-x-4)}$ complexes has not been considered here since data concerning such complexes is unavailable or incomplete.

It must be noted here that the quantitative effects of the resin cannot, at present, be adequately treated mathematically because much of the thermodynamic data required is not available. The application of this method to analytical separations is accomplished with this background as a guide, and with sufficient experimental data to predict the conditions required for a given separation. The best approach, then, would be to obtain data showing the distribution of the metal ions in question between resin and solution containing excess EDTA as a function of pH, while maintaining all other factors constant. To obtain this data, however, requires that the pH of the resin phase as well as that of the solution be controlled. The resin is charged with an exchangeable ion which can affect the pH of the solution as well as the resin phase. Control of pH was effected by the use of pH buffers in the sample solution, and by pretreating the resin columns with the same buffer solutions.

EXPERIMENTAL NECESSITIES

Reagents

Ion exchange resins: Dowex 50-X4 nuclear sulfonic acid type cation exchange resin in the sodium form was used throughout this work except in the case of the investigation of the effects of varying crosslinkage. In this case Dowex 50-X16 resin was used where noted. In all cases 50 - 100 mesh resin was used.

EDTA [disodium dihydrogen (ethylenedinitrilo)tetraacetate dihydrate]: Sequestrene Na2 recrystallized, as marketed by Geigy Industrial Chemicals Co.

Zinc: Primary standard zinc metal of 99.99% purity was obtained from the Platt Bros. and Co., Waterbury, Conn.

Glycine (ammonia-free): Eastman Kodak white label

Formic acid: Baker and Adamson reagent grade

Phenol: J. T. Baker Chemical Co. "analyzed" reagent

Ammonium citrate [$(NH_4)_2HC_6H_5O_7$]: J. T. Baker Chemical Co. "analyzed" reagent

Hydrochloric acid: Baker and Adamson reagent grade

Perchloric acid: Baker and Adamson reagent grade

Nitric acid: Baker and Adamson reagent grade

Ammonium hydroxide: Baker and Adamson reagent grade

Ammonium chloride: Baker and Adamson c.p. grade

Eriochromeblack T: J. T. Baker Chemical Co. "analyzed" reagent

Arsenazo [3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalene disulfonic acid trisodium salt]: Eastman Kodak white label

Naphthyl azoxine [7-(1-naphthylazo)-5-sulfo-8-hydroxyquinoline]: Supplied by Analytical Group II of the Ames Laboratory. The preparation and properties of this indicator are given by Fritz, Lane and Bystroff (21).

Alizarin red S (sodium alizarin-3-sulfonate): Allied Chemical and Dye Co. certified biological stain

Bromcresol green: Hartman-Leddon Company, Phila., Penn.

Sulfosalicylic acid: Mallinkrodt Chemical Works

Triethanolamine (2,2',2" nitrilotriethanol): Eastman Kodak white label

Pyridine: Baker and Adamson reagent grade

Bismuth: Baker and Adamson 99.8% pure bismuth metal

Thiourea: Baker and Adamson reagent grade

Sodium chloride: Baker and Adamson reagent grade

Water: All water used in preparing solutions was distilled and deionized.

The metal ions investigated in this work were obtained from the following sources: Rare earths, yttrium and scandium from the Ames Laboratory of the United States Atomic Energy Commission. All others except those specifically noted above were reagent grade laboratory chemicals.

Solutions

EDTA (0.05 M): Dissolve 18.6 grams of reagent grade EDTA in one liter of water. Standardize against a standard zinc solution using eriochromeblack T indicator and pH 10 buffer (ammonia-ammonium chloride). A second 0.05 M EDTA solution is prepared in the same manner, but is not standardized. This solution is used to add to the samples before passing them through the resin columns. Since an excess of EDTA is used here, rigorous standardization is not necessary.

Zinc (0.05 M): Pure zinc metal is accurately weighed out and dissolved in a small amount of 1:1 nitric-acid-water in a covered beaker. After dissolution of the zinc, the solution is transferred to a 1 liter volumetric flask and diluted to the mark with water. 3.2690 grams of zinc are required for an exactly 0.05 M solution. This solution is used to standardize the EDTA solution and for experimental work involving zinc.

Eriochromeblack T: Prepare the indicator for use by mixing the powdered dye with dry sodium chloride in a weight ratio of 20:1, NaCl:dye. The indicator prepared in this manner is stable indefinitely. It is added to the solution prepared for titration by means of a small spatula in an amount necessary to give just sufficient color intensity for easy visual observation of the end-point.

Ammonia-ammonium chloride buffer solution: 67.5 grams of ammonium chloride is mixed with 570 ml. of concentrated ammonium hydroxide and diluted to 1 liter. One ml. of this buffer is used with each aliquot of the zinc solution used in standardizing the EDTA.

Naphthyl azoxine (1%): One gram of the indicator is dissolved in 100 grams of dimethylformamide.

Alizarin red S (0.2%): 200 mg. of the indicator is dissolved in 100 ml. of water.

Bromcresol green (0.1%): 100 mg. of the indicator is rubbed in an agate mortar with sufficient volume of 0.1 M sodium hydroxide solution to neutralize the sulfonic acid group of the indicator. The formation of a permanent blue coloration indicates this neutralization. The resulting solution is diluted to 100 ml. with water.

Arsenazo (0.33%): 330 mg. of the indicator is dissolved in 100 ml. of water.

Glycine (0.2 M): 60 grams of glycine is dissolved in 4 liters of water. 4 grams of phenol is added to inhibit mold growth in the solution during prolonged storage.

Formic acid (0.2 M): 30 ml. of 98-100% formic acid is diluted to 4 liters with water. 4 grams of phenol is added to inhibit mold growth in the solution during prolonged storage.

Metal ion solutions (0.05 M): The required amount of the metal, or the salt or oxide of the metal, is dissolved in water or acid, as required, and diluted to 1 liter with water.

Apparatus

Burets: Kimble Normax burets were used throughout this work.

Stirrer: A magnetic stirrer was used with teflon-covered stirring bars.

Pipets: Kimble Exax pipets were used throughout this work.

pH meter: All pH measurements were made on a Beckman model G pH meter equipped with Beckman 1190-80 glass and 1170 calomel reference electrodes.

Spectrophotometer: A Beckman model B spectrophotometer with 1 cm. borosilicate glass cells was used for all spectrophotometric measurements.

Ion exchange columns: Three ion exchange columns as illustrated in Figure 1 were used for all work except in the case of the investigation of the effect of column length. For that purpose similar columns were used, but the height from the glass frit to the top of the column was 13 cm. The columns were fitted with a 60° funnel with a top diameter of about 8 cm.

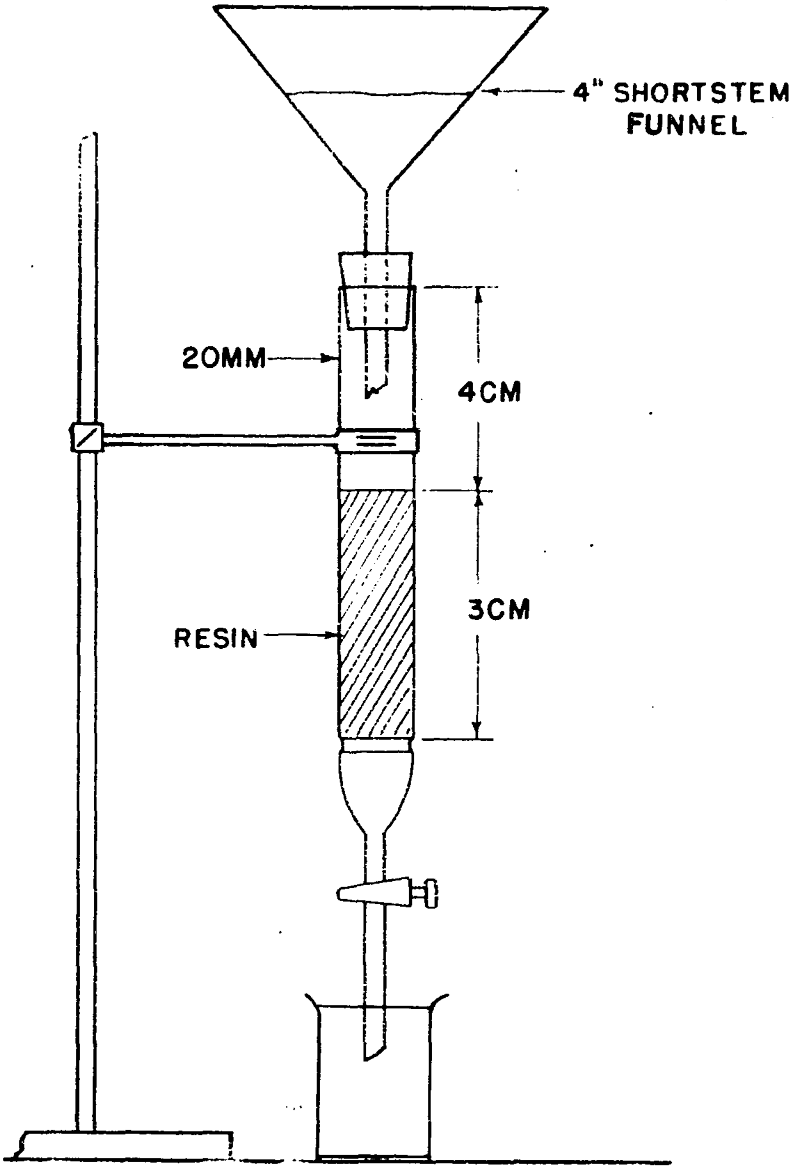


Figure 1. Ion exchange column

EXPERIMENTAL

Preparation of the Ion Exchange Resin

Since the ion exchange resins as received from the manufacturers contain some contaminants as a result of the production processes, and since the resin can be re-used indefinitely when properly regenerated; proper treatment of the resin is of prime importance in analytical applications. A study of the processes of resin regeneration is presented by Samuelson (69). Specific recommendations for complete regeneration of ion exchange resins are given by Djurfeldt and Samuelson (13). The principles defined by these authors have been followed in large measure in the preparation of resins for this work.

Specifically, the resin was prepared in the manner described below, and used resin was regenerated by the same processes. A 400 ml. beaker was filled to the top with the wet resin, and this amount of resin was transferred to a large ion exchange column similar to that illustrated in Figure 1. This column was 7 cm. in diameter and 30 cm. high. It was fitted with a 24/40 standard taper glass joint at the top and was brought down to 15 mm. glass tubing below the glass frit. This tubing was fitted with rubber tubing and a screw clamp. After the resin was placed in this column, it was backwashed with distilled water to remove the fines and other loose solids. When the solution above the resin had become clear, the water was allowed to drain out the bottom until the water level in the column was about 2 cm. above the resin level, and the screw clamp was closed. A 500 ml. separatory funnel fitted with a 24/40 standard taper glass joint below the stopcock was then inserted in the top of the ion exchange column. This was used to control the flow of regenerating solution and to prevent its intermixing with the solution in the column as would accur if the regenerating solution were merely poured into the column. The regeneration is accomplished in two steps.

First, to remove tri-and tetravalent ions, particularly, 1500 ml. of a 10% by weight ammonium citrate solution, adjusted to pH 3 to 3.5 with hydrochloric acid, was passed through the column by means of the separatory funnel. The rate of flow of this solution through the column was regulated by the stopcock on the separatory funnel after the screw clamp at the bottom of the column was opened fully. The rate of flow was so regulated that at least one hour of continuous flow was required to pass all the regenerating solution. This solution was then rinsed through the column by passing distilled water from the separatory funnel at the maximum attainable flow rate. This required about 2 liters of water, or four refills of the separatory funnel. This treatment leaves the resin in a mixed ammonium and hydrogen form, but free of all other contaminants.

Second, in order to obtain the sodium form of the resin, which was found to be most useful for this work, the processes described above were repeated using 1500 ml. of a 10% by weight sodium chloride solution. The completeness of the rinsing of the sodium chloride solution from the column was checked with a dilute solution of silver nitrate acidified with 1 drop of 3 M nitric acid. The rinsing was continued until no turbidity was produced when a small amount of the effluent solution was added to the silver nitrate solution.

Following this, the separatory funnel was removed from the column and an aspirator was attached to the bottom of the column. The aspirator was then operated for about 3 minutes at the maximum rate to remove most of the water in the column and then turned off. Absolute ethanol was then poured into the column until the liquid level was about 2 cm. above the resin. A considerable amount of bubbling occurred in the resin at this point, with a resultant channelling which would hinder the effectiveness of the ethanol rinse. To eliminate this channelling, the column was swirled vigorously until the resin settled out homogeneously. An additional 200 ml. of ethanol was then added, and the aspirator was again turned on until all the ethanol was withdrawn from the column. This process was repeated once again with ethanol, and then twice with acetone.

After this, the resin was poured out of the column onto paper towels on the lab bench and allowed to dry while agitating it slightly with a spatula. When completely dry (about 15 minutes) the resin was transferred to a clean 250 ml. erlenmeyer flask and closed with a rubber stopper. The resin thus prepared was weighed out for experimental purposes.

The importance of the above procedures cannot be overemphasized. Less rigorous preparations have resulted in many difficulties in the experimental procedures. The specific amounts of materials noted, and the flow rates mentioned should be closely reproduced. When resins with crosslinkages greater than X4 are used, the final product does not flow free with this treatment, and must be dried further in an oven for a short period at temperatures below 110° C.

Procedures

The procedures used to obtain the data to be presented were essentially the same for all the metal ions studied. Since many factors affect the systems investigated here, rigorous attention to the mechanical details of the procedures must be maintained.

Preparation of the ion exchange column

Dowex 50-X4 nuclear sulfonic acid type cation exchange resin prepared as directed was used except where otherwise noted. Five grams of the resin was weighed on a triple beam balance and poured into the top of each of three ion exchange columns which contained water to a depth of about 4 cm. with the funnels removed. After the resin had settled and swelling had ceased, the columns were tapped lightly to level the resin. The water level was then adjusted to be about 1/2 cm. above the resin. The funnels were inserted so that the tip of the funnel was about 1 cm. above the water level. The appropriate buffer solution [glycine (0.2 M) for pH 1-3.6, formic acid (0.2 M) for pH 2.7-4.2, or acid for pH below 1] was poured into a 1 liter beaker to within 1 inch of the top. Fifty ml. of the unstandardized 0.05 M EDTA solution was measured out in a graduated cylinder and added to the buffer. The pH was adjusted with hydrochloric or nitric acids or ammonium hydroxide to the desired value using the pH meter. The funnels on top of the ion exchange columns were filled with this solution, and it was passed through the columns at a rate of 10-15 ml./minute, regulated by the stopcock on the bottom of the column. The effluent solution was collected in a 250 ml. beaker until the solution level had fallen to the top of the neck of the funnel. The pH of this effluent solution was then measured. If it was within 0.1 pH unit of the desired value, the column was ready for use. If the pH was off by an amount greater than 0.1 unit, the pH of this solution was readjusted to the desired value and it was again passed through the column in the manner described, collected, and the pH again measured.

Each solution could be re-used twice in this manner. If the desired pH value had not been attained by the time this solution had been re-used twice, it was discarded, and new buffer solution added as described. This process was repeated until the desired pH of the effluent solution had been attained and the column was ready for use. The used buffer solutions were discarded, and the beakers replaced under the columns. The sample was then prepared for passage through the column as described below.

Preparation of the sample

Again, in all cases, the sample size was maintained constant with all of the metal ions investigated, except where specifically noted otherwise. To a 10 ml. aliquot of the 0.05 *M* metal ion solution in a 150 ml. beaker, 30 ml. of the buffer solution was added and a stirring bar was placed in the beaker. Three samples were prepared for each experimental point. The sample was then placed on the stirrer, and 15 ml. of the unstandardized 0.05 *M* EDTA solution was added from a graduated cylinder. While stirring continuously, the pH of the sample was adjusted, using the pH meter, to the desired value with the appropriate acid or ammonium hydroxide. When the correct pH had been attained, the sample was poured into the funnel at the top of the column, and passage through the column was started immediately with the rate of flow controlled by the stopcock. The second and third samples were successively prepared in this manner and passed through the columns, matching the flow rate of each to that of the first by noting the rate of fall of drops from the funnel tip. The effluent solutions were collected in a 250 ml. beaker. When the level of the sample solution in the funnel had dropped to the top of the neck of the funnel, a 30-40 ml. rinse of the buffer solution, which had been used to rinse out the sample beaker, was poured into the funnel without stopping the flow of solution through the column. This process was repeated two additional times with each sample, giving a total volume of 90-120 ml. of effluent in addition to the volume of the original sample. When this total volume had passed through the first two columns, they were turned off. When the level of rinse solution in the third column had reached the top of the neck of the funnel, the funnel was filled with distilled water. The collecting beaker was removed and replaced with a 50 ml. graduated cylinder. ~~The~~ time required to fill this cylinder from the 5 to the 45 ml. levels was measured with a stopwatch, and the rate of flow calculated from this information. The pH of the effluent solutions collected in the 250 ml. beakers was measured on the pH meter and recorded. These effluent solutions were retained for analysis as described in the next section.

When the portion of the sample that was retained by the column was of interest, it was eluted from the column in the following manner: The funnel at the top of the column was filled with 4 M hydrochloric acid (about 80 ml.) and this solution was passed through the column at a very slow rate of flow such that at least one-half hour was required to pass this solution and an additional 10 ml. which was added when the level of solution in the funnel had dropped enough to accomodate the additional amount. The effluent solution was collected in a 150 ml. beaker and retained for analysis as described in the next section.

Analysis of Samples

Wet ashing of organic materials in the sample

Since the preferred method of analysis, wherever applicable, was titration with EDTA, the removal of the EDTA and other complexing substances present in the sample was imperative. This was accomplished through use of a wet ashing with nitric and perchloric acids. The principles of this process are very adequately treated by Smith (75).

The original effluent portions of the samples (the fraction unaffected by the resin) was evaporated on a hot plate while covered with a ribbed watch glass. The temperature was maintained near, but below, the boiling point of the solution. When the volume of solution had been reduced to less than 50 ml., 25 ml. of concentrated nitric acid and 10 ml. of concentrated perchloric acid were added. The solution was evaporated to fumes of perchloric acid, and then to near dryness to reduce, as much as possible, the acid concentration of the sample. The sample fractions that were eluted from the column were treated in the same manner except that the volume of solution was first reduced to less than 30 ml., in the 150 ml. beakers, and 15 and 8 ml., respectively, of concentrated nitric and perchloric acids were added. The fuming was continued to near dryness as before.

These procedures have been applied to all the samples used in this work without difficulty as long as the specified conditions of sample size and buffer volume and concentration were rigorously followed. If these conditions are altered, it is imperative to follow closely the fuming operation throughout. A keen awareness of all the warning signals described by Smith (75), and the corrective measures prescribed will prevent occurrences of the much-publicized perchloric acid explosions. Wet ashing by this method is a valuable analytical tool, and is quite safe when properly executed.

It is also important to note that the fuming is carried out to near dryness, but not to complete dryness. In certain cases, particularly when fuming down solutions of divalent metals, explosions may occur when the sample is fumed to dryness. This is likely due to the thermal instability of some metal perchlorates. Copper was found to be particularly susceptible to this decomposition.

Whenever the warning signs of blackening, or relatively rapid color changes from yellow through red to brown or brownish-black become evident, a quick addition of cold water will stop the reaction. A need for more nitric acid in the reaction mixture is indicated by this behavior. The ashing procedure can be continued after addition of more nitric acid. Again, close attention to all stages of the process must be maintained.

A few compounds are quite stable to nitric acid oxidation. They are not attacked until all the nitric acid has evaporated, and the primary reaction is that of perchloric acid oxidation. When these compounds are present in more than milligram amounts, the wet ashing procedure is not recommended as it will nearly always present difficulties. Two of these compounds which have been encountered during the course of this work are citric acid and pyridine.

When the wet ashing process had been completed, the sample was diluted with water, and the cover glass and the sides of the beaker were rinsed down. The sample was then ready for analysis of the metal ion. The analyses for the various metal ions were made by the methods described in the next section.

Methods of analysis

Thorium. Thorium was analyzed by titration with EDTA using the method of Fritz and Ford (19). The indicator used was a mixture of equal volumes of 0.2% alizarin red S and 0.1% bromcresol green solutions instead of the 0.2% alizarin red S solution recommended by the authors.

Rare earths, scandium and yttrium. These metals in 0.05 M and 0.005 M concentrations were analyzed by the method of Fritz, Oliver and Pietrzyk (23) using titrant of equivalent molarity. Colorimetric analyses of microgram amounts were carried out by the method of Fritz, Lane and Richard (22) using the Beckman model B spectrophotometer.

Copper and zinc. Copper and zinc were analyzed by the method of Fritz, Lane and Bystroff (21).

Zirconium. Zirconium was analyzed by the method of Fritz and Johnson (20).

Iron. Iron was analyzed by titration with EDTA. Sulfosalicylic acid was used as indicator, and the titration was carried out at pH 2.0-2.5. The end-point was taken as the last discernible change in color from red through yellow-orange to the pale yellow-green of the iron (III)-EDTA complex. This titration is not recommended for purposes other than its use here to obtain the desired data. For the purposes of this investigation it was only necessary to obtain a reproducible equivalence between the titrant and the iron solution. The sample fractions from the columns were then determined as the fraction of titrant consumed in the analysis compared to the amount required for the total original sample of 10 ml.

Data

Table 1 and Figure 2 summarize the data on what have been designated as standard curves in this study. These data describe the distribution of metal ions between resin and solution as a function of pH when the samples are treated by the procedures previously described. The designation of standard curves defines the data obtained under a fixed set of conditions for all samples. All data presented here was obtained using 5 grams of X4 resin in the columns. Flow rates through the columns were all in the range of 8 to 11 ml./minute. No evident complexing of the metal ions, due either to the buffer compound, or to the anion of the acid used to adjust pH, was shown. This is the reason for the particular choices of buffers indicated. The complexing effects of some of the buffer components will be described in the discussions on the effects of variables. The average of the analyses of each of three independent samples was used to define each experimental point except where otherwise noted. The analyses were carried out on the fraction of the sample which passed through the column at the specified pH. The pH of the effluent solutions which were collected were within ±0.05 unit of the specified value except where noted in the table. The pH values recorded and plotted are those of the original sample and buffer solution. Because the sodium form of the resin was used, the tendency to variation in pH was generally toward higher values. The effects of varying conditions other than pH or metal ion are described in a later section.

Several points should be noted here concerning these

Table 1. Retention of metal ions as a function of pH

pH	Metal ion	Per cent on column	Buffer[a] used	pH	Metal ion	Per cent on column	Buffer[a] used
0.9	Th	100.0[b]	HCl	0.9	Yb	100.0	HCl
1.2	Th	87.5[b]	GH	1.2	Yb	99.5	GH
1.5	Th	47.3[b]	GH	1.5	Yb	47.6	GH
1.8	Th	3.3	GH	1.8	Yb	0.9	GH
2.1	Th	0.1	GH	2.1	Yb	0.1	GH
0.6	Sc	61.9	HCl	0.6	Cu	15.9[b]	HNO_3
0.9	Sc	46.4	HCl	0.9	Cu	4.2[b]	HNO_3
1.05	Sc	0.3	GH	1.2	Cu	0.0[b]	GN
1.2	Sc	0.0	GH	0.6	Fe	0.0	HNO_3
1.5	Y	100.0	GH	1.2	Zn	99.1	GN
1.8	Y	94.6[b]	GH	1.5	Zn	83.5	GN
2.1	Y	60.2[b]	GH	1.8	Zn	39.4[c]	GN
2.4	Y	10.0[d]	GH	2.1	Zn	0.0[c]	GN
2.7	Y	2.4[d]	GH	0.6	Zr	5.5[b]	HCl
3.0	Y	0.0	GH	0.9	Zr	0.8[b]	HCl

[a] The designations of the buffer solutions are as follows: GH for glycine buffer acidified with HCl; GN for glycine buffer acidified with HNO_3; F for formic acid buffer adjusted with ammonia

[b] Average of only 2 samples

[c] pH of effluent solution less than 0.1 unit above the stated value

[d] pH of effluent solution less than 0.2 unit above the stated value

Table 1. (Continued)

pH	Metal ion	Per cent on column	Buffer[a] used	pH	Metal ion	Per cent on column	Buffer[a] used
2.1	Sm	100.0[d]	GH	2.7	La	100.0	GH
2.4	Sm	75.5[d]	GH	3.0	La	92.0	F
2.7	Sm	42.3[c]	GH	3.3	La	70.4	F
3.0	Sm	13.9	GH	3.6	La	18.6	F
3.3	Sm	0.1	F	3.9	La	0.0	F

data. They are best discussed in reference to Figure 2. It should be evident that if these conditions are repeated, choosing a particular pH value, that those metals which pass quantitatively through the column at this pH could be separated from those which are quantitatively retained by the column. For example, if the pH value of 1.2 were taken, scandium could be quantitatively separated from yttrium, samarium and lanthanum. The separation of scandium from ytterbium or zinc would be nearly quantitative, but not perfect. The separation of scandium from thorium would not be complete, although a reasonable estimate of the degree of separation could easily be predicted from these data.

A second significant point which is evident in these data concerns the valence effect. Thorium and ytterbium are good examples. The formation constant of the thorium-EDTA complex is about 10^{23}, while that of the ytterbium-EDTA complex is about 10^{19}. Since the two curves fall in

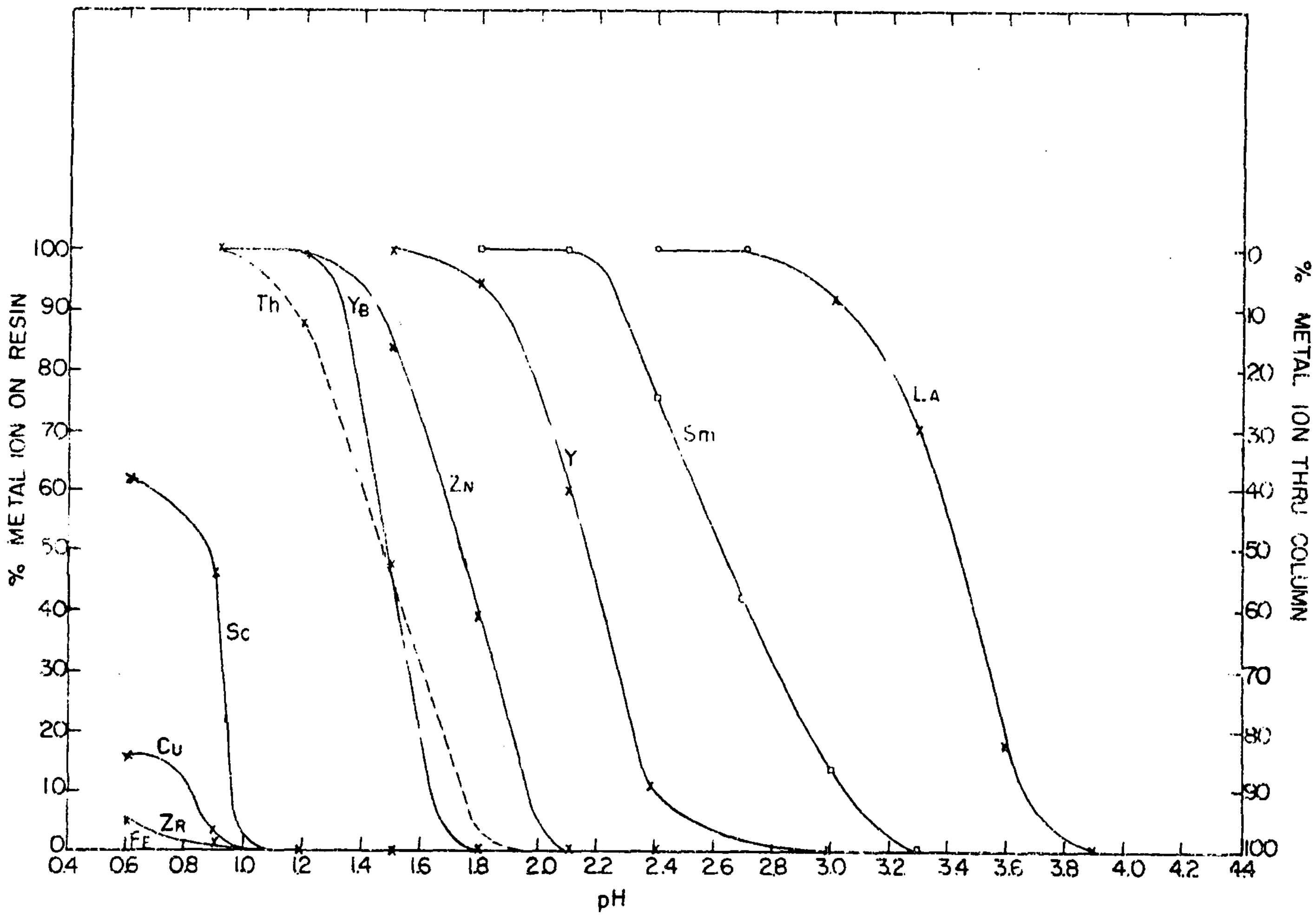


Figure 2. Retention of metal ions as a function of pH

nearly the same pH range, the difference of 10^4 in their formation constants must be largely nullified by the levelling effects of the resin. In semi-quantitative terms, the apparent distribution coefficient of thorium between solution and resin must be about 10^4 greater than that of ytterbium. This figure, of course, is not totally accurate, because equilibrium is not attained in these systems.

The effects of concentration of foreign ions in the solution are illustrated by the curves of scandium, copper and zirconium. To attain pH values much below 1, the concentration of buffer cations (hydrogen ions in this case) must be increased considerably over the 0.2 M level that was prescribed for the buffer solutions. The result of these high concentrations of hydrogen ion is to displace the metal ions of the sample that are initially adsorbed by the resin, and a type of chromatographic elution of the sample ions occurs. This prohibits the complete adsorption of these metals under the prescribed conditions.

Applications

The principles of this method and the data described have been applied to several synthetic binary mixtures of metal ions. Data for these separations are summarized in Table 2. The sample size was governed to adhere to the previously specified conditions by using a mixture of 5 ml. of each of the metal ion solutions concerned. The magnesium-aluminum separation was performed previous to the fixing of conditions, but is included here for comparison with Table 3 which summarizes data obtained by Analytical Group I of the Ames Laboratory, who have used this method for their purposes. The inclusion of the data of Tables 2 and 3 is intended to illustrate the possible applications of the method.

Table 2. Separation of metal ions[a]

Metal added m. mols.		Metal found m. mols.		No. of samples	pH
		On resin	Through column		
La	0.242_4	0.242_9		3	2.2
Th	0.248_4		0.247_4		
Sm	0.245_9	0.245_4		3	1.8
Fe	0.247_4		0.247_4		
Y	0.244_8	0.245_0		3	1.35
Sc	0.258_0		0.257_7		
Mg	0.996_2	0.996_9		2	4.0
Al	0.999_4		not analyzed		

[a] Glycine buffer acidified with HCl was used in all cases except the Mg-Al mixture which was unbuffered.

Effects of Variables

Effect of complexing action of the buffer

Because most compounds which serve as buffers also have

Table 3. Analysis of synthetic samples[a]

Metal added, mg.[b]				Metal found, mg.			
Al	Mg	Th	Y	Al	Mg	Th	Y
33.32	7.65	----	----	33.32	7.64	----	----
33.32	7.65	----	----	33.36	7.65	----	----
33.32	7.65	10.5	----	----[c]	7.65	10.5	----
33.32	7.65	10.5[d]	----	----[c]	7.77	10.5	----
33.32	7.65	10.5[d]	----	----[c]	7.67	10.5	----
33.32	7.65	10.5[d]	----	----[c]	7.65	10.5	----
33.32	7.65	10.5[d]	----	----[c]	7.64	10.6	----
----	7.65	----	201.2	----	7.65	----	201.2

[a] From analytical procedures of the Ames Laboratory, Mg-1

[b] Metals added from pure solutions standardized by titration with a standard EDTA solution

[c] It was assumed that 33.32 mg. of Al was found, then the Th value was calculated by difference.

[d] Uranium present

complexing properties, the effects of these compounds on the systems investigated has been encountered in several cases during the course of this work. The buffer concentration is highest of any component of the sample. Therefore, even though the buffer forms relatively weak complexes compared to the EDTA complexes, a mass action effect can be shown. Two possibilities arise when conditions are such that the complexing action of the buffer competes favorably with the EDTA complexes.

If the metal complex formed with the buffer compound is positively charged, the retention versus pH curve of the metal ion should be shifted toward higher pH values where the EDTA complexes are generally stronger. The curve may also be slightly distorted from the near-symmetry of the standard curve. If the positively charged metal-buffer complex is sufficiently strong, the trend toward less retention by the resin at higher pH values can actually be reversed by adsorbing this positively charged metal-buffer complex. This effect was shown by glycine buffer with both lanthanum and samarium, and is well illustrated in Figures 3 and 4 where the standard curves for the two metals are reproduced with the curves obtained by the same procedures using formate buffer. As before, each experimental point represents the average of three independent sample analyses. Note that in the case of both metals, the evident effects of the glycine are shown in the same pH range. The effects of glycine on the systems were not investigated further, because as a buffer it is relatively useless beyond pH 3.6, and further investigations along this line did not serve the current purposes of this work. Table 4 summarizes the data of Figures 3 and 4 for the points of interest.

The second possible effect of the complexing action of the buffer would be the formation of a negatively charged complex. This requires that the buffer anion show complexing properties. When this occurs, the pH versus retention curve

Table 4. Effect of buffer

pH	Per cent lanthanum on column		Per cent samarium on column	
	Formate buffer (standard)	Glycine buffer	Formate buffer (standard)	Glycine buffer
3.0	92.0	99.9	---	13.9
3.3	70.4	94.8	0.0	9.9
3.6	18.6	92.5	---	17.1

Table 5. Effect of anion

pH	Per cent zinc on column	
	Chloride in buffer	Nitrate in buffer (standard)
0.9	100.0	---
1.2	88.0	99.1
1.5	77.2	83.5
1.8	0.2	39.4
2.1	---	0.0

should move toward lower pH values because a second reaction, competing with the metal-resin reaction, is being introduced by the formation of negatively charged complexes. This effect was shown by the experimental work with zinc. Glycine buffer was used, but it was acidified with hydrochloric acid to obtain the desired pH value for the sample. Because the effect shown was opposite to the previously demonstrated effect of glycine, it was concluded that this variation in the zinc system was due to chloride ion forming a negatively

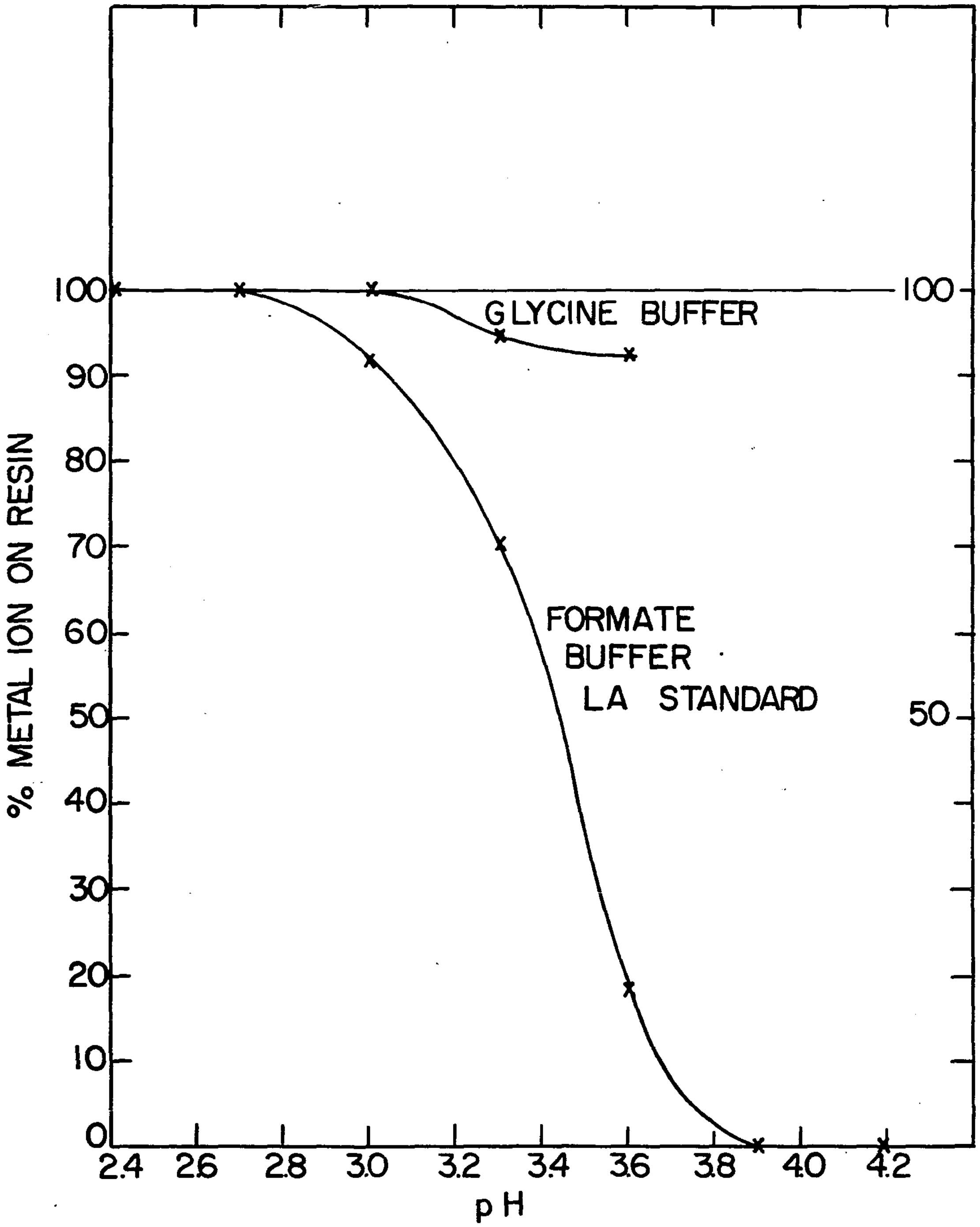


Figure 3. Effect of buffer

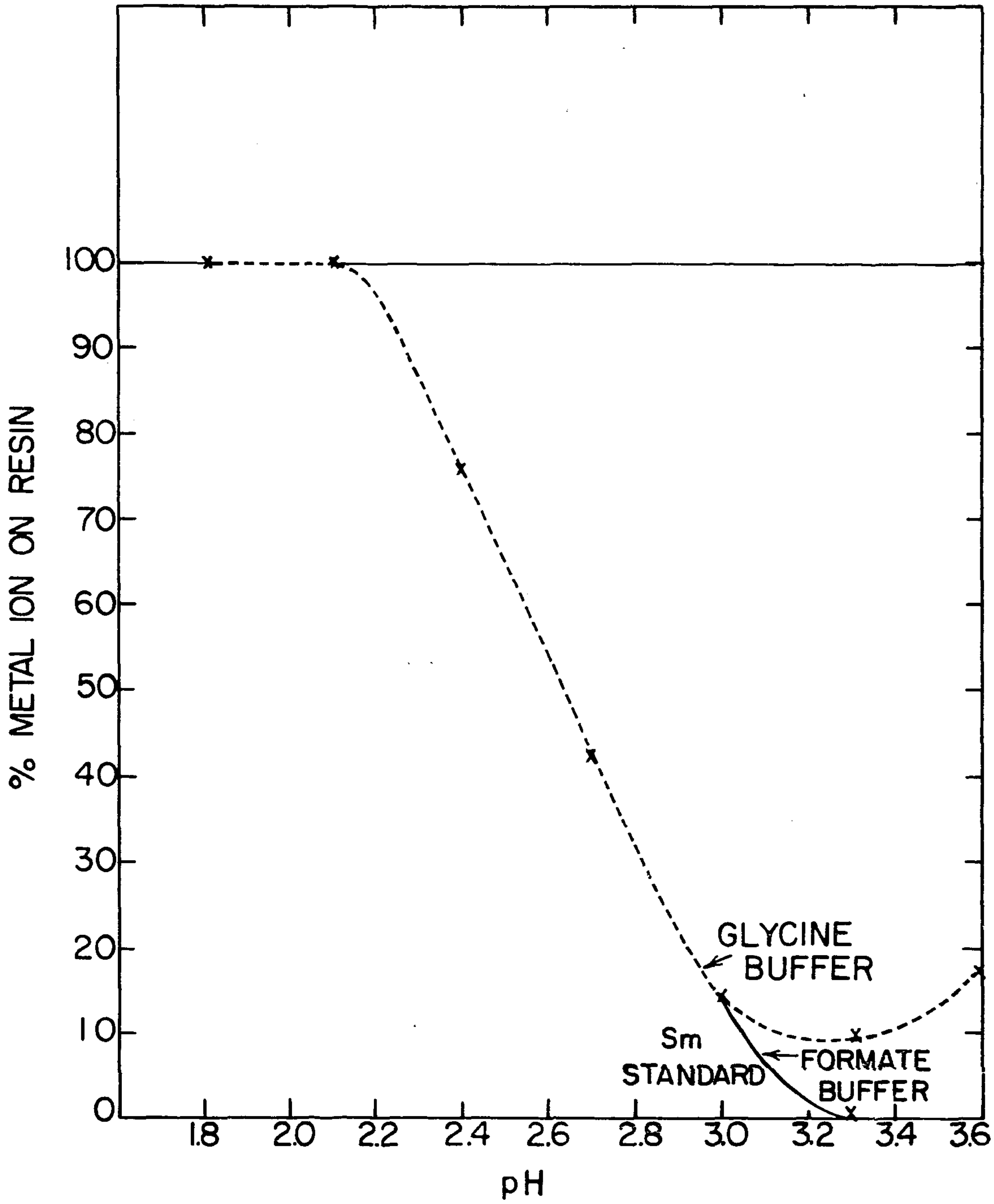


Figure 4. Effect of buffer

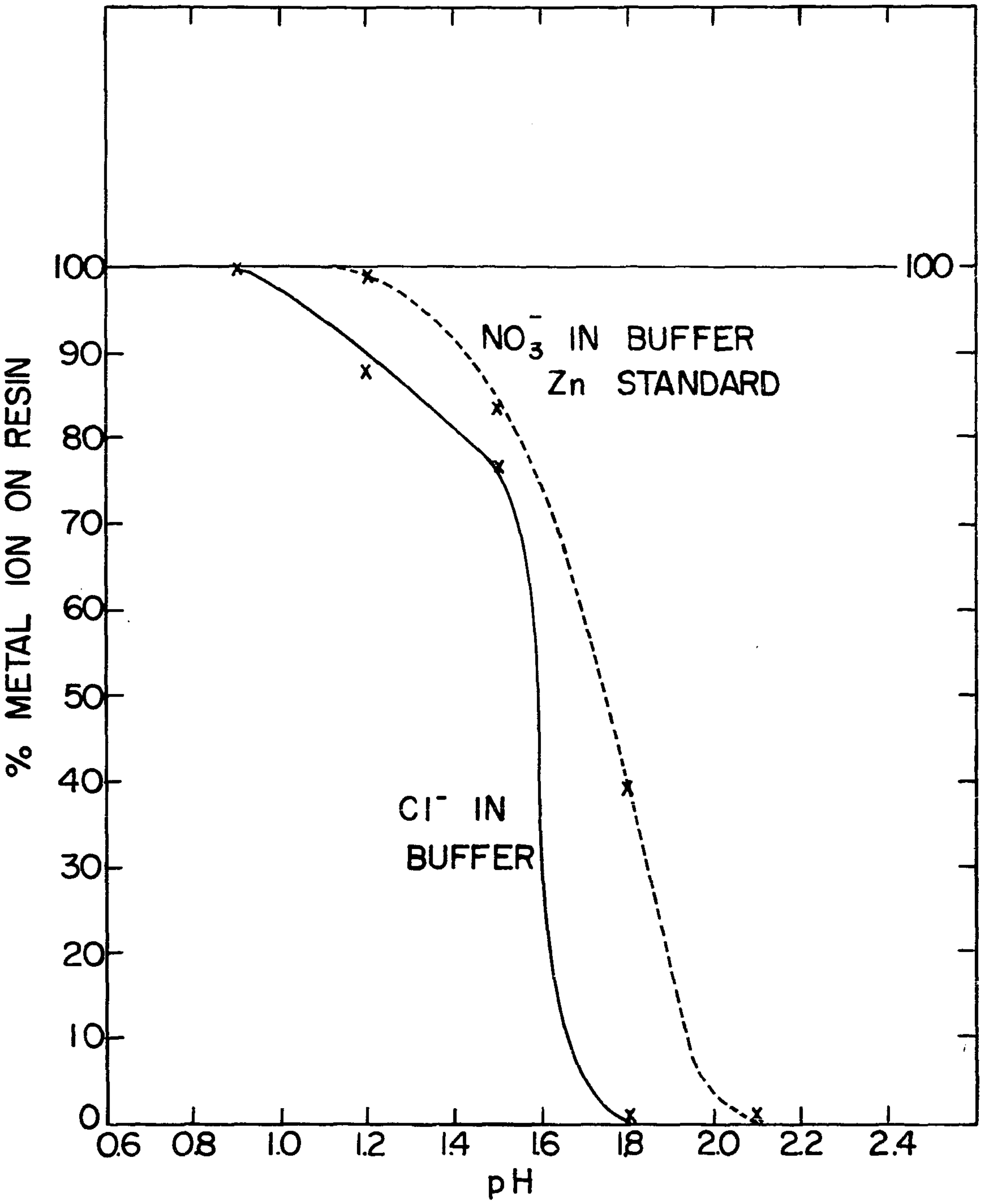


Figure 5. Effect of anion

charged complex with zinc. This effect is illustrated in Figure 5. The data of interest are included in Table 5.

Effect of column length

The effect of varying the column length was investigated using zinc for the sample system as shown in Table 6 and Figure 6. It was felt that this effect would be similar in the case of other metal ions. The effect was studied by doubling the weight of X4 resin used in the columns. This doubling results in a resin bed depth of about 7 cm. as compared to the 3 to 4 cm. bed depth used for the standard procedures. The actual effect shown was less than had been expected, but it points out at least two significant features.

Table 6. Effect of column length

	Per cent zinc on column[a]	
pH	Standard column	Double-length column
1.2	99.1	---
1.5	83.5	96.5
1.8	39.4	35.3
2.1	0.0	2.4

[a] Glycine-HNO_3 buffer used throughout

It is felt that one reason that ion exchange procedures are not more prevalent in analytical work is a fairly common misconception that inordinately long columns must be used, and that the procedures are tedious at best. The very small

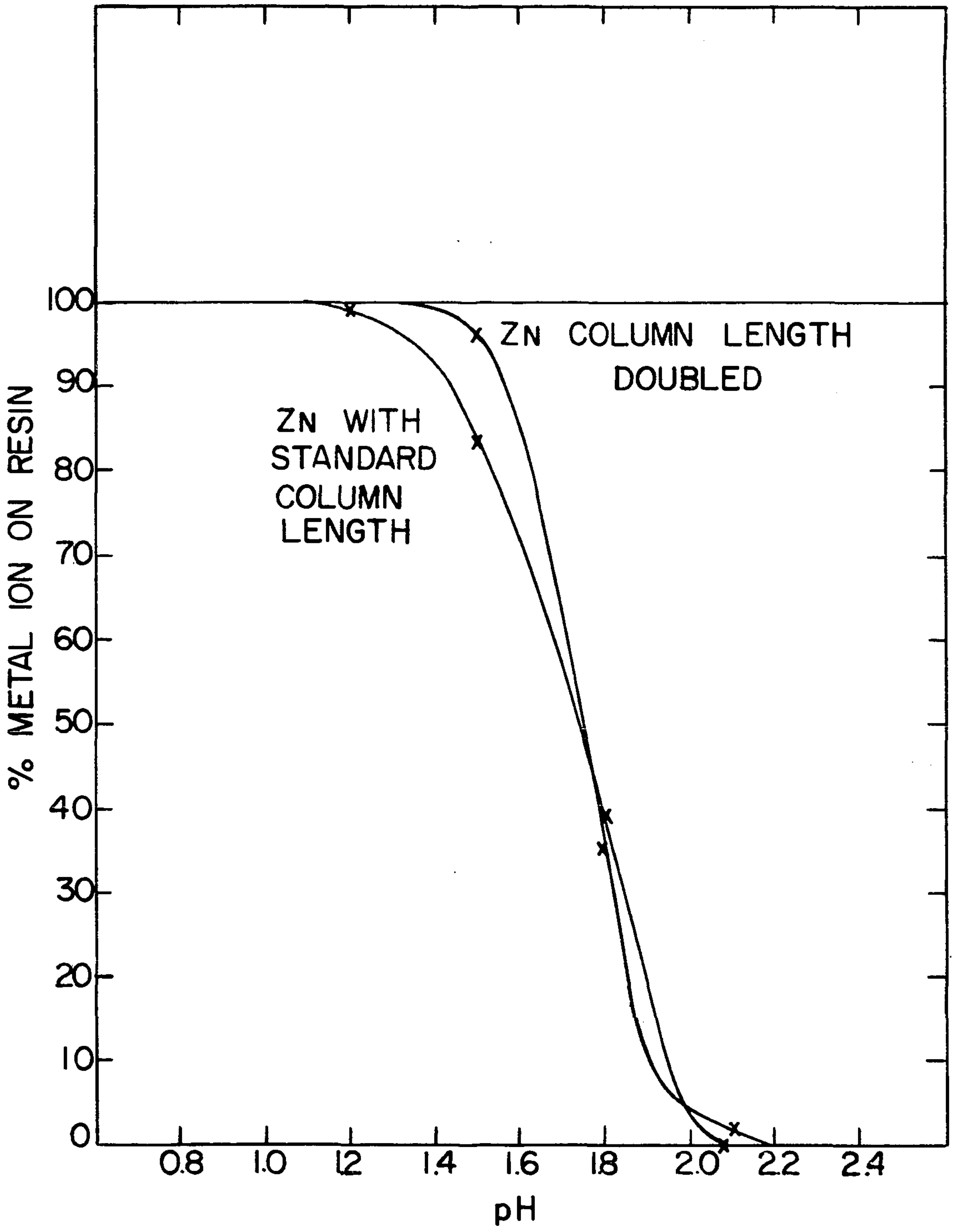


Figure 6. Effect of column length

difference in behavior between the 4 cm. and the 7 cm. column lengths illustrates the usefulness of these very short columns. One of the better examples of the use of very long columns where short ones would serve is reported by Gordon _et al_. (27) in which the separation of lanthanum from thorium was carried out using a 30 cm. column. The procedure reported by these authors was almost identical in other respects to that described here. As listed in Table 2, this separation has been carried out quite successfully using 4 cm. columns.

The rounding of the top of the standard curve indicates a slight chromatographic eluting action of the rinsing solution which is not evident in the curve for the longer column. It follows that the greater column length serves to retain the sample longer, and since the amount of rinsing solution is limited, the portion of the sample retained is not re-eluted off the column. This effect is shown also in the lower portion of the curve. The small amount of sample which is retained by the column is not carried through until higher pH values are reached.

Effect of resin crosslinkage

The crosslinkage of the particular resins used is designated by the manufacturer as the percentage of divinyl benzene in the original styrene-divinyl benzene reaction mixture from which the resin polymer is formed. The sulfonation process is carried out after the polymer has been formed. The fraction of the originally added divinyl benzene that is carried through to the final product is not accurately known, but is assumed to be proportional to the original amount. The greater the crosslinkage, the smaller are the channels through the resin beads which give access to the major portion of the reactive sites of the resin. This shrinking of the resin pores with increasing crosslinkage will show its greatest effect with ions of large radius and high charge. Because of this, thorium was chosen as the metal ion to demonstrate these effects. The data obtained for this purpose are summarized in Table 7 and Figure 7 where a comparison is made of the retention *versus* pH curves for thorium with X4 (standard) and X16 resins. The X16 resin was added to the columns so as to give the same column length as with the X4 resin.

Table 7. Effect of resin crosslinkage

pH	Per cent thorium on resin	
	X4 resin (standard)	X16 resin
0.9	100.0	97.6
1.2	87.5	59.7
1.5	47.3	29.5
1.8	3.3	11.6
2.1	0.1	---

It has become apparent in the course of this work that the resin not only adsorbs the free metal ion that is

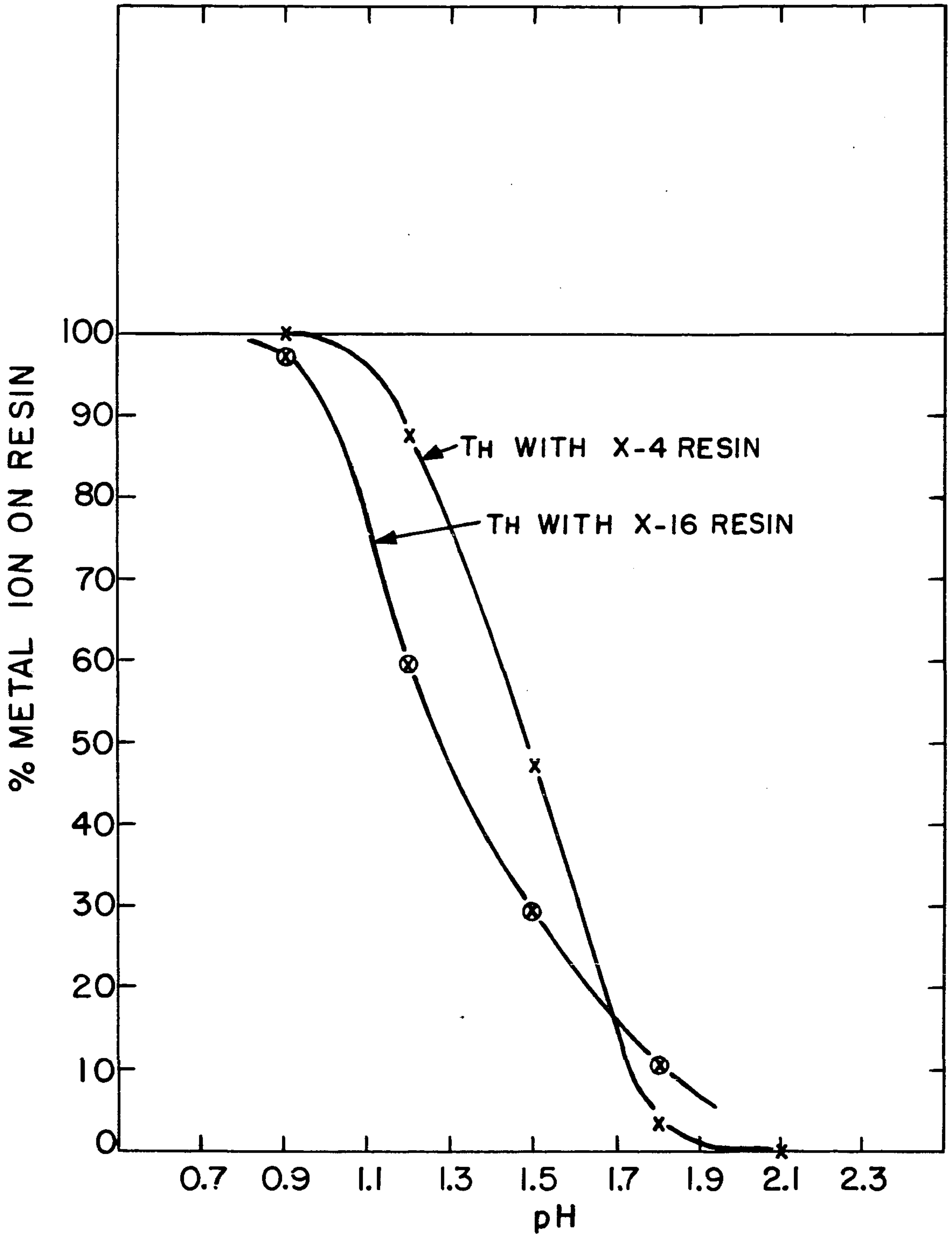


Figure 7. Effect of resin crosslinkage

available in the solution from the partial dissociation of the EDTA complexes, but also contributes to the breaking-up of these complexes. For this action to be significant, the complex itself must diffuse into the interior of the resin particles. If the resin pores restrict this diffusion, it will be necessary to supply more free metal ions by use of greater acid concentrations in order to attain the same distribution with X16 resin as was attained with X4 resin. Because of this, the upper portion of the curve obtained with X16 resin is shifted toward lower pH values.

Similar reasoning explains the tailing-out of the curve for the X16 resin at higher pH values. If the thorium-EDTA complex is once dissociated and the thorium adsorbed by the resin, the rinsing solution components must diffuse into the reactive sites of the resin in order to displace the thorium ions from the column. Because the EDTA in the rinsing solution is mainly responsible for this movement of the thorium ions, and because it is a relatively large molecule, this action is hindered, and the curve tails out toward higher pH values. Figure 7 illustrates these effects.

Effect of flow rate

Increasing the rate of flow of the sample through the column to approximately twice the normal rate has an effect which appears similar to that of increasing the crosslinkage of the resin used. A comparison of Figure 8 with Figure 7 clearly shows this. That the effect should be similar follows from an examination of the variations in the system which are introduced by the increase in flow rate.

Table 8. Effect of flow rate

pH	Per cent samarium on resin Flow rate 8-11 ml./min. (standard)	Flow rate 22-26 ml./min.
1.97	---	100.0
2.1	100.0	---
2.15	---	92.0
2.4	75.5	---
2.43	---	56.0
2.7	42.3	---
2.78	---	39.7
3.0	13.9	---
3.3	0.1	---
4.0	---	0.0

When the sample passes through the column at a faster rate there is less contact time between resin and sample. To attain the same distribution of metal ion between resin and solution as with the slower flow rate, the metal-EDTA complex must be dissociated to a greater extent by pH control before the sample is passed through the column. Thus, a lower pH value is required. The effect of the resin on the complex is reduced, since the greater rate of flow introduces stream-lines in the column and the sample

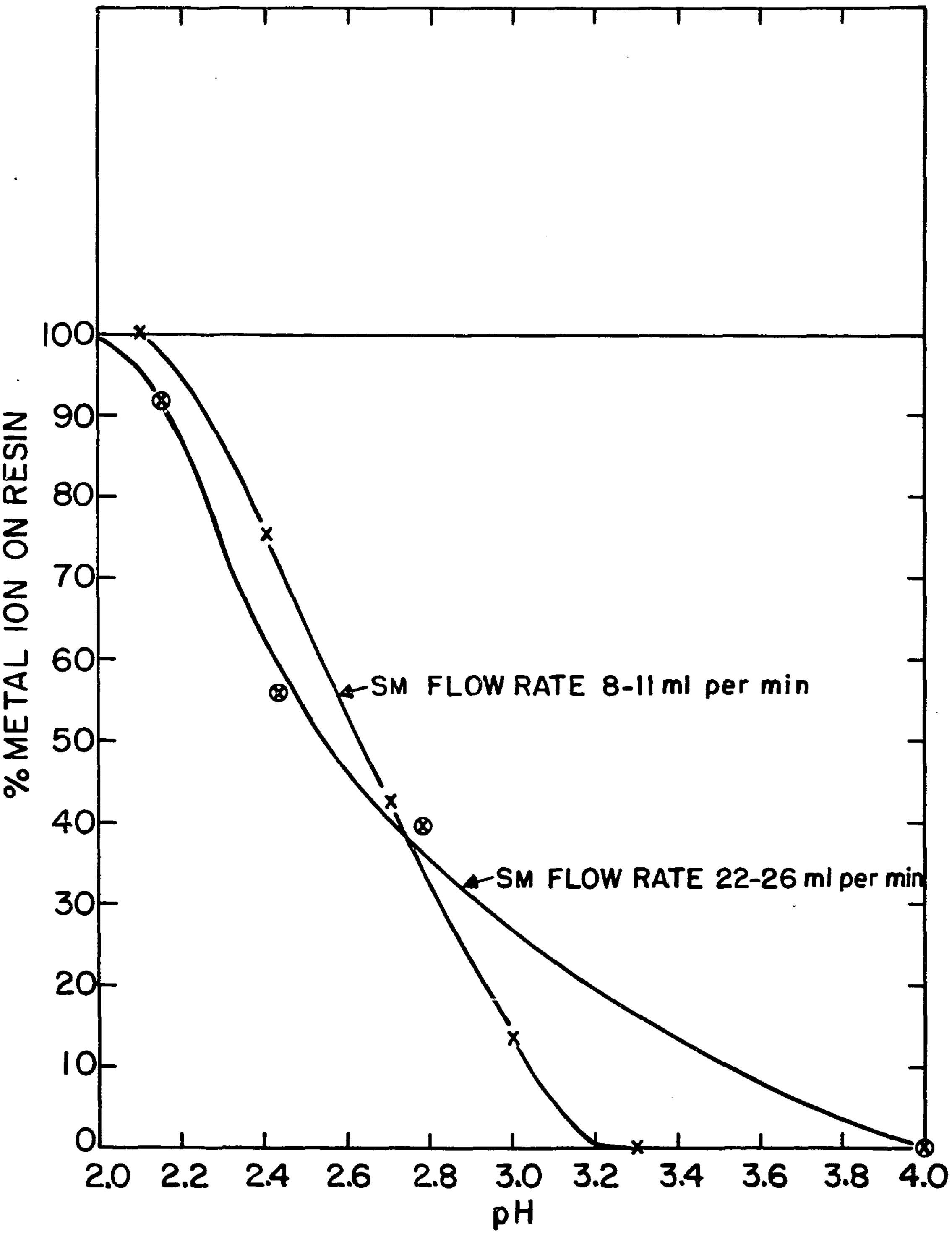


Figure 8. Effect of flow rate

constituents tend to follow these lines rather than diffuse into the resin pores.

The curve tails out at higher pH values for similar reasons. Because small amounts of the metal ion are inevitably adsorbed by the resin, they must be re-eluted down the column by the rinsing solution. For this to occur requires again that the components of the rinsing solution diffuse into the resin pores. Under conditions of this faster flow rate, this diffusion is decreased, and the pH must be raised to enhance the complexing effect of the EDTA to permit as little dissociation of the complex as possible. Table 8 summarizes the data illustrated by Figure 8. No significant change from the standard curves was noted by decreasing the rate of flow.

Effect of concentration

The behavior of samples which were considerably less concentrated in metal ions was of importance to demonstrate the possibilities of separating sample mixtures where one component is present in minor amounts. The net result of this is to increase the resin to metal ratio. It follows that the pH *versus* retention curves should move uniformly toward higher pH values due to the enhancement of the metal-resin reaction by the mass effect.

One series of samples was prepared using 10 ml. aliquots of 0.005 *M* yttrium solution and adding 15 ml. of 0.005 *M* EDTA solution to each while maintaining other factors constant. The decrease in concentration of the EDTA added to the sample was necessitated by the fact that at some of the pH values used in the investigation the more concentrated EDTA solution precipitated rather heavily. The net effect of this decreasing of the sample concentration by a factor of 10 was to move the entire curve approximately 0.12 units toward higher pH values. This is shown in Figure 9.

Table 9. Effect of concentration

pH	Per cent yttrium on column		
	0.05 M sample (standard)	0.005 M sample	1 x 10^{-4} M sample
1.5	100.0	---	---
1.8	94.6	100.0	100.0
2.1	60.2	82.5	90.6
2.4	10.0	25.8	55.7
2.7	2.4	6.3	---
3.0	0.0	0.8	---

A second series of samples was prepared using 10 ml. aliquots of a 1 x 10^{-4} M yttrium solution. The amount of EDTA added to the samples was the same as in the case of the 0.005 M samples. The analyses were made colorimetrically by the method of Fritz, Lane and Richard (22). As expected, the curve was displaced further toward higher pH values. This is also shown in Figure 9.

Some of the difficulties encountered in the spectro-

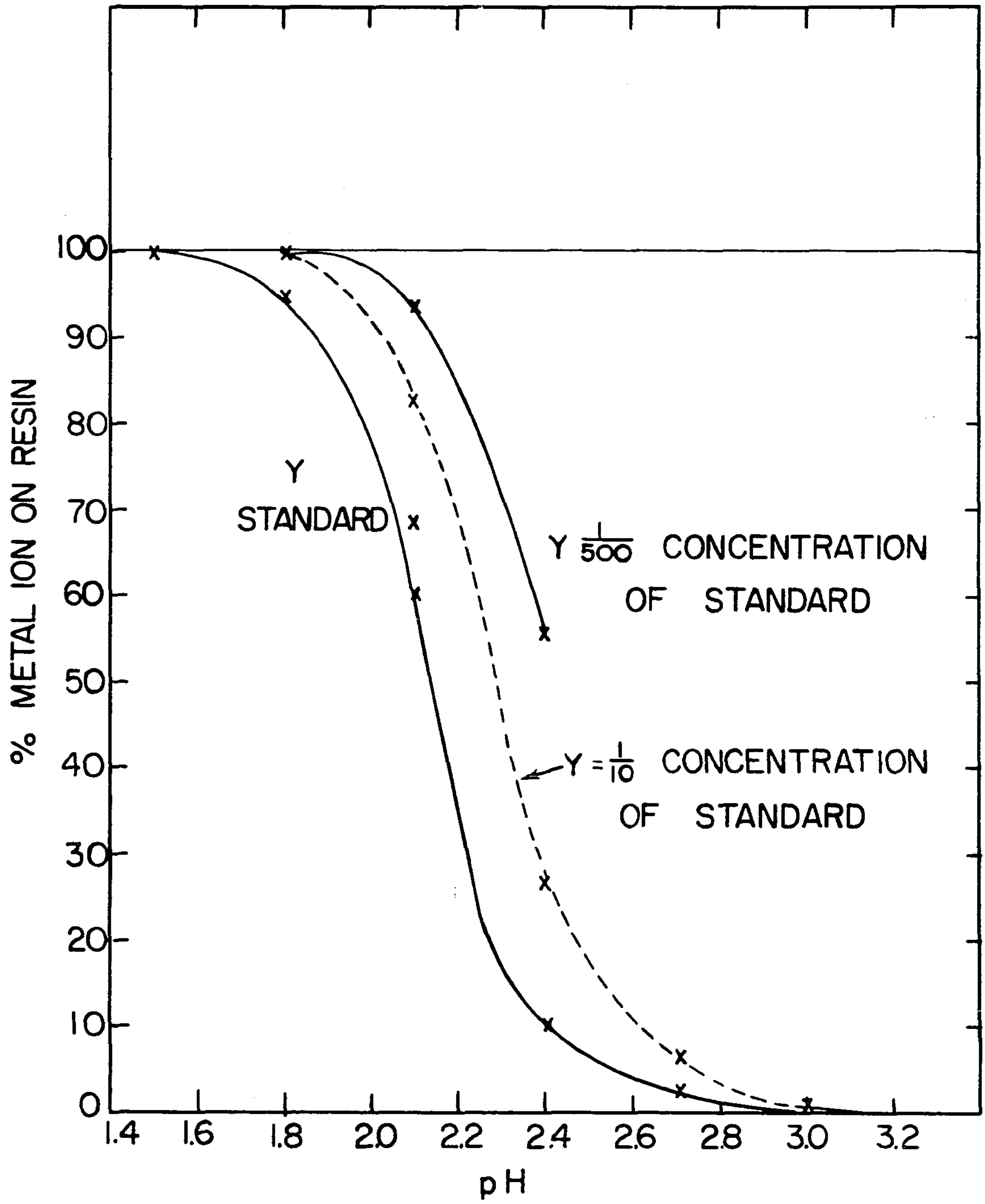


Figure 9. Effect of concentration

photometric measurements should be noted here. A method of colorimetric analysis for rare earths and yttrium is described by Rinehart (66) using alizarin red S as the color-forming reagent. A satisfactory Beer's law plot was not obtained in attempts to reproduce Rinehart's data, and the method was dropped in favor of the method of Fritz et al. When this method was applied to analysis of the fractions of the sample which were unaffected by the resin, very erratic results were obtained. No satisfactory explanation for this has been found, but certain factors must be considered as contributing to the erratic results. Among these are the high concentration of acid in the sample as a result of the fuming operation, and the fact that the method of analysis is sensitive to several other metal ions which may be introduced, as trace contaminants, with the reagents used in the ion exchange process. Trace contaminants become significant at the sample concentrations used here.

As a result of this, the entire set of samples was repeated, but the fraction of the sample retained by the resin was eluted and analyzed. This was done with the expectation that fewer contaminants would be present in this fraction of the sample, and that a smaller amount of acid would result in the final fraction used for analysis. This was found to be the case, though even here a blank correction had to be made. This was done by analyzing a sample run at a pH where 100 per cent of the yttrium should be retained by the column. The measurement of the absorbance was taken to represent 100 per cent of the sample, as determined from the Beer's law plot, and the absorbance in excess of this amount was taken as the blank. This value was subtracted from the subsequent measurements on other samples. The data in Table 9 and Figure 9 represent the values obtained in this manner.

DISCUSSION

Because no research project goes as smoothly as it appears on paper, some of the difficulties that have been encountered during the course of this investigation should be mentioned. The difficulties that were noted in the previous section concerning the spectrophotometric determination of yttrium are pertinent to another aspect of this work.

The separation of yttrium from iron was attempted using an iron to yttrium ratio of 1000:1. The resulting analyses on these samples showed such a high blank that the data was questionable. It is firmly believed that this separation can be accomplished, but the method of analysis for the yttrium fraction of the samples would have to be chosen to be less susceptible to interferences of other metals, particularly calcium and magnesium, which are believed to be the chief contaminants encountered in this system.

The use of radioactive tracers is one approach that would appear to be useful. This was the method used by Gordon et al. (27) to follow the concentration of microgram amounts of rare earths in thorium. Banks and Klingman (4), and Banks, Spooner and O'Laughlin (5) have described spectrophotometric methods for the analysis of rare earths using the ionic absorbance of the simple rare earth ions. These methods are quite selective and would be applicable in many cases, but they require samples of considerably greater concentration than the normal colorimetric levels.

It would have been very desirable to have demonstrated the separation of trace amounts of rare earths from thorium by this method. Most of the procedures available in the literature for accomplishing this separation are extremely tedious in execution. The procedure of Carron et al. (11) is a good illustration where several reprecipitations with close pH control are required. The work of Stine and Gordon (91) is another example of this. Radhakrishna (63) reports the separation of lanthanum and thorium, but gives no supporting data. Lerner and Petretic (46) accomplished the separation of the major amount of trace rare earths from thorium by an extraction of the nitrate solution with "pentaether". A check of the manufacturer (Union Carbide) of the "pentaether" shortly after the appearance of this paper brought the reply that production of this solvent had ceased and would not be resumed. An amperometric titration of thorium in the presence of rare earths is reported by Gordon and Stine (28), but the determination of the rare earths is not considered.

The separation of trace amounts of rare earths from thorium is not reported here, even though it was attempted and showed reasonable promise of success. The reasons for this lie in the fact that the experiments indicated that the reagent grade thorium nitrate commercially available was already contaminated with 200 to 300 ppm. of cerium alone. It could be assumed from this that significant amounts of other rare earths, particularly lanthanum, would also be present. Because the method of analysis was sensitive to all rare earths, the problem of analyzing synthetic samples with trace amounts of added rare earths was greatly complicated by blank corrections which were larger than the actual samples.

One difficulty encountered in this work which was very successfully overcome was the problem of maintaining the specified pH of the sample on passage through the column. The use of buffers as prescribed in the procedures solved this problem.

The first experiments on this method were carried out without any attempt at buffering other than to adjust the pH of the sample. The rinsing solution was water, containing a small amount of EDTA, adjusted to the same pH. The pH of the sample on passage through the column was increased by 1 to 3 units. Later, the resin was pre-equilibrated to the pH of the sample by a batchwise process before pouring it into the column. Other conditions were the same as above, but the pH still increased 0.5 to 1 unit. The substitution of hydrogen form resin for the sodium form was attempted, but here the high concentration of hydrogen ions in the interior of the resin was so great that nearly all the metal ions were adsorbed regardless of the initial pH of the sample. The procedures finally adopted, using buffers, have proven very successful for the purpose of this pH control.

This investigation has opened many avenues of further research which should prove quite interesting. An extension of the effects of the glycine buffer on some of the metals at pH values beyond the range covered here should be of interest. An investigation of the behavior of some of the metal ions such as aluminum and chromium, which are slow in forming complexes and likewise slow in dissociating, would be of value. The possible combinations of this method with the other types of ion exchange separations should permit the separation of many metal combinations that are very difficultly separable by other means. The extensions and variations of this method appear to be nearly unlimited when the number of complexing agents available is considered.

PART II. AN AUTOMATIC RECORDING TITRATOR

INTRODUCTION

The increasing need of modern industry for rapid, accurate and dependable methods of quality control, along with the increasing pace of research in recent times have made the instrumentation of analytical procedures a subject of prime interest. In-line instruments that not only record, but also are capable of controlling the composition of a plant stream are being used in ever increasing numbers. Of the standard analytical methods in use, potentiometric measurements are among the most readily adaptable to this type of instrumentation.

The amount of information obtainable from a complete potentiometric titration curve, and the speed with which an automatic titrator can perform the titration make these instruments extremely valuable as analytical tools. Robinson (67, p.447) says of potentiometric titrations:

> When performed manually so as to give a detailed plot versus reagent volume, the potentiometric titration is a tedious and time-consuming operation having two distinct disadvantages. For exploratory work involving unknown samples, the human tendency to accelerate the operation often results in plots lacking needed detail, whereas, for routine analytical operations, the method does not have the speed and simplicity of comparable procedures employing visual indicators. Accordingly, many of the modifications and improvements in potentiometric technic have been directed toward the development of electrode systems or end-point detection devices which reduce or eliminate the need for plotting, enhance the ease and precision of end-point detection, and generally increase the speed with which the titration can be performed.

In general, there are two types of automatic titrators that are described in the literature or are available from commercial sources. These can be classified as recording instruments or end-point sensing devices. The designation as a recording instrument is restricted for purposes of this discussion to the type of instrument that records the entire titration curve as it would normally be determined by manual methods. End-point sensing devices are instruments that control a valve or stopcock on a titrant reservoir either by reacting when a pre-set end-point potential is reached, or by reacting to the sharp change in potential which is encountered at the end-point.

For general applications, the recording type of instrument requires automatic performance of several functions. It must incorporate a potentiometric recorder which may also be equipped with certain warning or controlling devices, and is generally equipped with a motor-driven strip chart on which the titration curve is recorded. An amplifier must be included in addition to that which is normally a part of the recorder to prevent loading of the electrode circuit by the recorder. Means must also be provided to deliver the titrant and to correlate the titrant delivery with chart spacing. A commercial instrument that fulfills these requirements is manufactured by the Precision Scientific Company (61, 62). This instrument is based primarily on the specifications of a similar titrator described by Robinson (67) and patented by Robinson and Briggs (68). Other instruments of this type for general applications are described by Duggan and Stevens (14), by Kordatzki and Wulff (39) and Neilands and Cannon (58). Lingane (48, 49) described an instrument which is applicable to all types of potentiometric titrations except where the use of the glass electrode is involved. Eades et al. (16) describe an instrument that records the results of up to 225 samples consecutively by means of an automatic sample changer.

Several instruments of this type are reported that have been designed for specialized applications (1, 15, 98-100). In general, these instruments have been designed for remote operations with radioactive systems, or for analytical control applications where only one component of the system is analyzed.

Some of the earlier attempts at instrumentation of this type are rather interesting. Kordatzki and Wulff (39) described such an instrument in 1932. In principle, its operation was as follows: Titrant is forced into the sample slowly but continuously by means of a falling steel cylinder which successively displaces mercury, paraffin oil and titrant. The potential change is continuously recorded on a chart whose travel is proportioned to the volume of titrant delivered by having the falling cylinder drive the chart drum. Several excellent titration curves plotted by this instrument were reproduced in the paper. Still earlier, in 1922, Keeler (36) described an instrument that was designed to control the composition of a plant stream. The functions of the instrument were the same as the titrators described above, but it was so regulated that when the potential of the system being measured drifted beyond pre-set limits, the instrument opened a valve on a reservoir of acid. The instrument functioned well as a titrator when a suitable method of titrant delivery was used. Here also, several very good titration curves were reproduced in the paper. Hydrogen electrodes were used for measurements of acidity in both cases cited above, and elaborate amplifying systems such as are needed with the glass electrode, were not required.

The end-point sensing device is not generally designed to transmit a voltage signal which will permit the recording of the normal titration curve. This type of instrument is more specifically adapted to the routine type of work generally encountered in a control laboratory. Here the equivalence of titrant with sample is of prime importance, rather than the shape of the titration curve itself. Many of these instruments are equipped to drive recorders, but these are mainly for industrial purposes where the recorder also acts as a controller and operates other equipment whenever the potential of the system being measured drifts beyond pre-set limits. The principal requirement in this type of instrument is a method of stopping delivery of titrant from a reservoir at the exact end-point of the titration. There are two methods of accomplishing this which are inherently based on the electronic circuitry of the instrument

The circuit can be designed to trigger a relay when the input signal from the electrodes reaches a certain predetermined value. This requires a pre-setting of the instrument to respond to the end-point potential before the titration is attempted. Among commercially available instruments, the Beckman titrator is an example of this type. Others are described in the literature by several authors (12, 29, 56, 60, 71, 73, 92). Several of these authors describe instruments for highly-specialized applications, but all require this pre-setting of the end-point potential. Lingane (48, 49) described the alteration of a recording titrator to permit its use as an end-point sensing device of this type.

The circuitry may also be designed to react to the rapid change in potential produced at the end-point of the titration. The derivative circuit designed by Malmstadt (51) and adapted for several analytical applications (52-54) functions by computing the second-derivative voltage of the ordinary potentiometric curve. This triggers a relay system that stops delivery of titrant from the buret. An instrument adapted from Malmstadt's circuit is commercially available as the Sargent-Malmstadt Titrator. This instrument is equipped to drive a recording potentiometer for the purpose of recording the derivative curve.

These two basic types of instrument can be adapted for several other analytical measurements with slight alterations. Automatic photometric titrations are reported by several authors (31, 55, 72). Linde *et al.* (47) describe an apparatus for automatic thermometric titrations. Juliard and Van Cakenberghe (32) describe an instrument for automatically performing conductometric titrations. In all these cases the instrumentation required is the same as described for the recording titrator. The only difference being that the signal for operation of the instrument is obtained from sources other than the electrodes used for potentiometric titrations.

One of the most important components of any automatic titrator is a titrant delivery system. In conjunction with end-point sensing devices, this delivery system requires that the total volume used for the titration be measurable, and that the flow of titrant be accurately stopped at the end point. The rate of titrant feed should be regulated sufficiently that numerous false end-points are not obtained before the true end-point is reached. In general end-point sensing devices permit relatively rapid titrant flow for the major part of the titration. Titrant delivery systems suitable for these purposes are described by Audran and Dighton (3) and by Blaedel and Malmstadt (9) in addition to those described by some of the authors listed in the previous paragraphs.

The recording titrator requires rigid correlation of titrant delivery with chart spacing. In general, the chart is driven by a synchronous motor which moves the chart at a uniform rate. The simplest means of correlating chart spacing with titrant volume would then be the use of a constant-flow buret which is actuated by the same switch that controls the recorder chart motor. Of the several methods of accomplishing this uniform rate of delivery, two appear to be the most important.

The first of these is the constant-head buret. Burets of this type are described by Barredo and Taylor (6) and by Shapiro and Brannock (72). They are all based on variations of the familiar Marriotte bottle classically used in carbon-hydrogen determinations. The use of a calibrated orifice in conjunction with this constant-head titrant delivery system is described by Eades et al. (16). This type of titrant delivery system has not been too widely accepted because the accuracy of the system is generally inferior to that obtained by motor-driven syringe burets.

The most satisfactory method of obtaining constant titrant delivery is by means of a motor-driven syringe. The use of a well-made syringe driven by a synchronous motor virtually assures uniform delivery (32, 48, 67).

Allen (2) however, feels that imperfections in the barrel or piston of the syringe might introduce irregularities. He suggests a precision-ground glass rod driven through a gasket into an oversize barrel as an alternative.

The basic construction of a titrant delivery system of this type is quite simple. A threaded shaft is turned by a motor through a gear train or a belt and pulley system. The threaded shaft, in turn, drives a movable threaded block which pushes the piston of the syringe. A cam-driven syringe has also been described (55). The inclusion of a revolution counter on the motor or gear system adapts these systems ideally for use with an end-point sensing instrument (33, 48, 49).

One of the problems of automatic titrations is the finite rate of attainment of equilibrium near the end-point. With some end-point sensing devices this results in over-titrating the sample by 0.1 to 0.3 ml. (29, 73) If the titrant is standardized instrumentally rather than manually, this difficulty is avoided.

A method of slowing the rate of titrant delivery near the end-point while maintaining the titrant volume to chart spacing correlation is a desirable feature of some of the recording instruments. This is accomplished by two different approaches. Lingane (48) and Neilands and Cannon (58) use a clutch and gear shift system for changing the rate of titrant delivery. The gear train driving the chart is shifted simultaneously, and the volume to spacing ratio is maintained. Duggan and Stevens (14) accomplish this change in rate similarly, by use of two synchronous motors of different speeds incorporated in the syringe drive. The second method is described by Robinson (67) who uses a Selsyn motor-generator combination on the buret drive, and a Selsyn motor actuated by the generator for the chart drive. The recorder is equipped with an unbalance detector that stops delivery of titrant whenever the balancing potentiometer is more than 5 mv. behind the input signal. A brake is provided on the buret driving motor-generator combination to prevent motion when the power is turned off by the unbalance detector. This method is more complicated mechanically and electrically, but appears to be superior in operation.

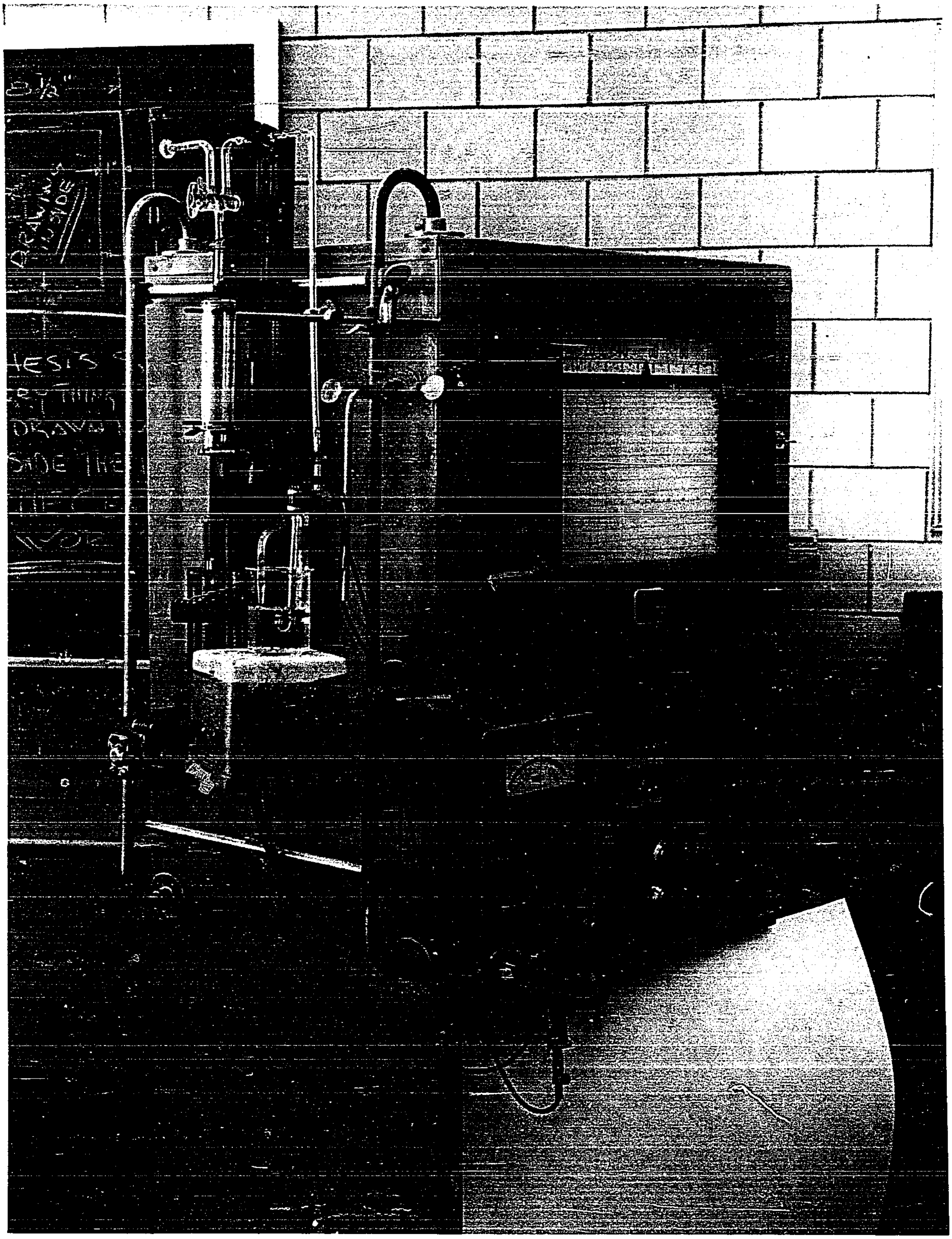
The instrument to be described in this thesis is of the recording type as defined earlier. It represents an attempt to provide this type of instrumentation with maximum flexibility in application at minimum cost. It is also designed to exemplify simplicity of construction such that it could be reconstructed by the average analytical chemist who has only a brief acquaintance with electronic circuitry.

DESCRIPTION OF THE INSTRUMENT

The instrument that has been constructed incorporates several component parts. These are an amplifier, a strip-chart recording potentiometer, a constant-flow syringe-type buret, a range and zero adjusting circuit which is self-contained, and a control circuit containing all the operating switches which is also self-contained. For the amplifying and recording functions, commercially available instruments are used. The complete instrument is pictured in Figure 10.

The amplifier is a Kay Lab model 202B microvoltmeter and amplifier. The manufacturer of this instrument has been succeeded by Kintel Laboratories, Inc. (38). This instrument was chosen primarily for its excellent adaptability for the purposes of the titrator, and secondarily for its flexibility for other uses. It has 14 voltage ranges from 300 microvolts to 1000 volts. The meter registers positive or negative values for any range so that the input signal leads do not need to be reversed. The amplifier output is 1 volt for full-scale deflection of the meter on any range. The stability and accuracy exceed the specifications of other instruments of the same type that were investigated (24, 25, 37). The input impedance for all ranges from 300 mv. to 1000 volts is 100 megohms. This is satisfactory for all electrode systems in common use except

Figure 10. Complete instrument



the glass electrode. The impedance of the glass electrode varies from 18 to 200 megohms (7, p.251) depending on the type used. It is felt that the glass electrode system is not overloaded by using this meter, but the voltage values registered are only proportional to the actual voltage of the electrode system. The use of electrode systems requiring the glass electrode is permitted by proper compensation of this proportionality in the range and zero adjusting circuits.

The recorder is a Bristol Model 560 wide-strip Dynamaster D-C potentiometer and D-C bridge. The choice of this recorder is somewhat arbitrary because there are several other commercially available instruments of this type that can meet the required specifications. The recorder has a 12 inch chart width of which 11 inches is calibrated from 0 to 100. The chart speed can be changed by interchange of gears to any of 7 speeds from 3/8 to 4 1/2 inches per minute. Full-scale deflection of the pen requires 1 second. The recorder has a fixed range of 10 mv. These specifications provide a recorder with great flexibility in application.

Some alterations have been made on the recorder to adapt it for these purposes without limiting its possible adaptations for other purposes. These alterations are noted in Figures 11 and 13. The internally-supplied power for the chart motor has been disconnected and power supplied to this unit from the control circuit. This is required

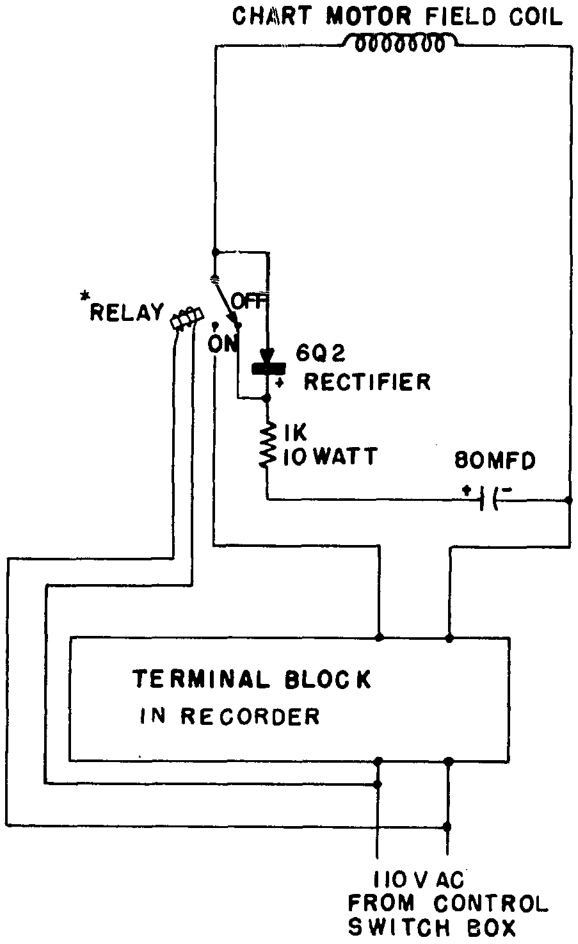


Figure 11. Electronic brake

*POTTER+ BRUMFIELD DPDT RELAY

to permit the synchronization of chart spacing with titrant delivery. An electronic braking circuit has also been added to the chart motor. The connections for this system are taken at the same terminal block in the instrument that was altered for the chart motor power supply. This circuit is easily placed inside most recorders. In this case it is inside the recorder door mounted on a plate behind the chart motor. This brake serves to stop the chart instantaneously whenever the power is turned off. It prevents backlash in the motor and gear train driving the chart, and maintains the volume to spacing ratio when the buret is turned off during the course of the titration. It functions by charging the large condenser while the instrument is in operation, and discharging this condenser through one of the field coils of the motor when the power is turned off. The D-C current produced momentarily stops the rotating armature within a quarter-turn or less.

The range and zero adjusting circuits provide for proper placement of the titration curve on the chart, and permit the recorded curve to cover the major portion of the chart width. The details of this circuit are illustrated in Figure 12. The range selecting portion of this circuit is essentially a voltage-dividing system that uses the amplifier output. The resistors are of the 0.1% precision wire-wound type. The actual values are chosen to correspond to

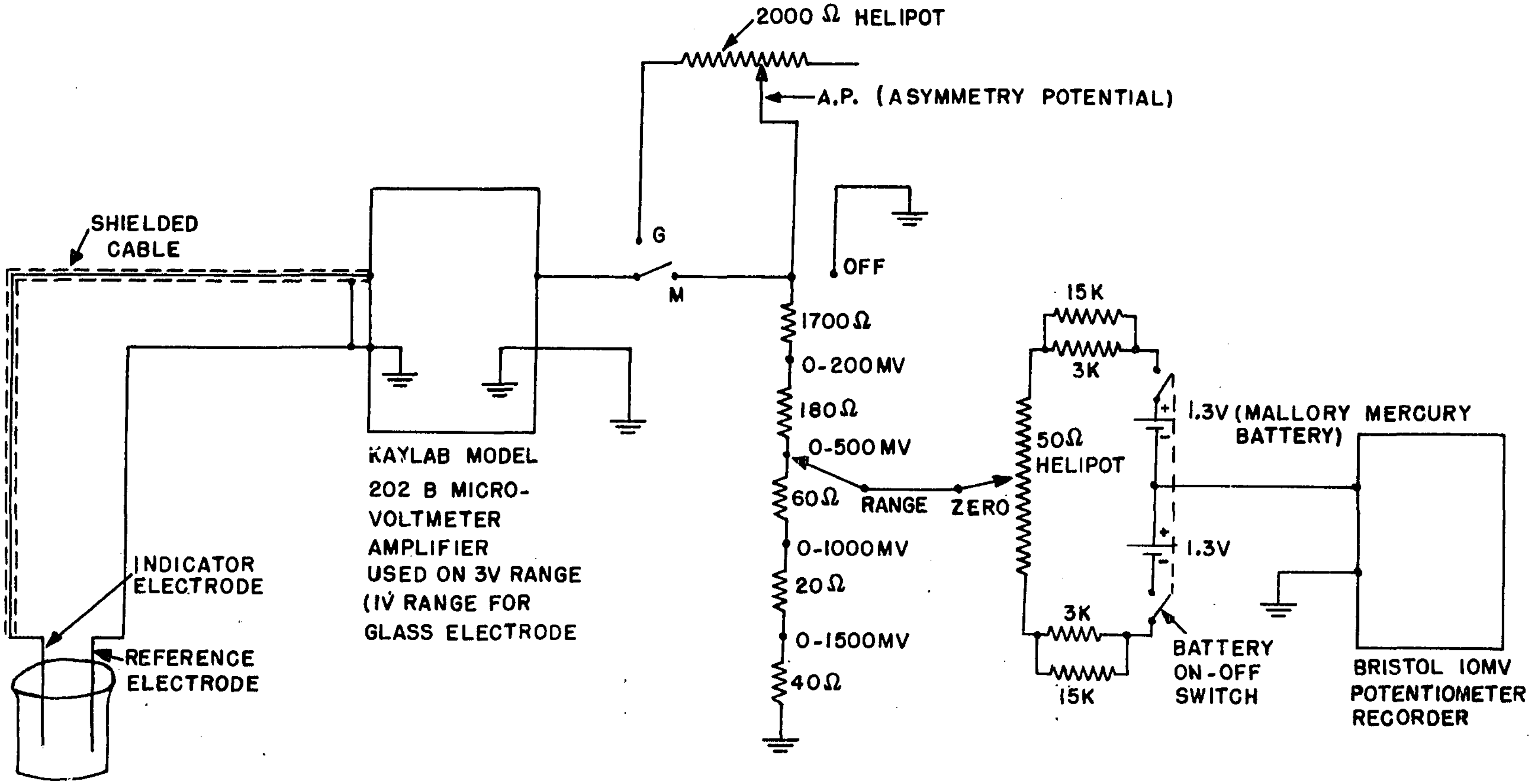
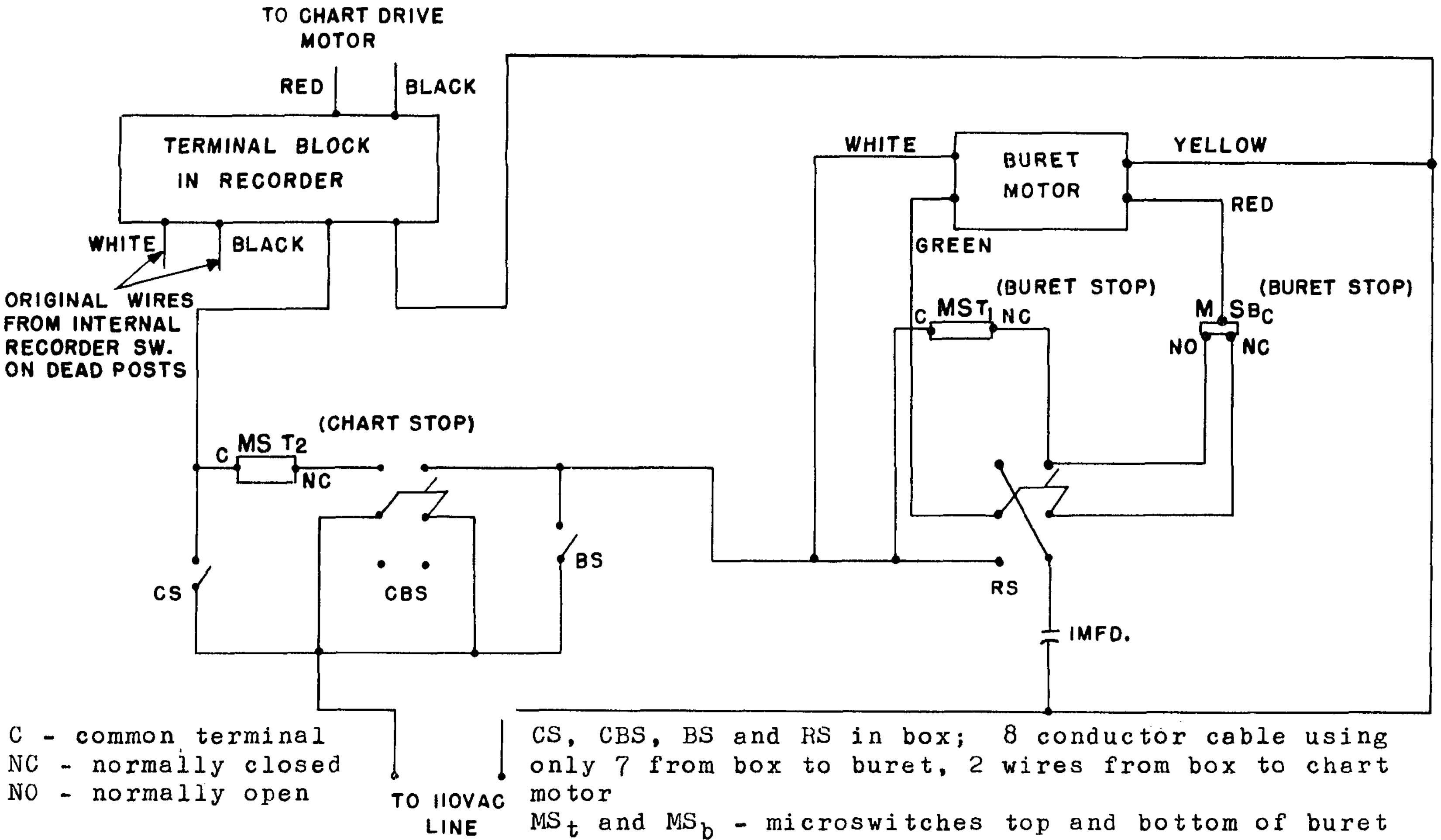


Figure 12. Range and zero adjusting circuit with complete signal circuit

the known amplifier output. The switch designated as G-M is used in the M position in all cases where the glass electrode is not required. The G position permits use of electrode systems requiring the glass electrode. The zero and asymmetry potential adjustments are used to standardize the instrument with standard buffer solutions in the same manner as with an ordinary pH meter. The details of standardizing will be discussed in a later section. The zero adjusting circuit is designed to permit the placement of the zero potential of the titration anywhere on the full chart width, or in the case of a titration in which the total range of the curve is above or below zero, the zero position can be set up to an equivalent of 1.25 chart widths beyond either limit of the calibrated portion of the chart.

The control circuit provides switching arrangements for independent or simultaneous operation of the chart and buret, and for reversing the buret for re-filling with titrant. The control circuit also contains provisions for limiting the forward and reverse travel of the buret to prevent breakage and to stop the chart at the upper limit of travel. These provisions are accomplished by the placement of microswitches at the top and bottom of the channel through which the threaded block moves. They are placed as shown in Figure 14, and included in the circuit shown in Figure 13. The upper microswitches are on a movable mount so that they can be pre-set to stop the instrument



C - common terminal
NC - normally closed
NO - normally open

CS - chart only on-off
BS - buret only on-off
RS - buret motor reversing switch

CS, CBS, BS and RS in box; 8 conductor cable using only 7 from box to buret, 2 wires from box to chart motor

MS_t and MS_b - microswitches top and bottom of buret frame

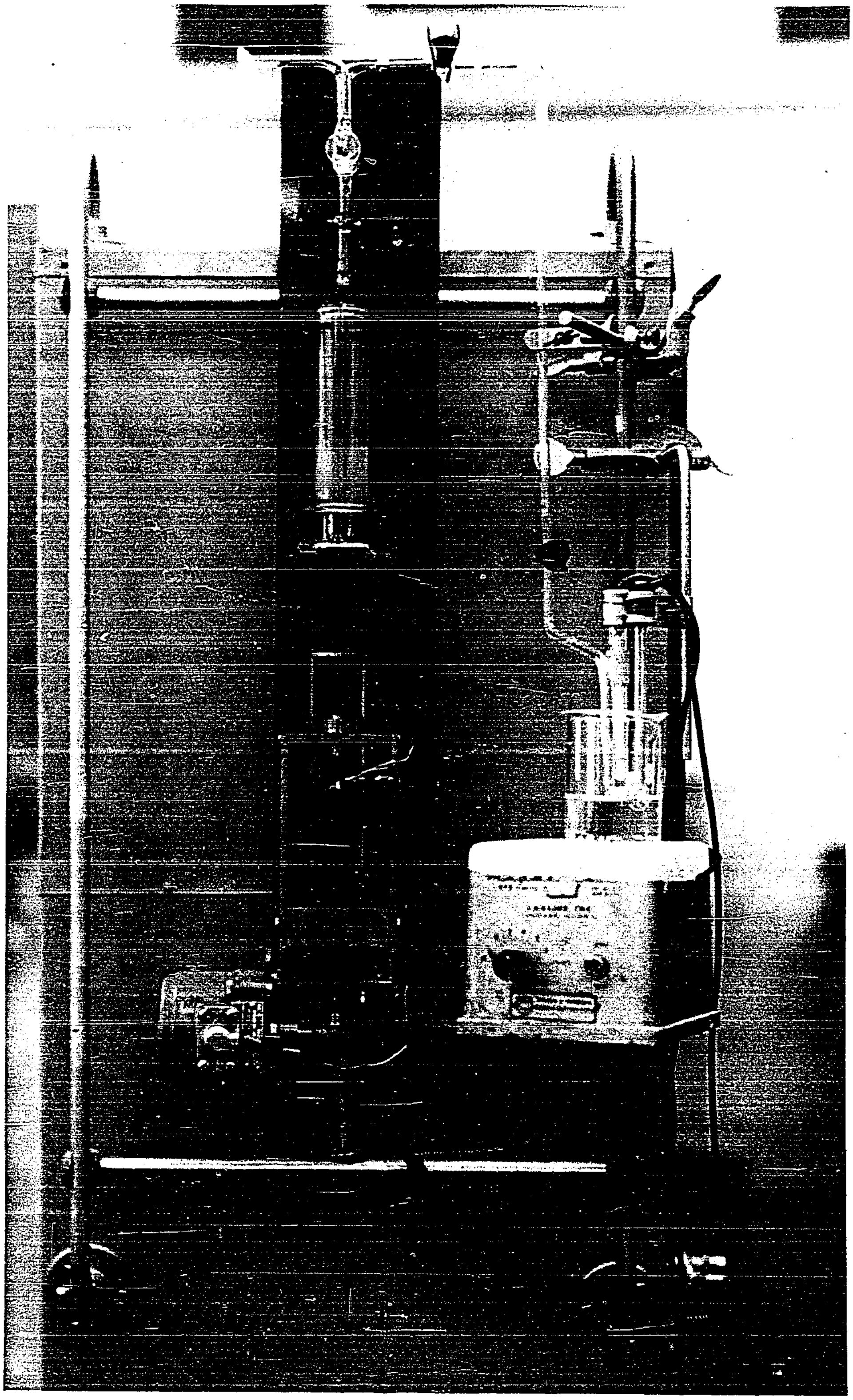
CBS - chart and buret on-off

Figure 13. Control circuit

when a desired volume of titrant has been delivered without wasting chart or titrant. The microswitch that controls the chart is set to trigger shortly before the buret-controlling microswitch because the buret movement operates both switches.

Figure 14 shows the syringe drive mechanism. The buret is a 50 ml. Luer syringe which is available from all laboratory suppliers. It is fitted with a ground-glass ball joint which is secured to the tip of the syringe with a small ground-glass joint and sealed with Dekhotinsky cement. A 3-way stopcock fitted with ground-glass sockets at all 3 positions fits the ball joint on the syringe. This permits filling the buret or delivery of titrant by turning the stopcock to the proper position. 1 mm. glass tubing is used to direct titrant into the sample beaker. 12/1 standard ground-glass ball and socket joints are used to keep the parts required for this purpose small enough for structural rigidity. The syringe piston is driven into the barrel in the following manner: A Brown 60 rpm. reversible synchronous motor fitted with a worm gear drives a shaft with 40 threads per inch by means of a 100-tooth spiral gear fixed to the bottom of the shaft. The worm gear passes 4 teeth of the spiral gear with every revolution of the motor. The shaft, in turn, drives a threaded block through the guiding channels. A disc fixed to this block by two rods pushes on the syringe piston. This arrangement provides a titrant delivery rate of approximately 1 ml. per minute.

The description of this instrument is intended to be a guide for construction of a similar instrument. Any number of variations may be adopted to suit the needs of a particular application. This instrument is designed primarily to carry out titrations requiring 5 to 20 ml. of titrant. The recorder chart speeds are chosen to provide a titration curve using about 10 inches of the chart length as compared to the 11 inch chart width. For these purposes the 1/2 or 1 inch per minute chart speeds are normally used. If other titrant delivery rates are desired, the specifications of the chart speed ranges on the recorder should be chosen to correspond to the titrant delivery rate so that the recorded curves are not greatly distorted in either dimension.



is done by placing the electrodes first in the sample solution, and noting the potential of the starting point of the titration on the voltmeter, using the appropriate range. The final potential to be encountered is then determined by placing the electrodes in an equivalent blank solution containing a small amount of the titrant, and noting the potential on the voltmeter as before. This fixes the potential range to be covered, and the position of the zero-potential point of the titration. The ranges available for use on the machine are 200, 500, 1000 and 1500 mv. The next larger range to the actual range of the titration must be chosen for the curve to be recorded in total on the chart. If the potential range of the titration encompasses the point of zero potential, the pen is moved to the appropriate position on the scale by use of the zero adjusting potentiometer, noting that the 0 to 100 calibration on the front of the recorder will represent the range to be chosen (e.g. If the range to be used is 1000 mv., each major division on the scale will represent 100 mv.). The stopcock above the syringe is turned to the delivery side, and slack in the buret driving mechanism is taken up by running it for a moment and wiping the delivery tip dry. The sample is then placed so that the electrodes and the buret delivery tip project below the surface of the sample solution. The recorder pen is released so that it rests on the chart, and the chart is turned manually until one of the calibration lines is directly under the point of the pen. The range switch is then turned to the desired range designation, and the buret and chart are started simultaneously by turning the chart and buret on-off switch (CBS) to the on position. When the titration is complete, the switch is turned off.

When the potential range of the titration is all above or below the point of zero potential, the zero adjustment is not made until after the range switch is turned to the appropriate position. At this point, the recorder pen will move rapidly to the upper or lower limit of its travel. It is brought back on scale as quickly as possible with the zero adjustment. The position to which the pen is brought will then represent the potential of the starting point. The pen should be positioned so that the remainder of the titration curve will fall on the calibrated portion of the chart. The titration then proceeds as before. In a few cases it will be necessary to reverse the electrode leads into the voltmeter in order for the pen to be positioned on the calibrated portion of the chart as described above. No titrations have been encountered where one or another of the procedures described does not permit recording of the total titration curve.

When the glass electrode is used, the voltmeter must be turned to the 1 volt range for the titration. If direct pH measurements are not required, the beginning and ending points of the titration are determined by use of the range switch and zero adjustment, and noting the pen position for the two points on each range. The range switch position that gives the greatest pen travel within the calibrated limits will be chosen, and the titration carried out as before. This will give an arbitrary potential range which is only proportional to the actual potential of the electrode system.

To record the titration curve in accurate pH terms, pH buffers must be used as with all pH meters. For this purpose, the voltmeter is used on the 1 volt range, and the G-M switch is turned to the G (glass electrode) position. Two buffer solutions are required, usually pH 4 and 7 or pH 7 and 9. If the total pH range of 0 to 14 is desired, the 1000 mv. range will be used. The asymmetry potential adjustment is turned to the limit so that the total resistance represented by the asymmetry potential potentiometer is in the circuit. The electrodes are immersed in the pH 7 buffer solution, and the range switch is turned to the 1000 mv. position. The pen is moved to give the desired placement of pH 7 with the zero adjustment. The range switch is then turned to the off position, and pH 4 or 9 buffer is substituted for the pH 7 buffer. The range switch is again turned to the 1000 mv. position, and the pen is moved to the desired placement of pH 4 or 9 with the asymmetry potential adjustment. When this has been accomplished, the sample can be titrated in the usual manner, and the pH of any point on the titration curve is accurately recorded. If lesser pH ranges are to be covered, the 500 or 200 mv. ranges can be used to permit the recorded curve to utilize most of the available chart width.

The electrodes should not be handled unless the range switch is in the off position. The extra procedures required for use of the glass electrode and the problem of the proportionality of actual to recorded voltages are easily eliminated by use of an electrometer-input voltmeter-amplifier in place of the Kay Lab voltmeter used here. This will be discussed in a later section. A Beckman 1190-80 blue label glass electrode has been used with this instrument, but a Leeds and Northrup electrode would be more satisfactory because the impedance is lower than that of the Beckman electrode. The ranges specified in the procedures for use of the glass electrode are correct when the Beckman electrode is used, but will change if the Leeds and Northrup electrode is substituted, and must be independently determined in that case.

APPLICATIONS

Figures 15 through 26 are reproductions of titration curves recorded on the titrator. A few points should be noted about these curves. Some of the detail is lost in the reproduction process that should be pointed out. The high-speed pen travel of the recorder results in the tracing of some of the extraneous signal that is inevitably present in all electronic systems. The level portions of the curves have varying degrees of waviness that are not reproduced. A rough comparison can be made to the appearance of a recorded polarogram before the half-wave potential is reached. This degree of waviness decreases as the range used is increased. The 1000 and 1500 mv. ranges give nearly smooth curves. As the range is decreased, the signal to noise ratio also decreases so that the greatest irregularity occurs with the 200 mv. range. No difficulty is encountered, however, in identifying a uniform curve. The break of the curve is always very neatly and smoothly defined. These irregularities in the tracing of the curve can be eliminated by using a recorder with a very slow pen speed, and incorporating the unbalance detector described by Robinson (67). This slow-speed pen does not respond to extraneous noise present in the signal, but a recorder of this type is very limited in other applications. The Precision Scientific Company instrument which incorporates this unbalance detecting system uses a recorder that requires 24 seconds for full-scale deflection of the pen.

Figure 15 illustrates standardization of the instrument so that the pH scale corresponds to the reduction potential scale using the glass electrode. The titrator was standardized using pH 4 and 7 buffers as described above, and checked with pH 9 buffer. The pen position with the pH 9 buffer was within 3 mv. of the theoretical -531 mv. that would be calculated on the basis of 59 mv. per pH unit. The correspondence of the inflections of the curve with pH for the titration of sodium carbonate with hydrochloric acid illustrates the reliability of pH measurements made in this manner.

Figure 16 shows an ordinary aqueous acid-base titration with an arbitrary potential scale. Methyl orange indicator was added to the sample, and the range of color change noted to show that the automatic titration gives essentially the same end-point as would be obtained by manual titration using an indicator. The non-symmetry of the curve indicates a slight over-sensing of the end point that illustrates still another point of interest in automatic titrations.

The factors involved in obtaining a normal potentiometric titration curve are the placement of the buret delivery tip in relation to the indicator electrode, the rate and direction of stirring, the rate of attainment of chemical equilibrium in the sample, and the rate at which the electrode detects the changes in the sample solution. The determination of whether the recording system is under-sensing or over-sensing the end-point can be accomplished by stopping titrant delivery abruptly in the end-point region of the titration. If the pen drifts back toward the starting potential, the end-point is being over-sensed, and the sample determination will be low. If the pen drifts in the other direction, the end-point is being under-sensed by the instrument, and results will be high. Slight drifting may be ignored, but drifting of an inch or more must be compensated. Three corrective measures are available. The buret delivery tip can be moved away from, or closer to the indicator electrode in terms of the direction of stirring to correct over-sensing or under-sensing, respectively. Stirring is generally maintained at a rate as fast as is permissable without loss of sample by spattering. Similar correction measures are obtained by interchanging the positions of the reference and indicator electrodes. A second method of compensating for these conditions is to slow titrant delivery in the region of the end-point. In the instrument described this is accomplished by stopping the buret drive and chart mechanism once or twice in this region. This is the primary purpose for installing the electronic brake on the chart motor. The third method of correcting these conditions is the use of a more, or less sensitive indicator electrode to compensate for under-sensing or over-sensing, respectively. This last method is illustrated in Figure 17 where the same acid-base titration has been carried out using an antimony electrode as the indicator electrode.

Figure 18 shows the titration of hydroxylamine in the presence of hydroxylamine hydrochloride and triethanolamine hydrochloride with hydrochloric acid. The solvent for both sample and titrant is isopropanol. The potential scale is arbitrary. This titration curve is included to illustrate the use of the instrument for non-aqueous acid-base titrations. This particular titration is one of the steps in the analysis of carbonyl compounds described by Yamamura (101).

One of the more familiar of oxidation-reduction titrations is reproduced in Figure 19, that of the titration of iron (II) with cerium (IV). The potential scale in this titration compares within 2 mv., at all points, with the same titration performed manually.

Figures 20 through 26 illustrate the application of the titrator to potentiometric complex-forming titrations. The use of various electrodes for this purpose is described by Siggia et al. (74). The theory and use of the mercury electrode for this purpose is described by Reilley et al. in a series of papers (30, 64, 65, 70). The mercury electrode has been employed in all the titrations illustrated in Figures 20 through 26.

Figures 20 and 21 demonstrate the proper use of the range switch to attain maximum use of the chart width. When mercury (II) is titrated with EDTA at pH 6 (Figure 20) the potential range of the titration is about 300 mv. Using the 500 mv. range, this titration utilizes approximately three-fifths of the chart width. If the titration is carried out at pH 4.6 (Figure 21), the range is slightly under 200 mv., but using the 200 mv. position of the range switch permits the recorded curve to utilize nearly the full width of the chart. It should be noted that the available ranges on the titrator have been very carefully chosen, and have proven very satisfactory in use.

Figure 22 showing the titration of zinc and Figures 23 through 26 showing titrations of thorium illustrate some of the many EDTA titrations that may be carried out automatically using the mercury electrode. The series of thorium titrations were carried out in conjunction with an investigation into the practical limits of dilution that could be attained while still providing a titration curve with an easily determined end point. In the series illustrated, the intersection of the extrapolation of the steepest portion of the break of the curve to the extension of the level portion of the curve before the end-point gives the same point of intersection for all of the titrations.

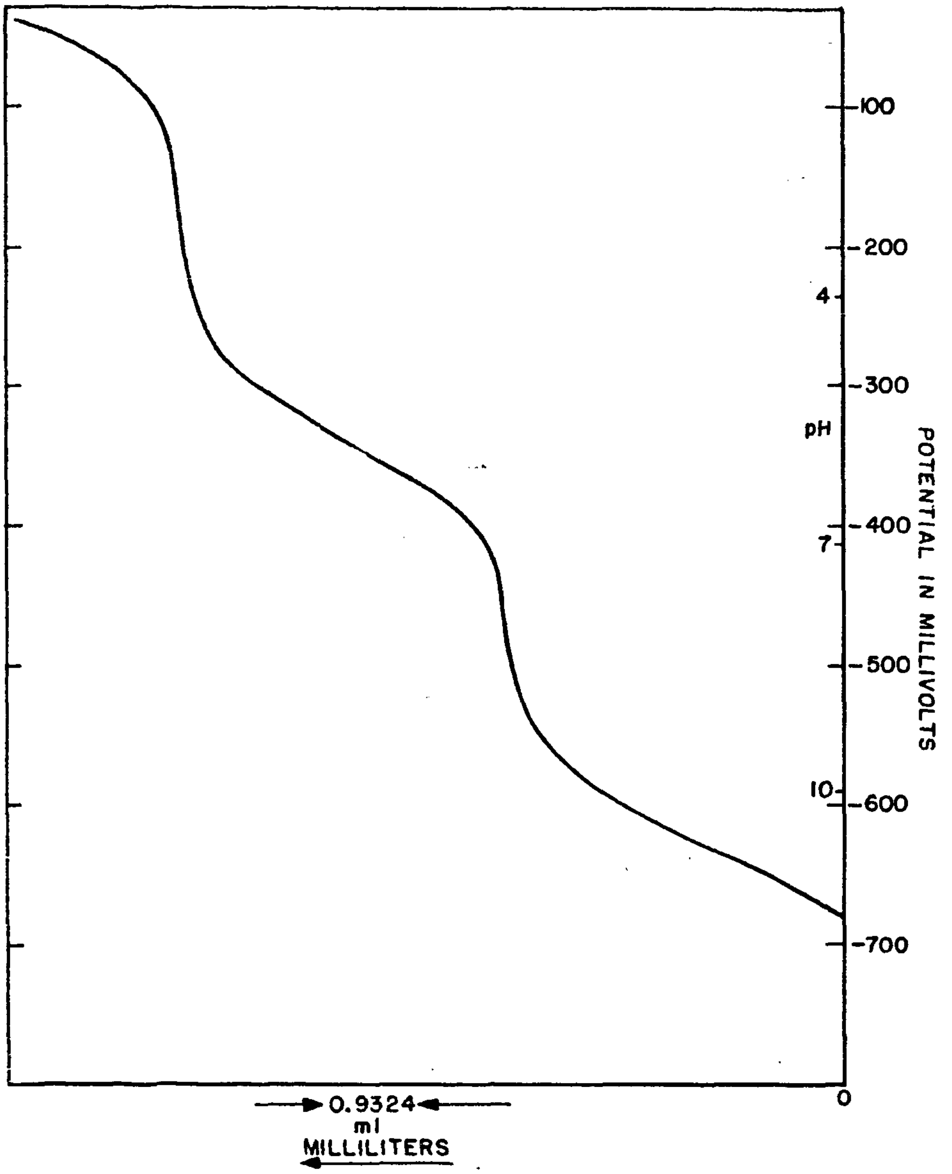


Figure 15. Titration of 0.05 M Na_2CO_3 with 0.1 M HCl
Glass-calomel electrode system
1000 mv. range correlated with pH scale

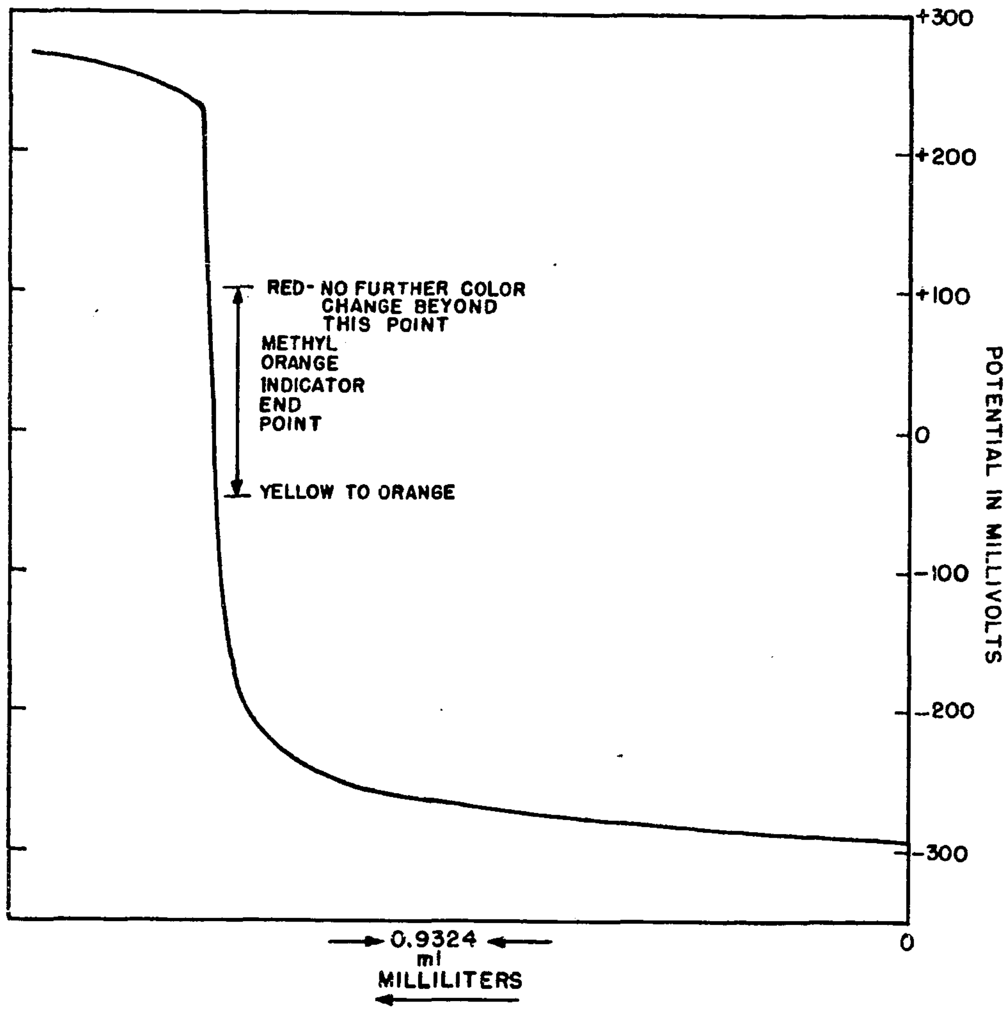


Figure 16. Titration of 0.1 M NaOH with 0.1 M HCl
Glass-calomel electrode system
1000 mv. range showing indicator end-point

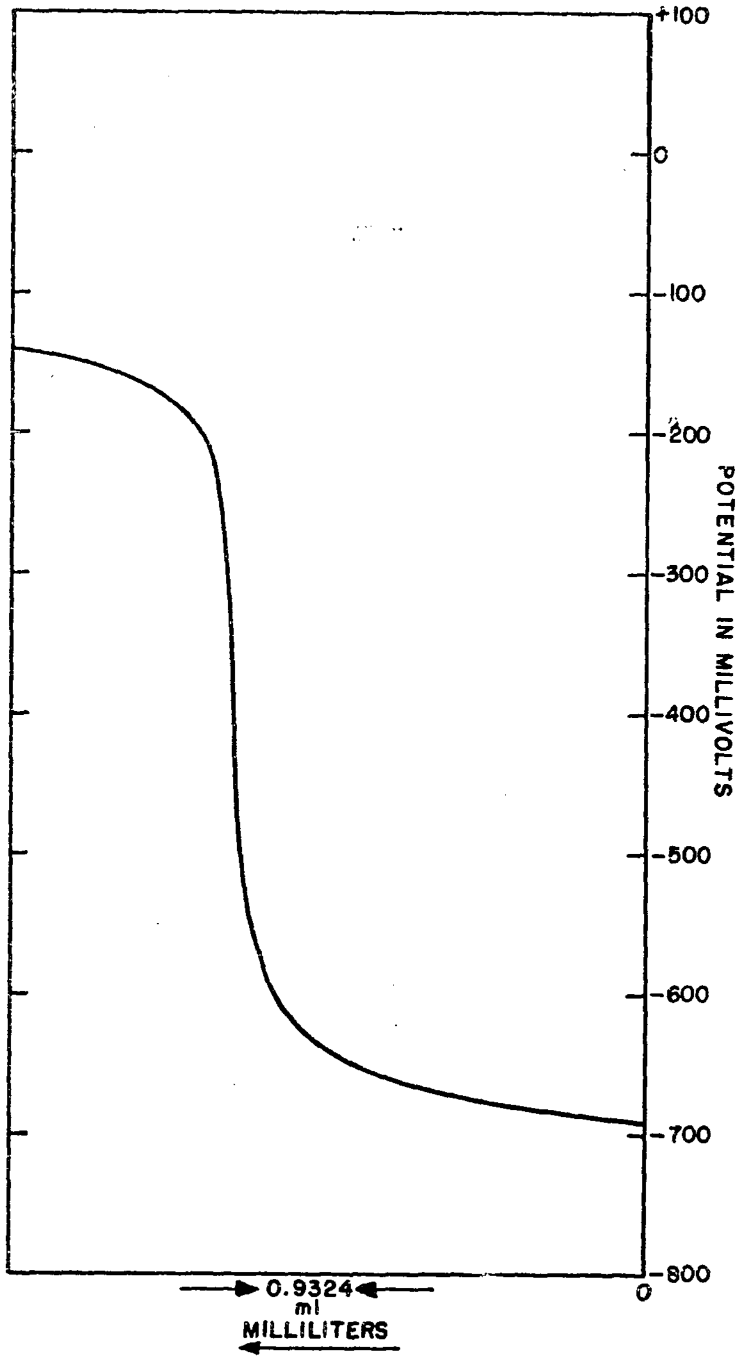


Figure 17. Titration of 0.1 M NaOH with 0.1 M HCl
Antimony-calomel electrode system
1000 mv. range

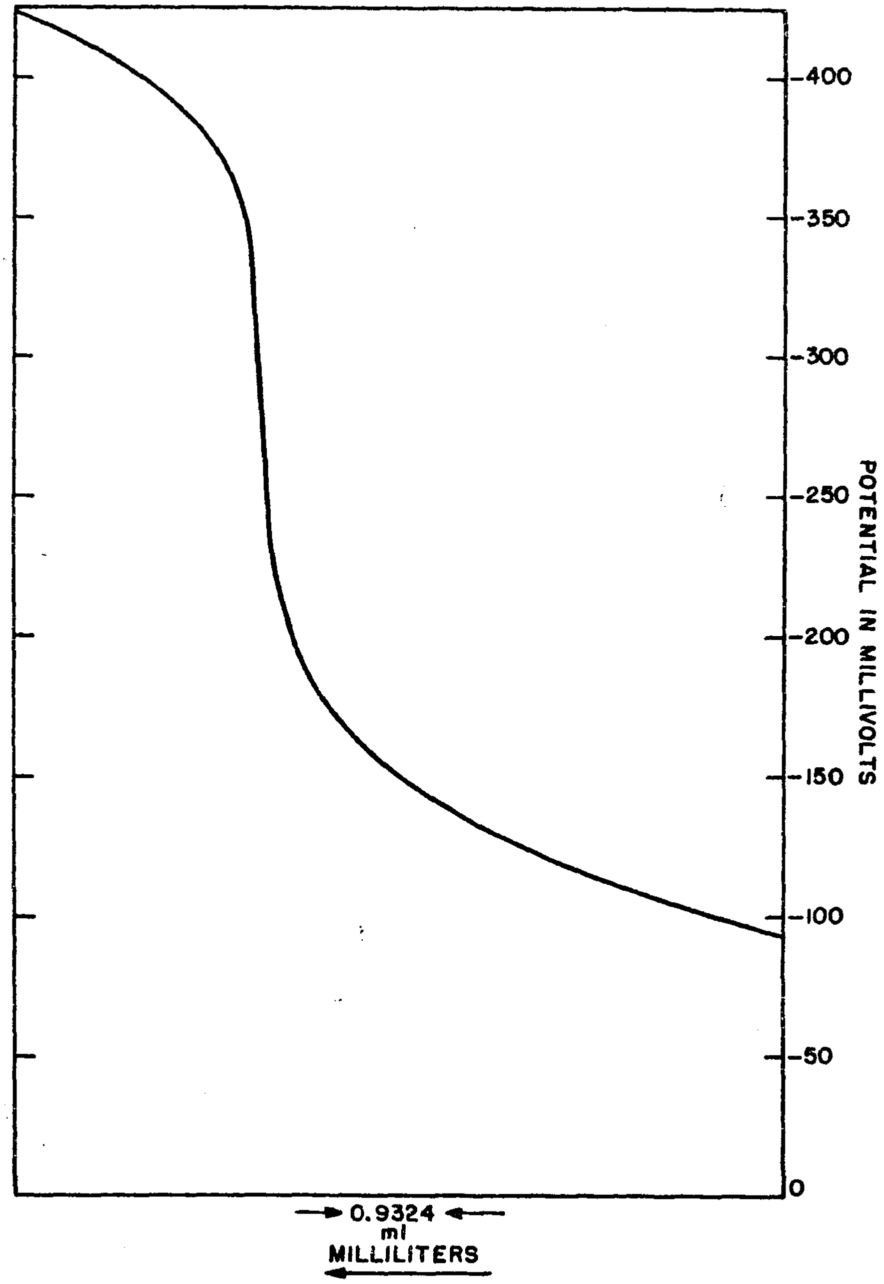


Figure 18. Titration of H_2NOH with HCl in isopropanol
Glass-calomel electrode system
500 mv. range

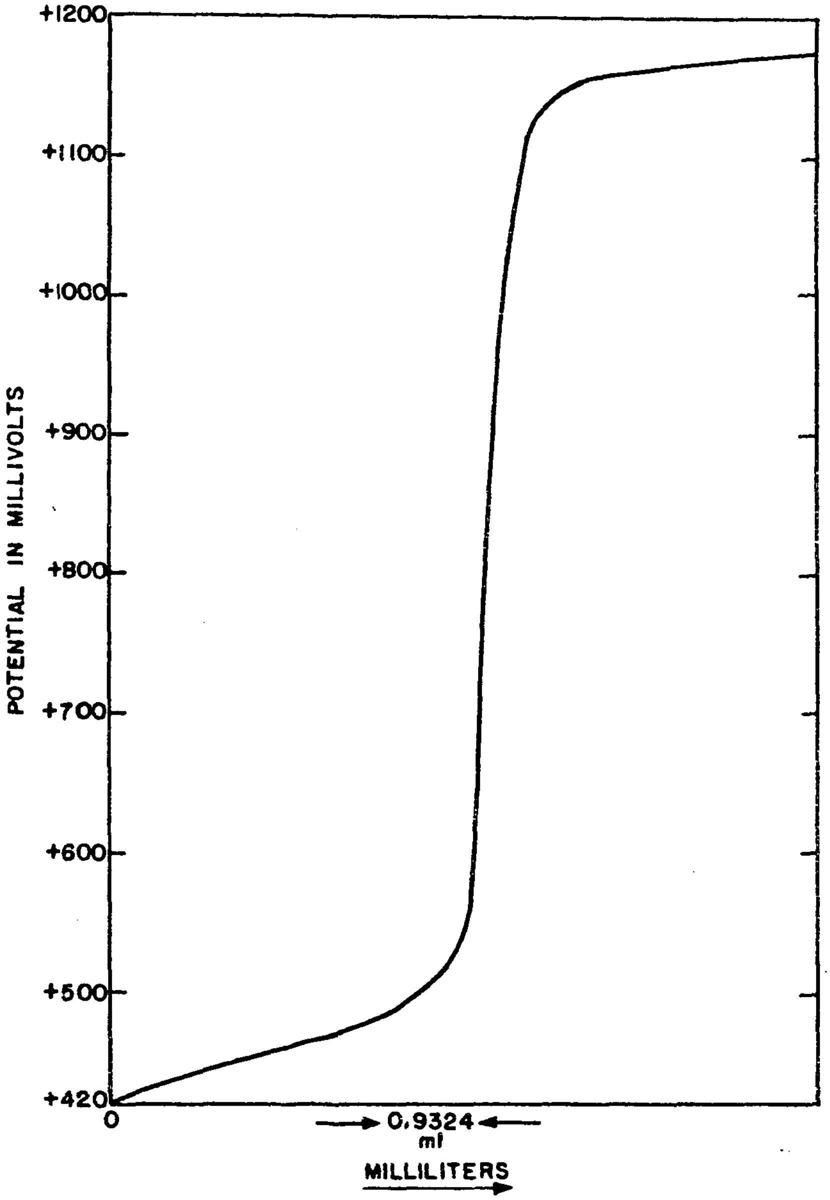


Figure 19. Titration of iron (II) with cerium (IV)
Platinum-calomel electrode system with leads reversed
1000 mv. range with zero potential off scale

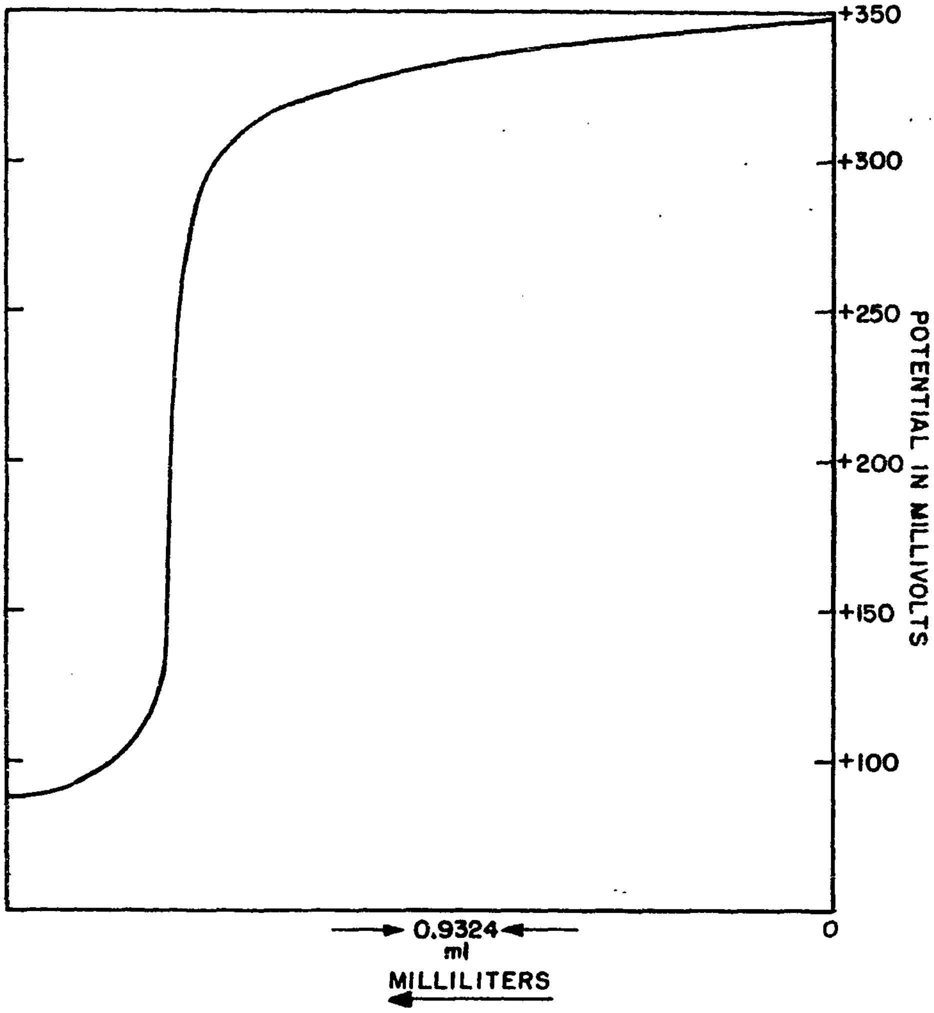


Figure 20. Titration of 0.05 M Hg (II) with 0.05 M EDTA at pH 6
Mercury-calomel electrode system
500 mv. range

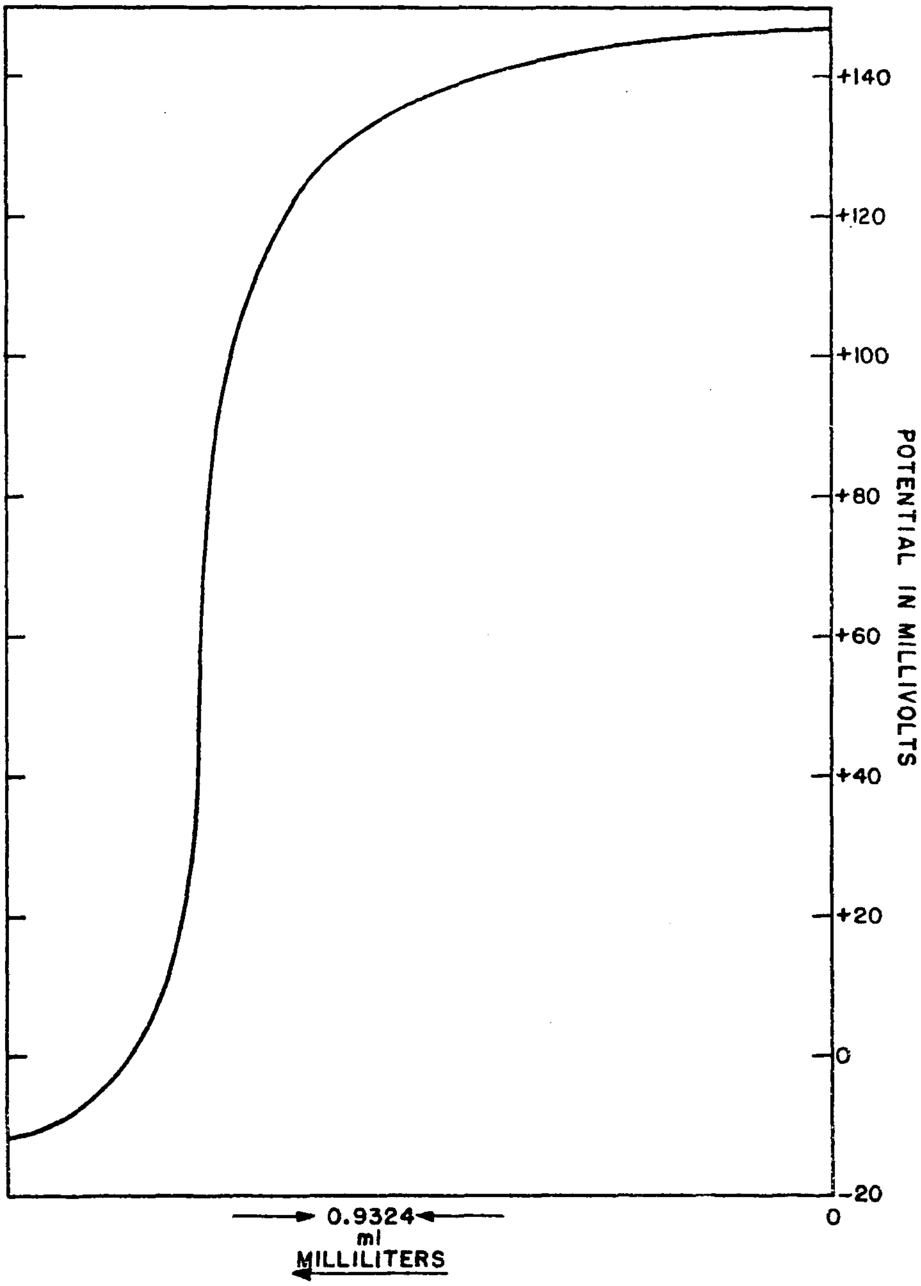


Figure 21. Titration of 0.05 M Hg (II) with 0.05 M EDTA at pH 4.6
Mercury-calomel electrode system
200 mv. range

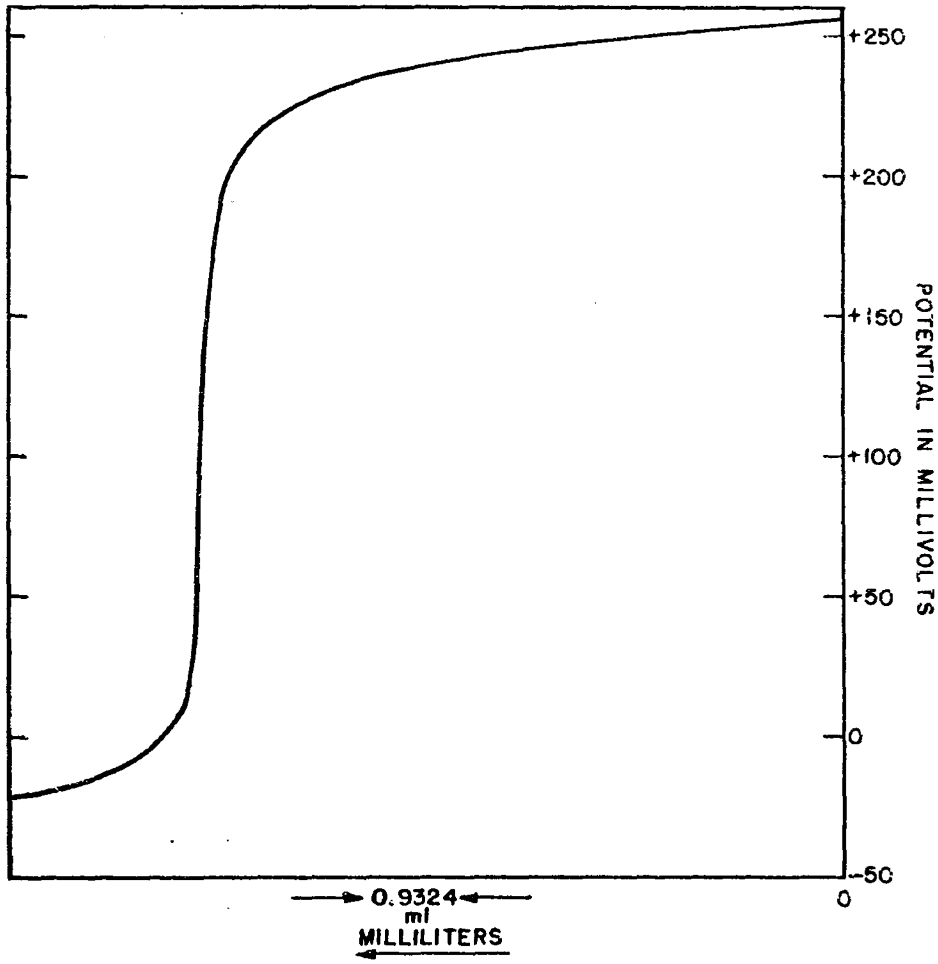


Figure 22. Titration of 0.05 M Zn with 0.05 M EDTA
Mercury-calomel electrode system
500 mv. range

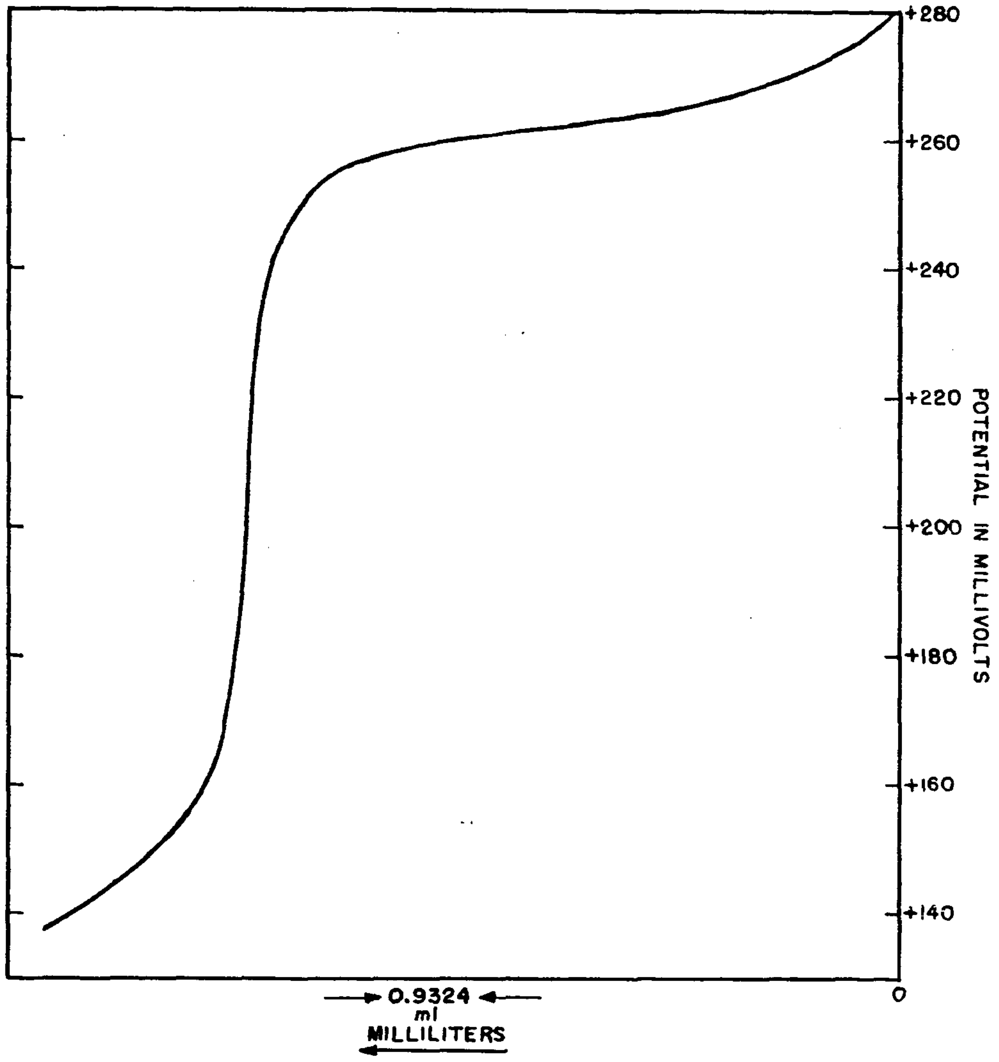


Figure 23. Titration of 0.05 M Th with 0.05 M EDTA
Mercury-calomel electrode system
200 mv. range

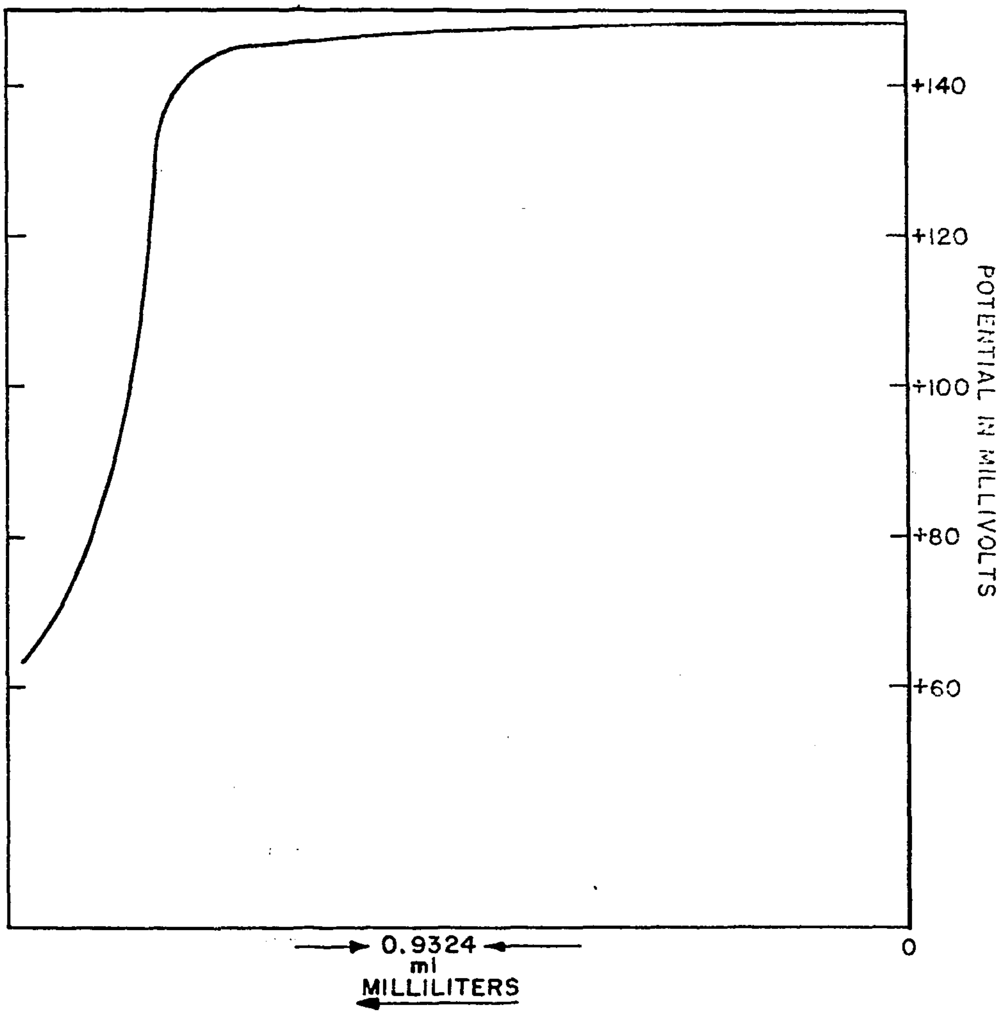


Figure 24. Titration of 0.005 M Th with 0.005 M EDTA
Mercury-calomel electrode system
200 mv. range

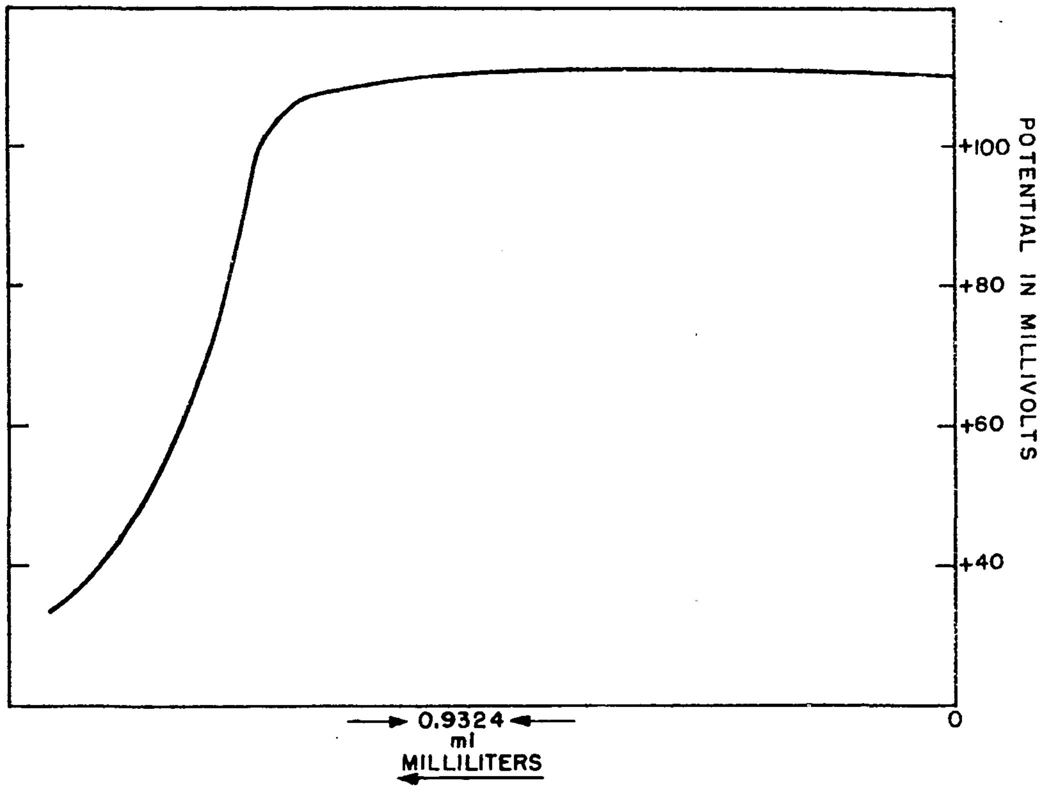


Figure 25. Titration of 5×10^{-4} $\underline{M}$ Th with 5×10^{-4} $\underline{M}$ EDTA
Mercury-calomel electrode system
200 mv. range

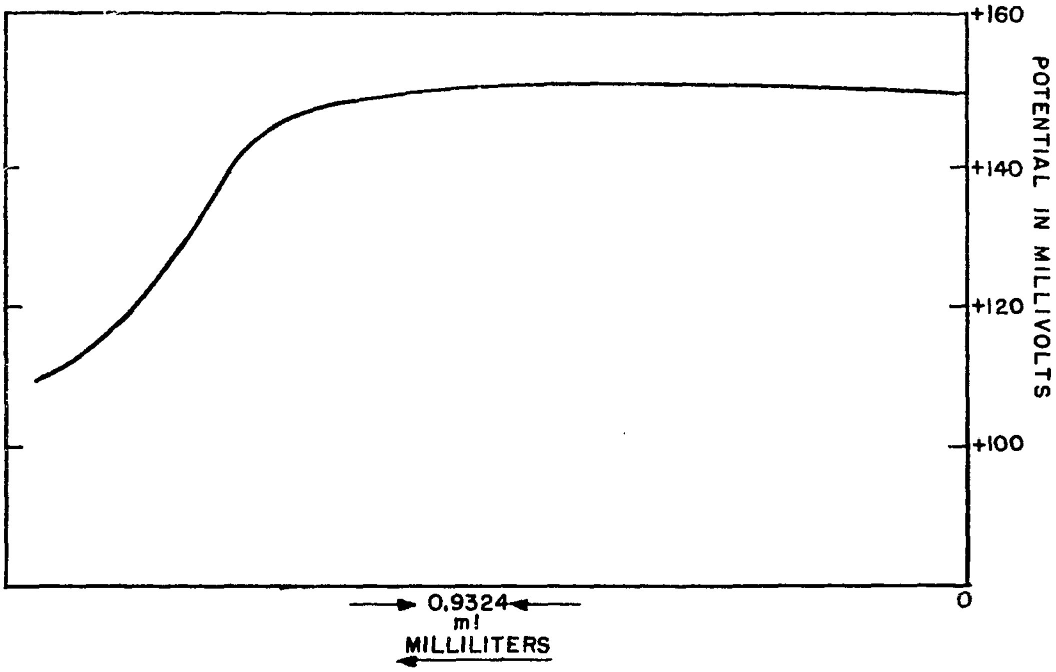


Figure 26. Titration of 1 x 10^{-4} M Th with 1 x 10^{-4} M EDTA
Mercury-calomel electrode system
200 mv. range

DISCUSSION

Recommendations for Improvements

The instrument that has been described is designed to give an accuracy of ±0.3% both in potential scale reading and in end-point determination as interpreted from the recorded titration curve. This has been demonstrated both in the determination of rate of titrant delivery and in actual titrations of known samples. As in any titration procedure, the titrant should be standardized by the method to be used for sample determinations. When this is done, the factors limiting the accuracy of the automatic titration are the limits of accuracy of the amplifier and recorder, and the accuracy of calibration of the resistors in the range selecting circuit.

In the instrument described, the recorder is the component of least accuracy. The actual electrical accuracy of the recorder is ±0.25% of full scale. This is further conditioned by the finite thickness of the line drawn by the recorder pen. The accuracy of locating the end-point is limited also by the finite thickness of the recorded curve, and the ability of the operator to start the titration with the pen exactly on one of the calibrated lines of the chart to assist in calculating the volume of titrant delivered. If the standardization of the titrant is carried out using the instrument, and the titrant is not to be used for any manual titrations, its concentration can be expressed in terms of equivalents per unit chart spacing, and the calculation of volume is not necessary

This instrument can be easily converted to an end-point sensing device by inclusion of a mercury or contact switch attached to the shaft of the balancing potentiometer of the recorder, or on a movable mounting where the pen movement can be made to actuate it. Electrically, this switch is inserted in the power line to the control circuit. Pre-setting the position of the switch to correspond to the end-point potential of the titration will result in stopping the titration automatically at the end point. The details of this alteration are described by Lingane (48). Addition of a revolution counter to the buret drive would be desirable for this purpose.

The flexibility of the components has been emphasized. This flexibility will permit the use of the instrument for photometric, thermometric or conductometric titrations by suitable substitution of the required signal sources for the electrodes. Appropriate choice of the ranges available on the voltmeter and range circuit can be made for these purposes.

The recorder-amplifier-range circuit system is ideally suited for adaptation to gas chromatography. The additional components required for this purpose can be purchased separately or assembled from commercial suppliers.

The inclusion of provisions other than the electronic brake for slowing the rate of delivery of titrant near the end-point would be desirable. Methods of accomplishing this have been described. The substitution of a nylon or teflon syringe for the glass syringe would be desirable for use with strongly basic titrant solutions. A teflon syringe has been constructed for this purpose, but has not yet been tested.

Acceptable Substitutes for Components

Several recorders are commercially available which can be supplied to fit the specifications described in previous sections. The Brown, Leeds and Northrup, Wheelco and Weston recorders are in this group. Recorders with narrower charts are manufactured by these organizations, and by Varian Associates. The narrower chart could be used in control applications where the exact potential values are of lesser importance. The end-points of titrations could still be determined with nearly the same accuracy as with the wide chart in most cases. Two recorders are available which would replace the range and zero adjusting circuit also. These are the Fisher Recordall (17) and the Sargent recorder. The Sargent recorder has been briefly tested by the author and shown to be usable for this purpose. When use of the glass electrode is not required, these two recorders can be used without the additional amplifier for most other electrode systems.

Most of the difficulties involved in the use of the glass electrode as described can be easily eliminated by substituting an electrometer-input voltmeter-amplifier for the Kay Lab instrument used in this titrator. This type of voltmeter will permit direct reading and recording of the actual voltage signal. Instruments of this type are made by the General Radio Company (24, 25) and by Keithley Instruments, Inc. (37). The substitution of either of these instruments for the Kay Lab voltmeter will result in a negligible reduction in the accuracy of the potential measurements. However, the advantages gained in operations with the glass electrode make this substitution desirable. The resistors used in the range circuit would have to be changed to conform to the voltmeter output unless the specification of 1 volt output for full-scale deflection is maintained.

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