



THE APPLICATION OF THE PHOTOMETRIC END POINT  
TO CHELOMETRIC TITRATIONS FOR THE RESOLUTION  
OF MIXTURES OF METAL IONS

A THESIS

Presented to

The Faculty of the Graduate Division

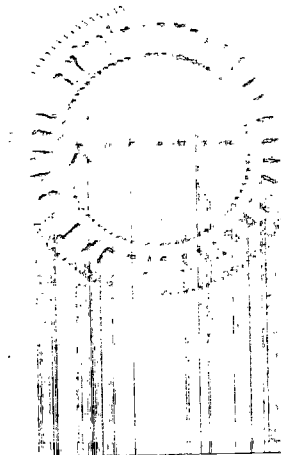
by

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## SUMMARY

The introduction of complexing agents (chelons) such as EDTA into titrimetry has aided in the analysis of aqueous solutions of metal ions. The chelometric titration is usually a simple and rapid technique. In addition certain mixtures of metal ions can easily be resolved by means of a chelometric titration. Selectivity in chelometric titrations is achieved by controlling certain important factors. In general these factors are the nature of the complexing agent, the pH of the solution to be titrated, the presence of masking agents and the method of end point detection.

Although the factors just enumerated have been studied, only recently the method of end point detection has been recognized as offering the possibility of increasing selectivity. Especially useful in chelometric titrations is the photometric titration. The titration curve for a photometric titration is a plot of the absorbance of the solution being titrated versus the volume of titrant added. Many aqueous solutions of metal ions undergo changes in absorbance in the visible region of the spectrum as a titration is performed with a chelon. Often, in very important cases, the human eye is unable to detect these changes and an instrument, the phototitrator, must be used. In this study an instrument constructed by other investigators was used to detect the changes in transmittance. The instrument was constructed to be mechanically, optically and electrically stable. An important feature of the construction of the instrument was that the titration cell

remained in the open during the titration. A collection of 15 interference filters spanning the visible region of the spectrum was available so that nearly monochromatic light could be used.

On the basis of both theoretical deductions and experimental verification four chelometric photometric titration methods were developed. Systems involving metal ions which are ordinarily difficult or impossible to resolve by any other titrimetric technique were studied. The following methods were developed: a consecutive titration of calcium and magnesium, a selective titration of cadmium, a consecutive titration of copper and nickel and a selective titration of cobalt.

Of the chelometric methods available for the determination of calcium in the presence of magnesium, none is completely satisfactory because a pH greater than 12 must be used to mask the magnesium as insoluble magnesium hydroxide. In addition certain restrictions with respect to use of masking agents and the method of end point detection limit these methods.

The chelometric titration with a photometric end point was found to be successful for determining calcium in the presence of large amounts of magnesium and for the consecutive titration of calcium and magnesium in the same solution. First the solution containing both calcium and magnesium is buffered at pH 10 with an ammonia-ammonium chloride buffer. Calcium is titrated with EGTA using murexide as the step indicator and a 505 mu interference filter. Calcium was titrated even when the calcium to magnesium ratio was 1:130. Magnesium is titrated next in the same solution using EDTA as titrant, Erio T as a step indicator and a 622 mu interference filter.

The presence of many foreign metal ions can be tolerated because masking agents can be employed which will not interfere with calcium or magnesium titrations. Nickel, zinc, copper, cadmium, mercury, cobalt and iron do not interfere when properly masked. Manganese does interfere, however, when present in greater than trace quantities. A few anions interfere due to the formation of insoluble calcium salts. Tartrate interferes if present in three-fold excess of the calcium. Barium and strontium are serious interferences since they will be cotitrated with calcium.

Cadmium was selectively titrated with EGTA using copper as the slope indicator at 742 m $\mu$ . The solution is buffered at pH 10 with an ammonia-ammonium chloride buffer. In the presence of ammonia, cadmium is titrated before copper. The ammonia concentration must be controlled (but only within wide limits) so that the slope of the copper titration curve is not decreased too much. Cadmium can be titrated in the presence of large amounts of zinc; satisfactory results are obtained when the cadmium to zinc ratio is 1:500. Cadmium can also be titrated in the presence of iron(II), cobalt(II), nickel(II), mercury(II), aluminum and magnesium. The alkali metals do not interfere. However, lead and calcium are cotitrated with cadmium. Other metal ions interfere by being cotitrated or causing kinetic problems. However, since the method is so satisfactory for determining cadmium in the presence of zinc and since the separation of both zinc and cadmium from almost all other metal ions is easily accomplished by ion exchange the problem of interfering metal ions is not a serious one. However, certain mixtures of metal ions can be analyzed by titrating several aliquots with different

titrants using different indicators. The analysis of a solution of cadmium, zinc, copper and lead was performed in this way.

Copper and nickel were analyzed in the same solution by means of the photometric end point. Both metals were titrated with trien and a 591 mμ interference filter was used to obtain nearly monochromatic light. The solution was first buffered at pH 7 with ammonium acetate. At this pH the copper was titrated selectively and the end point was obtained by means of the self-indicating copper-trien complex. The stability of this complex is very high and the end point break was very sharp. Nickel was titrated next after raising the pH to 10 and buffering the solution with an ammonia-ammonium chloride buffer. Murexide was used as the step-indicator. Again a very sharp break was obtained at the end point. The ammonia concentration must be controlled so that the nickel-murexide indicator complex is not prevented from forming. The following metals did not interfere: manganese(II), iron(II), aluminum, bismuth, lead and silver. Zinc and cadmium did not interfere with the copper titration but they were cotitrated with nickel. Cobalt interferes because of the slow conversion of cobalt(II)-trien to cobalt(III)-trien due to slow air oxidation. The standard trien solution hydrolyzes to a small extent but no error was detected when a three-month old solution was used.

A highly selective method for titrating cobalt was devised based on the conversion of cobalt(II) to the highly stable cobalt(III)-EDTA complex. The titration is performed at a pH less than 2 where most metal-EDTA complexes are completely or nearly completely dissociated. The cobalt was oxidized in the presence of an excess EDTA and the excess

EDTA was back titrated with a standard bismuth solution. For nearly all of the common metals this procedure is satisfactory. However, copper and nickel were slowly replaced from their EDTA complexes by bismuth. In order to overcome this kinetic problem an excess of bismuth solution was added instead of back titrating with bismuth. The replacement reaction occurred much more rapidly using this modification. The excess bismuth was then back titrated with a standard EDTA solution. Pyrocatechol violet was used as a step-indicator and gave excellent photometric titration curves.

Most metal ions did not interfere either because the pH was too low or they could be masked. The most serious interference which could not be prevented was due to iron. To use this method iron must be absent. Chromium interferes but the method was modified in such a way so as to enable the determination of both cobalt and chromium.

Nickel and cobalt can be determined in the same solution by performing two titrations. The sum of nickel and cobalt is obtained by performing the back titration of bismuth at  $0^{\circ}\text{C}$ . An excess of bismuth is then added and the solution warmed to room temperature. The bismuth then replaces the nickel and the remainder of the uncomplexed bismuth is back titrated with EDTA.

## CHAPTER I

### INTRODUCTION

#### Chemical Analysis versus Determination

One of the basic problems analytical chemists must solve is the estimation of a constituent in the presence of associated substances. The frank recognition of this situation either does not always occur or is not always made clear (1). To help clarify this problem it is necessary to introduce terms whose meanings are intended to distinguish " . . . between the analysis of pure substances and the analysis of mixtures" (2). Methods satisfactory for elements when they occur alone, as in pure compounds, are abundantly available. The suggestion has been made that these methods be called "determination." However, methods which yield results even though interfering elements are present are termed "analyses."

Of the several criteria required for an acceptable quantitative analytical chemical procedure, the extent to which interferences can be tolerated is of great importance. In practice, samples to be analyzed, such as rocks and alloys, will always contain several components. If the available methods cannot cope with this situation the only alternative is to subject the sample to a time consuming separation procedure. Even the techniques of chromatography, ion exchange or solvent extraction cannot always be relied on to resolve a complicated mixture perfectly or even partially. Thus, the elimination of the separation step can still be a significant attribute of an analytical procedure.

### Selectivity and Specificity

Methods can be described using terms which take into account the ability to tolerate interferences. Two accepted terms are "selectivity" and "specificity." The analysis of substances in aqueous solution by means of titrimetry is based on a chemical reaction between the titrant and the titrate. The terms selectivity and specificity are applied more accurately not to the method but to the titration reaction and to those conditions necessary to bring about this reaction. "Reactions (reagents) which under definite experimental conditions are quite unambiguous for one component, are termed specific; on the other hand, those reactions (reagents) which permit a narrow choice, because they are characteristic for a limited number of ions or compounds are termed selective" (3). Specificity is the extreme case of selectivity; a reaction is either specific or non-specific. If the reaction is non-specific then it may be more or less selective. The importance of selectivity or specificity both on a practical and theoretical basis need no justification.

### Object of Investigation

This study focuses attention on aqueous solutions of metal ions and the chemical analysis of these solutions by titrimetric procedures. Complexing agents are widely used to analyze solutions of metal ions. The factors which affect complexing reactions can be varied in many ways in order to increase selectivity. A review of these factors will be presented. However, some factors, although very useful for increasing

selectivity, have not been fully investigated. A study of some of these factors from a theoretical viewpoint and the application of these factors to practical analytical problems will be presented.

#### Complex Formation as the Basis of Titration

In the following discussion about complexometric or chelometric titrations a number of terms will be used which must first be defined. A metal complex is the substance formed when the water molecules surrounding the metal ion are replaced by other ions or molecules. The group replacing the water molecule is called a ligand. A ligand molecule which forms only one bond with the metal ion is called a monodentate ligand. Similarly, a reagent which forms two bonds is called a bidentate. A sexadentate reagent is one which binds the metal with six bonds. A chelate compound is a special type of complex. The term "chelate," first introduced by Morgan and Drew (4), was taken from the Greek term chele, meaning crab's claw. The reagent holds the metal ion much like a crab holds its prey with its claws. The chelating agent always has more than one position on the molecule through which a bond can form. It is important to note that in the chelate compound the metal is part of a ring. For the analytical chemist, the term chelon represents a special type of chelating reagent. The term chelon is a generic term for a class of reagents including polyamino-carboxylic acids, polyamines, and related compounds which form stable soluble and usually 1:1 complexes with metal ions and may consequently be used as titrants for metal ions (5).

The introduction of chelons into titrimetric analysis (the most widely known example being EDTA<sup>\*</sup>) has replaced many gravimetric procedures and many titrimetric procedures based on precipitation and redox reactions. This replacement has occurred because of the simplification of the analysis of metal ion solutions using chelons as titrants. But without the proper attention to a number of factors little can be said about the selectivity of the chelometric approach. An understanding of the nature of complex formation is helpful in recognizing what these factors are.

Previous to the introduction of chelons, the only widely known applications of complexation reactions as the basis of titrations were the titration of halides with mercury(II) and the titration of cyanide with silver(I). Most inorganic complexing reagents are not satisfactory as titrants because they fail in one or more of the criteria of titrimetric reactions: the reactions must be rapid, stoichiometric and quantitative. For example, the titration of ferric iron with thiocyanate would be unfavorable because after a portion of the total ferric iron has been transformed into the  $\text{Fe}(\text{SCN})^{+2}$  specie the further addition of titrant would cause the formation of  $\text{Fe}(\text{SCN})_2^+$ .

At any point during the titration, therefore, the solution would contain "free" iron(III) and several complex species of iron(III) and thiocyanate in ratios of 1:1, 1:2, etc. This would at least cause the stoichiometry to be complicated. Because of the occurrence of these step-wise reactions the change in pM as the equivalence point is approached would not be abrupt but "dragged out" and hence the equivalence point could not be easily located. A special type of complexing

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\* Ethylenediamine tetraacetic acid or (Ethylenedinitrilo) tetraacetic acid.

agent, one that reacts in a 1:1 ratio with the metal ion, is needed as the titrant. Chelons are compounds which generally react in the simple 1:1 stoichiometry. The complexing molecule in this case contains more than one atom in the molecule through which coordination can occur with the metal ion. This enables a single molecule, the chelon, to satisfy the coordination requirements of the metal ion and the result is the combination of the metal ion and the chelon in a 1:1 ratio. The metal ion is now a part of one or more rings depending on the number of coordinating positions in the chelon molecule. Chelons are generally organic molecules with basic and/or acidic groups on the molecule through which coordination or salt formation occurs both with metal ions and hydronium ions.

The stability constant is an important parameter to consider in estimating the success of a titration reaction based on complexation. A large value for the constant means complete or nearly complete reaction. Many factors will affect the value of this constant. Merely the presence of coordinating atoms (for example N, O and S) in the molecule does not guarantee a good reagent. Two effects, the size of the ring in which the metal atom takes part and the "chelate effect," have been found to be deciding factors. Schwarzenbach has studied these points in detail (6). In brief, chelates in which the metal ion is a member of a five-membered ring are most stable. Smaller numbered rings are less stable because of strain; larger rings are less stable because of an entropic effect. Furthermore it has been verified that replacement of  $n$  unidentate ligands by one  $n$ -dentate ligand results in an increase of stability. For example, the overall stability constant of

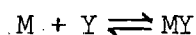
the copper-tetramine complex,  $\text{Cu}(\text{NH}_3)_4^{+2}$  is  $K = 10^{12.6}$ . If two ammonia molecules are now combined into a single molecule such as ethylenediamine and reacted with copper to form the copper-ethylenediamine complex,  $\text{Cu}(\text{en})_2^{+2}$ , the overall stability constant would be found to be  $K = 10^{20.5}$ . This increase in stability due to the decrease in the number of steps required to form the fully complexed metal ion is called the "chelate effect." The structure of the chelon is clearly related to the stability of the chelate. Another factor to consider about the chelon is its solubility in water. This requirement is usually adequately fulfilled if groups such as the carboxyl or sulfonic groups are present in the molecule.

#### Stability Constants. General Considerations.

The constant referred to in the previous discussion is the thermodynamic stability constant. The use of this constant is limited since the analytical chemist must deal with solutions which are more complicated than the conditions under which the thermodynamic constant was measured. The problem occurs because species are present in the solution which by means of competing equilibria can upset the primary equilibrium between the metal ion and the chelon.

The use of stability constant data is complicated by the existence of several kinds of stability constants. The "thermodynamic constant" is of most interest to physical chemists. The value of this constant is obtained by measuring molar concentrations and calculating activities by means of the activity coefficients which themselves may be either calculated from purely theoretical principles or experimentally

measured. The thermodynamic constant may also be obtained by measuring concentrations in successively dilute solutions and extrapolating to infinite dilution. The second kind of constant is called a "mixed constant" and involves both activities and molar concentrations in the stability constant expression. For example, acid dissociation constants may be determined by a pH measurement (which is nearly the same as measuring the activity of the hydrogen ion) and measurements of the molar concentrations of the other species involved in the dissociation. The calculation would be made with the activity of the hydrogen and the molar concentrations of the other species as terms in the dissociation expression. A third constant, the "absolute constant" (7) expresses a relationship solely in terms of molar concentrations. For the case of a metal chelate, MY, the absolute stability constant is based on the equilibrium



and is written as

$$K_{\text{abs}} = \frac{[MY]}{[M][Y]}$$

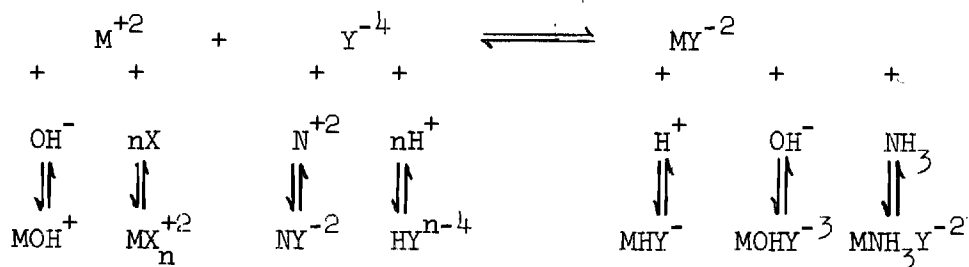
The terms in brackets are molar concentrations. Charges are omitted for simplicity. They are obtained by abstracting the influence of pH and other complex formers (other than the titrant). Only the molar concentrations of metal ion M, fully dissociated Y and complex MY are used in the calculation of the absolute constant. The fourth and last type of constant, the "apparent constant," is used mainly by analytical chemists because it will reflect the stability of the complex under conditions

which exist during an analysis. The calculation and use of the apparent constant will be discussed later.\*

In order to obtain accurate answers activities should be used instead of concentration terms. Because of the lack of activity coefficient data calculations made in this study will be carried out with concentration in terms of molarity. However, when pH is referred to the hydrogen ion activity is implied. Thus calculations of constants on this basis will really yield what may be called "mixed apparent constants" as described above.

#### The Effect of Side Reactions on a Titration

The scheme illustrated next designates some of the competing equilibria (side reactions) which can affect the main titration reaction (8).



$M^{+2}$  is the bivalent metal ion to be titrated,  $Y^{-4}$  is the chelon (titrant),  $MY^{-2}$  is the chelonate, X and  $OH^{-}$  are foreign complex formers,  $N^{+2}$  is a bivalent interfering metal ion,  $H^{+}$  is the hydronium ion,  $MHY^{-}$ ,  $MOHY^{-3}$  and  $MNH_3Y^{-2}$  are mixed complexes of  $MY^{-2}$  with  $NH_3$ ,  $OH^{-}$  and  $H^{+}$  in the scheme. It is obvious how these side reactions can be unfavorable for

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\* See below p. 10.

a titration. For example, since the chelon is an acidic substance, as the pH is decreased more of the undissociated forms of the chelon Y are formed. In the case of EDTA decreasing the pH below approximately 10 results in the successive formation of  $HY^{-3}$ ,  $H_2Y^{-2}$ ,  $H_3Y^{-1}$ , and  $H_4Y$ . This pH effect is not reflected in the thermodynamic constant. The effect of pH could be estimated by considering all of the pertinent equilibria, setting up the proper algebraic equations and solving for the concentration of the desired ion. The information could be calculated but the labor is not always worthwhile. Schwarzenbach has devised a simplified approach on the basis of the apparent stability constant (9).

#### The Apparent Stability Constant and the Influence of pH

The absolute stability constant is defined in terms of only the chelon that is present in the completely dissociated form. This is true only in strongly alkaline solution at a pH greater than 10 for most of the chelons to be dealt with. At lower pH values the uncombined chelon will be present in its protonated forms  $HY^{-3}$ ,  $H_2Y^{-2}$ ,  $H_3Y^{-1}$ , and  $H_4Y$ . These forms will vary in their amounts according to the pH of the solution. To account for this fact, the stability constant under the actual solution conditions must be calculated and the resulting constant is called the apparent stability constant. A factor  $\alpha_H$  can be used to calculate the apparent constant from the absolute constant. The subscript H denotes that the hydrogen ion concentration dependence is being considered. For the remainder of this discussion, however, the subscript will not be used.

All calculations will be made on the basis of molar concentrations as symbolized by brackets. The error introduced by not using activities will be neglected.

At any pH the apparent stability constant may be expressed by:

$$K_{app} = \frac{[MY^{+n-4}]}{[M^{+n}][Y]'} \quad (1)$$

where  $[Y]'$  denotes the total concentration of chelon not combined with the metal, but including all dissociation forms which may exist at a particular pH. This  $[Y]'$  may be related to  $[Y^{-4}]$  by the formula

$$[Y]' = [Y^{-4}] \cdot \alpha_H \quad (2)$$

Since  $[Y]'$  is the total concentration of the uncombined chelon in its various forms, overall balance gives

$$[Y]' = [Y^{-4}] + [HY^{-3}] + [H_2Y^{-2}] + [H_3Y^{-1}] + [H_4Y] \quad (3)$$

It is possible to express the various terms in Equation (3) by introducing the stepwise acid dissociation constants of the chelon. For practical purposes it is more suitable to use the reciprocal of the dissociation constant, namely the "proton stability constant" of the "proton complexes" of the chelon. The expressions are for a tetrabasic acid such as EDTA:

$$K_1 = \frac{[HY^{-3}]}{[H^+][Y^{-4}]} \quad (4)$$

$$K_2 = \frac{[H_2Y^{-2}]}{[H^+][HY^{-3}]} \quad (5)$$

$$K_3 = \frac{[H_3Y^{-1}]}{[H^+][H_2Y^{-2}]} \quad (6)$$

$$K_4 = \frac{[H_4Y]}{[H^+][H_3Y^{-1}]} \quad (7)$$

Now  $[H_4Y]$  may be expressed in terms of  $K_4$ ,  $[H_3Y^{-1}]$  in terms of  $K_3$  and so forth, thus

$$\begin{aligned} [Y]' &= [Y^{-4}] + K_1[Y^{-4}][H^+] + K_2[HY^{-3}][H^+] + K_3[H_2Y^{-2}][H^+] \\ &\quad + K_4[H_3Y^{-1}][H^+] \end{aligned} \quad (8)$$

Substituting now all terms other than  $[Y^{-4}]$  by the expressions for the above constants the result is

$$\begin{aligned} [Y]' &= [Y^{-4}] + K_1[Y^{-4}][H^+] + K_1K_2[Y^{-4}][H^+] \\ &\quad + K_1K_2K_3[Y^{-4}][H^+]^3 + K_1K_2K_3K_4[Y^{-4}][H^+]^4 \end{aligned} \quad (9)$$

Combining this equation with (2) and dividing by  $[Y^{-4}]$  the expression for  $\alpha_H$  is obtained

$$\alpha_H = 1 + K_1[H^+] + K_1K_2[H^+]^2 + K_1K_2K_3[H^+]^3 + K_1K_2K_3K_4[H^+]^4 \quad (10)$$

This formula enables the calculation of  $\alpha_H$  for any pH value since the four acidity constants (and therefore their reciprocals) are known. It is convenient to plot  $\alpha_H$  versus pH so that the value of  $\alpha_H$  is conveniently available at any pH. Once  $\alpha_H$  is known, the apparent stability constant can be calculated by combining (1), (2) with the equation for the absolute constant

$$K_{app} = \frac{MY^{+n-4}}{[M^{+n}]\alpha_H[Y^{-4}]} = \frac{K_{abs}}{\alpha_H} \quad (11)$$

or

$$\log K_{app} = \log K_{abs} - \log \alpha_H \quad (12)$$

Note that this formula contains only the normal complexes  $MY^{+n-4}$  and none of the hydrogen ( $MHY^{+n-3}$ ) or hydroxo ( $MOHY^{+n-5}$ ) complexes. Under extreme conditions of pH, one or the other of this type of complex may be formed in appreciable amounts.

Thus the effect of pH on the equilibrium between the metal ion and the chelon is reflected in the lowering of the MY concentration and is represented by  $K_{app}$ . For example the absolute constants (logarithms) of iron(III) and calcium with EDTA are 25.1 and 10.7 respectively (10). The value of  $\log \alpha$  at pH is 10.6 (10). Thus the apparent constants of iron and calcium at pH 3 respectively are 14.5 and 0.1. The stability constants are decreased the same amount but the calcium now is nearly completely dissociated.

The Influence of Other Complex Formers. The  $\beta$  Factor.

When another complex-forming substance is present the metal ion is distributed between the complexes formed with this substance and the titrant. The apparent stability constant which takes into account the influence of this substance, Z, is given by

$$K_{\text{app}} = \frac{[MY^{+n-4}]}{[M]^{'} [Y^{-4}]} \quad (13)$$

$[M]^{'}$  is now the concentration of the metal ion not combined with the chelon, Y, including the "free" metal and also all complexes possibly formed with Z. The relation between  $[M]^{'}$  and  $[M^{+n}]$  is analogous to that in (2) and is given by

$$[M]^{'} = [M^{+n}] \beta_Z \quad (14)$$

The complex between M and Z is seldom a 1:1 complex (e.g., the ammine complexes of copper, zinc, nickel, etc., in ammoniacal solution).

Therefore the total amount of the metal ion not combined with the chelon, Y, is given as

$$[M]^{'} = [M^{+n}] + [MZ] + [MZ_2] + \dots + [MZ_n] \quad (15)$$

Charges are omitted for the sake of simplicity. The stability constants of the various complexes between M and Z are given by the following equations

$$K_1 = \frac{[MZ]}{[M^{+n}][Z]} \quad (16)$$

$$K_2 = \frac{[MZ_2]}{[M^{+n}Z][Z]} \quad (17)$$

$$K_M = \frac{[MZ_n]}{[MZ_{n-1}][Z]} \quad (18)$$

Replacing the terms  $[MZ]$ ,  $[MZ_2]$  ...  $[MZ_n]$  in (15) by the appropriate expressions derived from the stability constants the following expression results

$$[M]' = [M^{+n}] + K_1[M^{+n}][Z] + K_1K_2[M^{+n}][Z]^2 + \dots K_1K_2\dots K_n[M^{+n}][Z]^n \quad (19)$$

Combination of the last equation with (14) gives

$$\beta_Z = 1 + K_1[Z] + K_1K_2[Z]^2 + \dots K_1K_2\dots K_n[Z]^n \quad (20)$$

The apparent stability constant is then obtained by combining (13), (14) with the equation for the absolute constant

$$K_{app} = \frac{[MY^{+n-4}]}{[M^{+n}]\beta_Z[Y^{-4}]} = \frac{K_{abs}}{\beta_Z} \quad (21)$$

or

$$\log K_{app} = \log K_{abs} - \log \beta_Z \quad (22)$$

Note that  $[Z]$  is the concentration of the "free" compound, that is, not combined with the metal. Therefore the concentration of total Z is equal to  $[Z]$  only if a sufficient excess is present so that the relatively small amount combined with the metal may be neglected. Since Z is usually

contained in buffers or is added deliberately in excess the condition holds closely enough to equate  $C_Z = [Z]$ .

If several complex formers are present in the solution the total  $\beta$  factor can be calculated according to

$$\beta_{\text{total}} = \beta_1 + \beta_2 + \dots + (n-1) \quad (23)$$

where  $n$  is the total number of  $\beta$  factors. Usually only one of the  $\beta$  factors is significant and need be considered.

The Influence of pH and Complex Forming Substances.  
Other Than the Titrant.

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If both the pH effect and complex due to foreign complexing reagents effect occur simultaneously, the apparent stability constant is obtained by combining the derivations given above

$$K_{\text{app}} = \frac{[MY^{+n-4}]}{[M]^1 [Y]^1} = \frac{K_{\text{abs}}}{\alpha_H \beta_Z} \quad (24)$$

or

$$\log K_{\text{app}} = \log K - \log \alpha_H - \log \beta_Z \quad (25)$$

Note that the constants for the complexes between M and Z should also be the apparent ones. They can be calculated for the particular pH in a way similar to that given for the chelon Y.

### Other Influences

Most stability constants are measured at a certain temperature (20°C) and for a specified ionic strength. By changing these parameters the analytical chemist can change the absolute stability of the complex. Increasing the salt concentration with non-complexing species decreases the stability. The addition of organic solvents will change the stability. However, these effects are usually considered important only when extreme conditions are encountered (11).

### Selectivity in Chelometric Titrations

A selective titration reaction will occur if the side reactions of the titrant with other foreign metal ions is prevented. Several possibilities exist which can bring this about. It is unlikely that a selective reaction can be discovered solely on the basis of the structure of the chelon. With few, although important, exceptions, those chelons that are widely known are not selective in their reactions. The factors that are very useful for increasing selectivity are pH, use of masking agents, kinetic effects, mode of addition of titrant and the method of end point detection. The  $\alpha$  and  $\beta$  factors are very useful in predicting how conditions can effect the selectivity of a reaction. It is clear that if two metal ions differ considerably with respect to the stability of their complexes with the chelon, they will react with the titrant in discrete steps. It is only necessary then to be able to locate the end points. The requirement that a selective or specific set of indicators be available is possible

for some mixtures of cations but in general this requirement is difficult to fulfill. The only alternative is recourse to an instrumental method of end point detection.

### The pH Effect

When the difference of stability of metal chelates is sufficiently great, it is possible to conduct the titration at a pH sufficiently low that the less stable chelates do not form under the reaction conditions employed. Many chelometric titrations are performed at pH 10 since the protonated forms of the chelon will be almost entirely dissociated. One group of metal ions, Bi(III), Fe(III), Cr(III), V(III) and Th(IV) for example form such stable EDTA chelates that practically no dissociation occurs even at pH 2. Thus it is possible to titrate these ions in the presence of many bivalent cations. The effect can be estimated very conveniently with the  $\alpha$  factor. For the titration of metal M in the presence of metal N using a visual type of indicator the stability constants should differ by about 8 - 10 log units in  $\log K$  (12). This difference can be decreased to 3 if the end point is detected instrumentally, without using a step indicator.\* The stability constants used in these estimations should be the apparent constants. Although the  $\alpha$  factor cancels out in the ratio it is necessary that  $K_N$  is lowered sufficiently so that none of it reacts with the titrant.

### Masking

Masking is a process in which a substance is transformed so that certain of its reactions are prevented. The masking process occurs

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\* See below p. 31.

without physical separation of either the substance being masked or the reaction products of the masking reaction. Demasking is the process in which a masked substance is released from its masked form and regains its ability to take part in certain reactions. The description of the masking procedure should clearly state which species is masked and against what reaction. For example, silver ion can be masked with ammonia against chloride ion but silver iodide will precipitate in the presence of ammonia.

The masking-demasking procedure is used very effectively for the titration of zinc and magnesium mixtures. Zinc is masked against EDTA with cyanide but the magnesium remains unmasked. The magnesium is titrated with EDTA using Eriochromeblack-T as the indicator. The zinc-cyanide complex is demasked by the addition of formaldehyde which destroys the zinc-cyano complex thus freeing zinc ion which can now be titrated with EDTA using Erio-T.

The effect of the masking agent can be evaluated with the  $\beta$  factor. The masking agent must decrease the apparent stability of the complex between titrant and foreign metal so that it does not react with the titrant. The masking agent should not adversely affect the main titration reaction.

By converting a metal ion to a different oxidation state, a masking action can be brought about. Generally, metal ions in lower oxidation states form weaker complexes. For example the logarithms of the EDTA complexes of iron(II) and iron(III) are 14.3 and 25.1 respectively (10).

Cheng has reviewed the use of masking reagents and presented some principles which can be used to evaluate masking reagents (13).

#### Kinetic Effects

The kinetic requirements for a titration reaction are covered generally by the term rapid. However, the fact that some complexation reactions are slow can be used to advantage. For example, chromium(III) reacts extremely slowly with EDTA. This situation is unsatisfactory for titrating chromium. However, since the reaction is so slow other metal ions can be titrated in the presence of chromium. Similarly, nickel reacts slowly with EDTA but at room temperature the reaction is not quite slow enough to enable a selective titration by "kinetic" masking. However, it is possible to lower the solution temperature to 0°C and decrease the rate of reaction of the nickel sufficiently to prevent its reacting during the period required to titrate the other metal ion (14).

#### Mode of Addition of Titrant

A titration method can be modified with regard to the order of addition of reagents to enable a titration which might not otherwise be possible. Several general types of titrations are possible on the basis of treating the solutions with one or more standard solutions (15).

Direct Titration. The most common approach to titrations is the direct addition of increments of a standard solution to the unknown solution until the stoichiometric amount of ligand has been added.

Back Titration. An excess of a standard ligand solution is added to the unknown solution and the excess is titrated with a standard solution of a suitable metal ion. This procedure is generally used when

the titration must be carried out under conditions whereby the metal would be precipitated (e.g., as the hydroxide) and when a good indicator is available for the metal in the standard solution but not for the metal being determined. The method might be used in cases where a slow reaction occurs. The excess of titrant is added and the solution warmed until reaction is complete. The excess is then back titrated.

Replacement or Substitution Titration. The metal being titrated is treated with an excess of a solution containing a metal chelate which is less stable than that of the unknown in the solution. Thus the second metal is quantitatively displaced and may then be titrated with a standard ligand solution.

#### Method of End Point Detection

The last factor, the choice of end point detection, has been recognized as influential in gaining selectivity and only recently investigations have shown that less rigid requirements in the factors discussed above can be tolerated if the proper end point detecting method is chosen. Methods of end point detection can be divided into two groups: visual detection and instrumental detection.

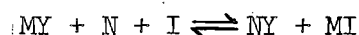
Visual Indication and Metal Indicators. The detection of the end point in a chelometric titration depends on the recognition of the change in color which occurs when the "metallized" or complexed indicator is converted to the "unmetallized" or free indicator. Only a limited number of compounds are of value as metal indicators. Most of the known indicators fall within a few structural types (e.g., azo dyes, phthaleins and sulfonphthaleins, triphenylmethane dyes and phenolic substances) (16).

In order to obtain a good end point, one that is sharp, the ratio of the stability constant of the metal-chelate to the stability constant of the metal-indicator complex must be of the order of  $10^4$  and the value of the metal-indicator constant must be greater than  $10^5$ . These values can be shown to be true as the result of the introduction of some simplifying assumptions into a more rigorous derivation (17). When making these estimates one should use the apparent stability constants.

The selective titration of one metal, M, in the presence of another metal, N, using an indicator, I, which is specific for the metal M is possible using the following relation

$$\frac{K_N}{K_M} = \frac{10^{-2}}{K_I}$$

The stability constants of the two metals are  $K_N$  and  $K_M$ . The stability constant of the metal indicator is  $K_I$  and for metal indicator complexes the values are seldom less than  $10^6 - 10^7$ . Thus the ratio  $K_N/K_M$  must be of the order of  $10^{-8} - 10^{-9}$  in order that metal M is selectively titrated (18). Flaschka and Barnard have pointed out a misunderstanding with regard to indicators (19). The statement is made occasionally that the problem of selectivity could be solved by the use of specific indicators. That this is not generally true can be understood from the equilibrium



In this system, N does not react with the indicator to any extent, otherwise, only the sum of N plus M could be determined. Selectivity

will be obtained only if the stability of the indicator complex,  $MI$ , is as low as possible. A selective or specific indicator is of value if its properties are such that the usual possibilities of increasing selectivity (pH effect and masking) can be suitably associated with its use.

A few redox indicators have been used as indicators in metal ion determinations. Variamine Blue B is the most common example of this type of indicator. The behavior of the indicator can be briefly described by its application to the titration of iron(III) with EDTA. In an iron(III) solution there is always some iron(II) present. The variamine blue will be oxidized by the iron(III), of course producing some iron(II), and the solution will be blue-violet. The iron(III) is titrated with EDTA and at the end point only some iron(II) remains. The indicator is reduced by this iron(II) and passes to the colorless form. Redox indicators are seldom used because of their sensitivity to small amounts of oxidizing and reducing materials. Further the presence of extraneous or added complex formers may alter the redox potential markedly (20).

Instrumental Detection of the End Point. The instrumental detection of the end point in chelometric titrations (or in titrimetry in general) often has significant advantages. If the use of a metal-complexing indicator is avoided then improved selectivity may result. In order to titrate metal  $M$  in the presence of metal  $N$  without using an indicator the ratio of the stability constants,  $K_M/K_N$  should be of the order of  $10^6$  when using a pM method of detection.\*

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\* See below, p. 23.

This should be compared to the ratio  $10^8$  to  $10^9$  when using a metallochrome indicator. The instrumental technique will also be more advantageous for dilute solutions and micro-titrations.

Four general types of instrumental methods are used in the detection of end points in chelometric titrations:

- (1) Potentiometry (Platinum or Mercury Drop Electrode)
- (2) Amperometry
- (3) Conductometry (High and low frequency)
- (4) Photometry

In addition chronopotentiometry has attracted some interest (21). These methods are not arranged in order of their usefulness.

Of the four methods three of them involve electrochemical measurements. A disadvantage of electroanalytical chemical measurements is the occurrence of slow electrode reactions. This is especially true in non-aqueous solutions and in precipitation titrations. Conductometric titrations are seriously hampered by the presence of a large excess of foreign ions in the form of the buffer which is invariably required for a chelometric titration. Considering these facts then would impel one to place photometric titrations at the head of the list.

#### Classification of Instrumental End Point Detecting Techniques

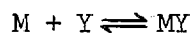
A titration curve is obtained by measuring or by calculating the change in a physical property of the solution as increments of titrant are added. Methods used to obtain the titration curve can be classified into two categories depending on the mathematical relationship between the property being measured and the concentration of the specie of interest.

The first group includes those methods based on the fact that the property measured is a function of the logarithm of the concentration. For example, potentiometric titrations are based on the Nernst Equation

$$E = E^{\circ} + \frac{RT}{nF} \ln[M^{+n}]$$

The potentiometric titration curve is obtained by plotting the potential of the indicating electrode versus the volume of titrant. The end point is generally the inflection point of the curve. These methods will be referred to as pM methods. It should be noted that the portion of the titration curve used to locate the end point results from the most unfavorable equilibrium position since at the end point the complex exhibits the highest degree of dissociation.

The second group of methods is based on a linear relation between the property measured and the concentration of the specie of interest. Amperometric, conductometric and photometric methods belong in this group. The property measured (diffusion current, conductance or absorbance) is a linear function of the volume of titrant. Ideally the titration curve consists of two straight lines having different slopes and intersecting at the end point. For an extrapolation procedure the points removed from the end point are the most important. The advantage is due to the shift in the position of the equilibrium



The position of this equilibrium is forced in the direction of the undissociated complex both at the start of the titration when M is in

excess and far after the end point when Y is in excess. The value of the extrapolative method over the pM method is due to the repression of the dissociation of the complex. Extrapolative methods locate the end point on the basis of points measured where dissociation occurs to the least extent while pM methods locate the end point on the basis of points measured when dissociation occurs to the greatest extent. For the selective titration of metal M in the presence of metal N it is necessary to have a difference of about 2 logarithmic units in the stability constants if the extrapolative technique is used.\*

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\* See below p. 42.

## CHAPTER II

## PHOTOMETRIC END POINT DETECTION

Definition and Example

Generally, the name of the end point detecting technique indicates the property to be measured. Thus, photometric titrations involve the measurement of the change in some optical property of the solution. For a reason to be considered later, this property is the absorbance. The concentration of the absorbing species changes as the titration progresses, hence, the absorbance changes. For example, copper(II) in an ammoniacal medium can be titrated with EDTA and transformed from the copper-tetramine complex to the copper-EDTA complex. The intensity of the light of the wave length which is absorbed by the copper-tetramine complex is measured after it passes through the unknown solution. As the copper-tetramine is converted to copper-EDTA the absorbance decreases, hence, the intensity of the light reaching the photodetector increases. After each increment of EDTA is added the corresponding absorbance value is recorded. Up to the end point the absorbance is continuously decreasing linearly because copper-tetramine is being removed. After the end point the absorbance remains constant since all of the copper-tetramine has been titrated and the EDTA added in excess does not absorb any light. A graph is then made of the absorbance versus the volume of titrant added.

Dilution must be corrected for if the concentration of the EDTA is of the same order as the concentration of copper or less. Two straight lines are drawn through the two series of points and the end point is found as the intersection of the two lines. Thus the end point is found by means of an extrapolation procedure. The titration curve would have a different appearance if the light used had been of the wavelength which the copper-EDTA complex absorbed. Before the end point the absorbance increases since more and more copper-EDTA is being formed. The absorbance remains constant after the end point since the EDTA added in excess would not absorb.

This example is a special case of a photometric titration in terms of a complexometric titration. The method can be applied to other types of titrations, e.g., acid-base, redox and precipitation titrations. The shape of the titration curve however will be different for different systems.

#### Advantages of the Photometric Methods Over Other Methods

These advantages have been discussed in several different sections but a summary at this point will be helpful in appreciating the photometric titration.

Since the end point is located by extrapolation, points in the vicinity of the end point are not important. This must be contrasted with the pM methods which depend upon the location of the inflection point to establish the end point. The photometric method has advantages over the electrochemical methods. In general slow electrode reactions are unsatisfactory for a titrimetric procedure. High concentrations of salts will hamper the measurement of conductance.

The photometric titration has several advantages over the absolute spectrophotometric determination. The presence of other substances absorbing at the same wavelength does not necessarily cause an interference, inasmuch as only the change in absorbance is significant. The precision of locating the titration line by using the information obtained from the measurement of several points is greater than the precision of any single point.

#### Applications of the Photometric Titration

In general, the method is applicable to the titration of solutions which are dilute or in which reactions tend to be appreciably incomplete at the end point, e.g., neutralizations of very weak acids and bases, redox reactions involving couples with similar potentials, metal ions which form weak complexes and reactions in general which are slow to come to equilibrium in the vicinity of the end point. All these circumstances tend to produce a rounding off of the end point breaks but only the points removed from the end point are necessary for the extrapolation procedure.

Using the photometric titrator to detect the end point in a titration which can be detected by the eye does not offer, in general, any increase in accuracy but increases the precision (22). When the eye cannot detect the end point using a visual indicator the photometric titrator is extremely useful.

In general, two cases can be considered when the eye is replaced by the photometric titrator to detect the end point when using a visual indicator (or step indicator).\*

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\* See below p. 31.

colored solutions which prevent the visual observation of the indicator change because of the deep background color of the solution can still be photometrically titrated. The human eye is neither sensitive nor selective enough to detect the "color change" through this optical barrier. A sensitive photoreceptor in combination with the selectivity gained by using monochromatic light will have no difficulty in locating the end point.

Second, the photometric titrator can be used to detect color changes of indicators which are described as "indistinct" or "dragging" when observed by the eye. The "dragging" end point is due to at least two factors; first the chemistry of the reaction which governs the color change, i.e., the rate of reaction and the equilibrium constants and second, the color phenomena in the solution and their relation to the detector. When the indicator complex is dissociated at the end point or when the rate of reaction at the end point is slow one needs only to depend on the points on either side of the end point and extrapolate to find the end point. When the end point is indistinct because of the nature of the colors of the indicator in its two forms one needs to depend only on the sensitive receptor and the nearly monochromatic light.

### Theoretical Background

#### Basis for a Photometric Titration

The fundamental law of the absorption of monochromatic light underlying photometric titrations is the Bouguer-Lambert-Beer Law,  $A = -\log T = \epsilon lc$ , where  $A$  is the absorbance,  $T$  is transmittance,  $\epsilon$  is molar absorptivity,  $l$  is the length of the light path through the

absorbing medium and  $c$  is the molar concentration of the absorbing substance. Those factors which affect this law must also be considered when the law is used as a basis for the photometric titration. The most important consequence of the law is that the absorbance is linearly related to the concentration of the absorbing specie. Theoretical titration curves can be derived from Beer's Law and the mass-action law if the appropriate equilibrium constants are known.

The general shape of the titration curve will depend on the optical properties of the reactant, titrant and products of the reaction at the wave length used. It is necessary to determine the spectral curves of all the pertinent species in the solution both before and after the end point in order to choose the appropriate wave length. The change in absorbance should be as large as possible. The wavelength can be chosen directly from the spectral curves or from a  $\Delta$ -curve. A  $\Delta$ -curve is a plot of the difference between the spectral curves of a specie at the start of the titration and after the end point versus the wavelength. The greatest difference in absorbance will occur at the maximum or the minimum in the  $\Delta$ -curve.

#### Types of Photometric End Point Indication

Flaschka and Sawyer have devised a new nomenclature for the three possible types of photometric indication (23). Both equilibrium and optical properties (absorbance) have been considered. The discussion will be limited to those titrations which involve the formation of a 1:1 complex.

Self-indication. A system is termed self-indicating when a metal ion initially present in a complex (B-complex) is progressively

transferred into the titration complex (T-complex) of differing absorbance upon addition of titrant. The conditions which must be satisfied so that a satisfactory titration curve is obtained are: the stability constant of the T-complex must be sufficiently greater than that of the B-complex so that transfer of the metal ion is essentially complete; the stability constant of the T-complex and also of the B-complex, when the latter is an optically significant variable, must be high enough to insure that neither is appreciably dissociated; the absorptivities of all species involved must be such that the slopes of the two straight branches of the titration curve are sufficiently different to permit a well defined intersection to be obtained upon extrapolation.

Example: The titration of copper in ammoniacal buffer of pH 10 with EDTA will give a curve as shown in Figure 1, Curve I. Copper initially is present as the less absorbing ammonia complex (at the wavelength chosen) and during the titration is transferred to the highly absorbing EDTA complex. Since ammonia and EDTA do not absorb in this region of the spectrum no account need be made of their optical properties.

Step-indication. The term step-indication describes a system which uses a complex-forming indicator which behaves in the same fashion as when acting as a visual indicator. In the photometric titration the curve that is obtained has the appearance of a step. The following conditions must be satisfied: the stabilities of the T-complex and I-complex (indicator complex) must be sufficient to prevent an unduly high degree of dissociation; the magnitude of the stability constants must be in the order  $K_B \ll K_I \ll K_T$ , where the subscripts refer to the

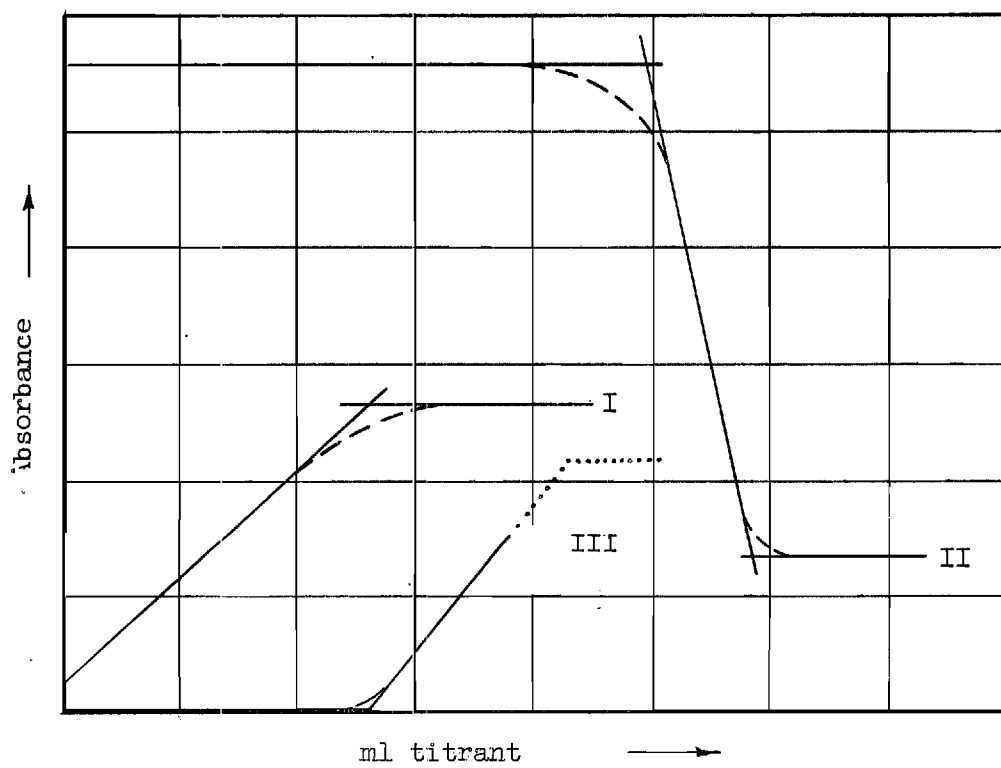


Figure 1. Photometric Titration Curves Obtained with Various Types of Indication.

appropriate complexes; the absorptivities of all species involved must be such that a well-defined intersection is obtained upon extrapolation.

Example: The photometric titration of copper at pH 4 with EDTA as titrant and PAN as indicator will give a curve similar to that in Figure 1, Curve II. The first horizontal portion of the curve is due to the transference of the copper from the aquo complex to the EDTA complex (T-complex), neither of which absorbs at the wavelength selected. In contrast to the self-indicating system this portion of the curve is not used for extrapolation and hence need not be plotted in practice. The second portion of the curve, where an abrupt change in absorbance occurs, is due to the transfer of the copper from the I-complex to the T-complex. The third portion of the curve results from the addition of colorless titrant after the end-point has been reached. It should be noted that this type of indication shows two intersection points, the second generally corresponding to the amount of metal present. The difference between the two intersection points is equivalent to the amount of indicator present.

Slope-indication. The term slope-indication will be used to describe end-point location via a self-indicating system, the metal of which is titrated after the metal to be determined. Again, the T-complex must be stronger than the corresponding B-complexes. The T-complexes and any optically significant B-complex must be strong enough to prevent any appreciable dissociation. In addition the condition

$$(K_T/K_B)_S \ll (K_T/K_B)_d$$

must be satisfied, i.e., the ratio of the stability constants of the T- and B-complexes of the self-indicating system (subscript "s") must be less than the ratio of the stability constants of the corresponding complexes of the metal to be determined (subscript "d"). These conditions insure that the metal to be determined is complexed before the metal in the self-indicating system. The absorptivities of all species involved must be such that the slopes of the titration curve before and after the end-point differ sufficiently to permit a precise location of the end-point by extrapolation.

Example: One of the first systems involving slope-indication was studied by Underwood when he titrated bismuth with EDTA using copper as the "photometric indicator," a term which he coined (24). Flaschka and Sawyer point out that this term is correct but that it may be confused with the general expression "indicator in a photometric titration," which includes step indication. Thus, the new term slope-indicator was introduced. In this example, it would be possible to determine both bismuth and copper since the titration can be carried out to a second change in slope where all of the copper has been titrated (see the dotted line in Fig. 1, Curve III).

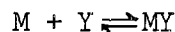
#### Photometric Titration Curves. Derivation and Discussion

Determining whether or not a reaction will be feasible for a titration can be accomplished by means of several calculations of varying degrees of complexity. Crude estimations can be made simply with the knowledge of the appropriate stability constants and the colors of the solutions. If necessary a very rough spectral curve is satisfactory for an approximation. On the other hand it is possible to calculate the

entire titration curve by using equations which have been derived in a rigorous manner.

Titration curves for acid-base systems have been derived by Goddu and Hume (25) and Higuchi, et. al. (26). Because of the increased number of equilibria, the calculation of complexometric titration curves is considerably more complicated than acid-base titration curves. The titration curves have been derived for all the cases of end point indication considered above. Step indicating systems have been theoretically investigated by Fortuin, Karsten and Kies (27) and by Ringbom and Wanninen (28). Reilley and Schmid have developed principles for determining the efficacy of metallochromic indicator. In general, they have shown that a sharp end point is obtained if the log of the ratio of the stability constant of the chelonate to the stability constant of the metal indicator complex is at least four, if the metal indicator complex stability constant is of the order of  $10^4$  to  $10^5$ , if the concentration of the indicator is low and if the concentration of the metal ion is high.

Flaschka (29) has derived equations for both the self-indicating and slope indicating mechanisms. The titration curve resulting from a mechanism involving step indication for the case of a single metal ion forming a 1:1 complex can be calculated from an equation which is derived in the following way. The titration reaction is



As usual the charges are omitted since they do not influence the manner of the derivation. If all species M, Y, and MY absorb at a given wavelength and Beer's Law is obeyed, the total absorbance, A, is equal to the sum of the absorbances of the individual species.

$$A = \sum_i \epsilon_i [i] l \quad (1)$$

Where  $\epsilon_i$  is the molar absorptivity of specie  $i$ ,  $[i]$  is the molar concentration of specie  $i$  and  $l$  is the light path length. During the titration both  $\epsilon$  and  $l$  remain constant, thus,  $\epsilon_i \times l = k_i$  and

$$A = \sum_i k_i [i] \quad (2)$$

At any point in the titration the following two equations are true:

$$C_M = [M] + [MY] \quad (3)$$

$$C_Y = [Y] + [MY] \quad (4)$$

From the equilibrium condition and the definition of the stability constant

$$K = \frac{[MY]}{[M][Y]} \quad (5)$$

This  $K$  should be the apparent stability constant which is related to the absolute stability constant according to the equation  $K_{app} = K/\alpha\beta$  where  $\alpha$  and  $\beta$  take into account the presence of hydrogen ions, other complex formers and other metal ions.\*

For convenience the units on the abscissa are defined in terms of  $\underline{a}$ , the complexation degree which is calculated according to

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\* See above p. 9.

$$\underline{a} = \frac{C_Y}{C_M} \quad (6)$$

At equilibrium the total absorbance is

$$A = [M]k_M + [MY]k_{MY} + [Y]k_Y \quad (7)$$

By appropriate substitution using (3), (4), (6) and (7), equation (8) results:

$$A = C_M [k_{MY} + k_Y(a-1)] + (k_M + k_Y - k_{MY})[M] \quad (8)$$

Using (3), (4), (5) and (6), M is written as a function of  $\underline{a}$  according to

$$[M] = \frac{[KC_M(1-a) - 1] + \sqrt{[KC_M(1-a) - 1]^2 + 4KC_M}}{2K} \quad (9)$$

Only the positive sign has physical meaning. This can be shown if the condition  $\underline{a} = 0$  is considered. The equation must then reduce to  $[M]=C_M$ . Combining (8) and (9) yields the final expression for the titration curve:

$$A = \frac{1}{2K} \left\{ 2KC_M [k_{MY} + k_Y(a-1)] + (k_M + k_Y - k_{MY}) \left[ KC_M(1-a) - 1 + \sqrt{[KC_M(1-a) - 1]^2 + 4KC_M} \right] \right\} \quad (10)$$

In many practical cases the complex former and the metal ion will either be colorless or at least will not absorb at the wavelength used. Then  $k_M = 0$  and  $k_Y = 0$ , and Equation (8) simplifies to

$$A = k_{MY}(C_M - [M]) \quad (11)$$

An examination of (10) will show the importance of the value of the parameter  $KC_M$  with regard to the shape of the titration curve. As  $KC_M$  becomes smaller the titration curve deviates more and more from a straight line before the end point. After the end point the curve becomes horizontal only after the addition of a large excess of the titrant if  $KC_M$  is small. However, for a value  $KC_M = 50$  it is still possible to obtain a useful titration curve as shown in Figure 2. The advantage of the photometric method is evident if it is compared to the pM curve which is shown in Fig. 2 also.

The value of the parameter  $k$  must also be considered. The previous example assumed a value of 100. If an insufficient value must be used then the situation might be improved practically by using an increased light path. Furthermore, in practice the parameter  $a$  cannot be used since  $C_M$  does not remain constant because of dilution when titrant is added. The usual volume correction may be applied:

$$C_M = \frac{C_M^0 V}{V+b} \quad (12)$$

where  $C_M^0$  is the starting concentration,  $V$  the initial volume and  $b$  is the volume of titrant added. Also

$$C_Y = \frac{mb}{V+b} \quad (13)$$

where the symbols have the same meaning as in the previous equation and  $m$  is the molarity of the titrant. Combining Equations (6), (12) and (13) yields

$$a = \frac{mb}{C_M^{\circ}V} \quad (14)$$

which is substituted in the equation for the titration curve. Thus

$$A = \frac{C_M^{\circ}V}{V+b} \left[ k_{MY} + k_Y \left( \frac{mb}{C_M^{\circ}V} - 1 \right) \right] + (k_M + k_Y - k_{MY})[M] \quad (15)$$

where  $[M]$  is calculated according to

$$[M] = - \left[ KC_M^{\circ} \frac{V}{V+b} \left( \frac{mb}{C_M^{\circ}V} - 1 \right) + 1 \right] \frac{\sqrt{\left[ KC_M^{\circ} \frac{V}{V+b} \left( \frac{mb}{C_M^{\circ}V} - 1 \right) + 1 \right]^2 + 4KC_M^{\circ} \frac{V}{V+b}}}{2K} \quad (16)$$

If only MY absorbs then the simplified equation results

$$A = k_{MY} \left( \frac{C_M^{\circ}V}{V+b} - [M] \right) \quad (17)$$

The simplified equations are used when  $V \gg b$ . The minimum value of  $KC_M^{\circ}$  which will give a titration curve from which the end point can still be established will not be calculated because of the mathematical difficulties. Instead  $KC_M^{\circ}$  values of about 200 to 500 will be assumed to be satisfactory and then the titrations will be performed and these assumptions tested by experiment.

In general dilution is handled experimentally in two ways. The titrant used may be very concentrated at least according to limits imposed by its solubility. It can be delivered with a micro-burette and hence dilution can be ignored. Dilution can be corrected by means of the equation presented above. However, this correction applies only to

the "color" dilution. Upon dissociation the color intensity decreases and this change will not be corrected. The effect is more important for the case of weaker complexes.

Flaschka (29) has also considered the case of slope indication or more generally the titration of two metals successively in the same solution without the use of an indicator.

Two metals, M and N, are to be titrated by the chelon Y. The effect of dilution will now be ignored. The stability constants are

$$K_{MY} = \frac{[MY]}{[M][Y]} \quad (18)$$

$$K_{NY} = \frac{[NY]}{[N][Y]} \quad (19)$$

The conservation equations which hold are

$$C_M = [M] + [MY] \quad (20)$$

$$C_N = [N] + [NY] \quad (21)$$

$$C_Y = [MY] + [NY] + [Y] \quad (22)$$

It is useful to estimate the possibility of titrating two metals in the same solution by the difference in their stability constants. In order to simplify the derivation, the quotient  $Q$  is used and defined as

$$Q = \frac{K_M}{K_N} \quad (23)$$

The photometric titration will be satisfactory only if the molar absorptivities of the metal ions (free or complexed) are such that they

can be differentiated. This factor is governed by the  $k$  value ( $k = \epsilon \cdot l$ ).

Because of the complicated nature of the system the derivation is made in the following manner. An expression for  $Q$  is derived using the previous equations so that the following form is obtained:

$$Q = \frac{C_M - [M]}{[M]} \times \frac{C_N - C_Y + (C_M - [M]) + \frac{C_M - [M]}{[M]K_M}}{C_Y - (C_M - [M]) - \frac{C_M - [M]}{[M]K_M}} \quad (24)$$

This expression is then solved for  $C_Y$ :

$$C_Y = \frac{C_M - [M]}{[M]} \left( \frac{C_N}{Q + \frac{C_M - [M]}{[M]}} + [M] + \frac{1}{K_M} \right) \quad (25)$$

Since this expression when solved for  $[M]$  is third order the following approach is made in calculating the titration curve. Values of  $[M]$  are assumed and  $C_Y$  calculated. Using  $C_Y$  and  $[M]$  a value for  $Q$  can be calculated. Then from the definition of the complexation degree  $\alpha$  may be calculated from

$$\alpha = \frac{C_Y}{C_M} = \frac{1}{C_M} \cdot \frac{C_M - [M]}{[M]} \left( \frac{C_N}{Q + \frac{C_M - [M]}{[M]}} + [M] + \frac{1}{K_N} \right) \quad (26)$$

All of the necessary relations are now available for calculating the photometric titration curve. However, the following simplifying assumptions are made; metal M forms the more stable complex and is titrated first and the only species absorbing at the chosen wavelength is NY.

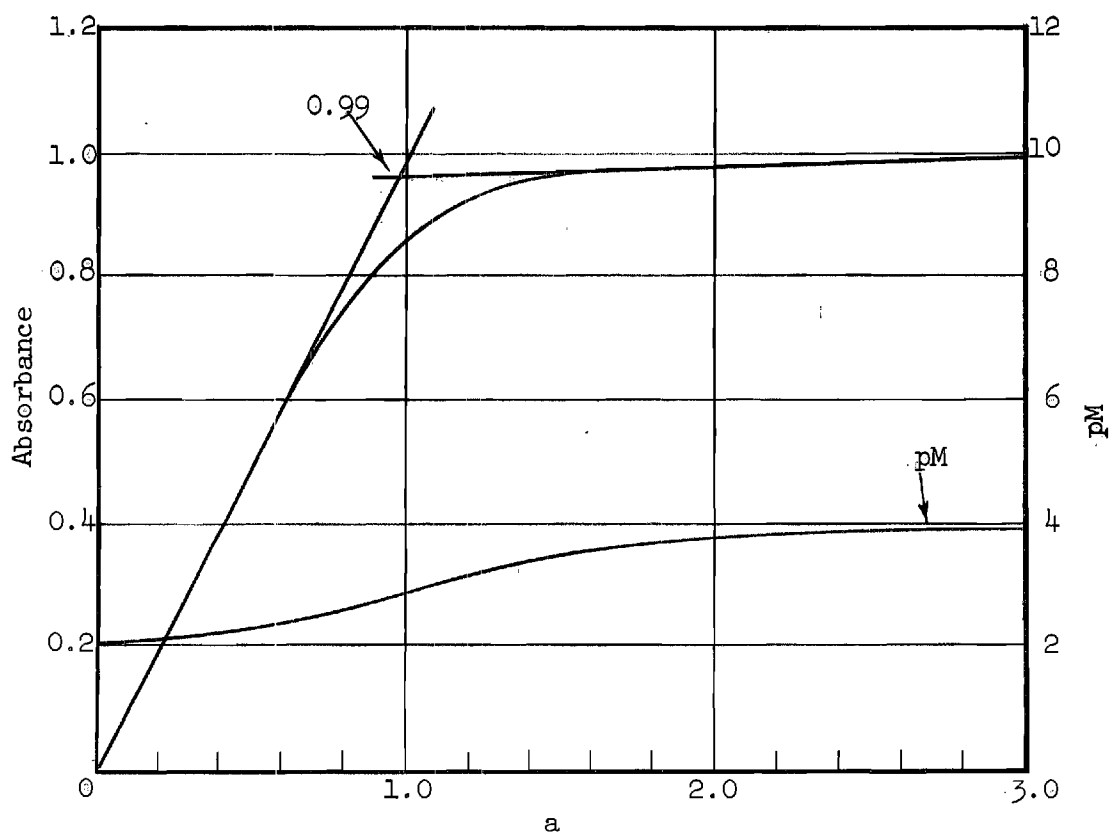


Figure 2. Photometric and pM Titration Curves for the Determination of a Single Metal.

$$K = 5 \times 10^3, C_M = 10^{-2}, k_{MY} = 100, KC_M = 50$$

Thus:

$$A = k_{NY} [NY] = \left[ k_{NY} \quad \alpha C_M - (C_M - [M]) - \frac{C_M - [M]}{[M]K_M} \right] \quad (27)$$

The assumed  $[M]$  values are substituted in the above equation to calculate  $A$  and  $a$ . A representative curve for a situation which definitely gives a poor pM curve but still is usable for the photometric titration is shown in Figure 3. The course of the titration curve depends on  $\alpha$ . For a large value of  $\alpha$  the titration curve will show a sharp break at the first end point. If  $\alpha$  is small the first end point shows a curvature which in a severe case might be difficult or impossible to locate. It can be shown that for a value of  $\alpha = 100$  (when a large  $K_{MY}$  is used) good curves still result. The situation described is an ideal one since concentration conditions and  $k$  values may be unfavorable.

Corrections for dilution increase the algebraic difficulties and since the results are limited by other factors the labor required may not be worthwhile. Since apparent stability constants are used and since they may have been determined for an ionic strength far different from the conditions to be actually encountered the calculation of the curve is not worthwhile. In addition the formation of proton and hydroxo complexes will cause the experimental results to differ from the calculated results. In those cases where such factors arise the most reasonable alternative is to determine by means of experiments whether or not the titration will be successful.

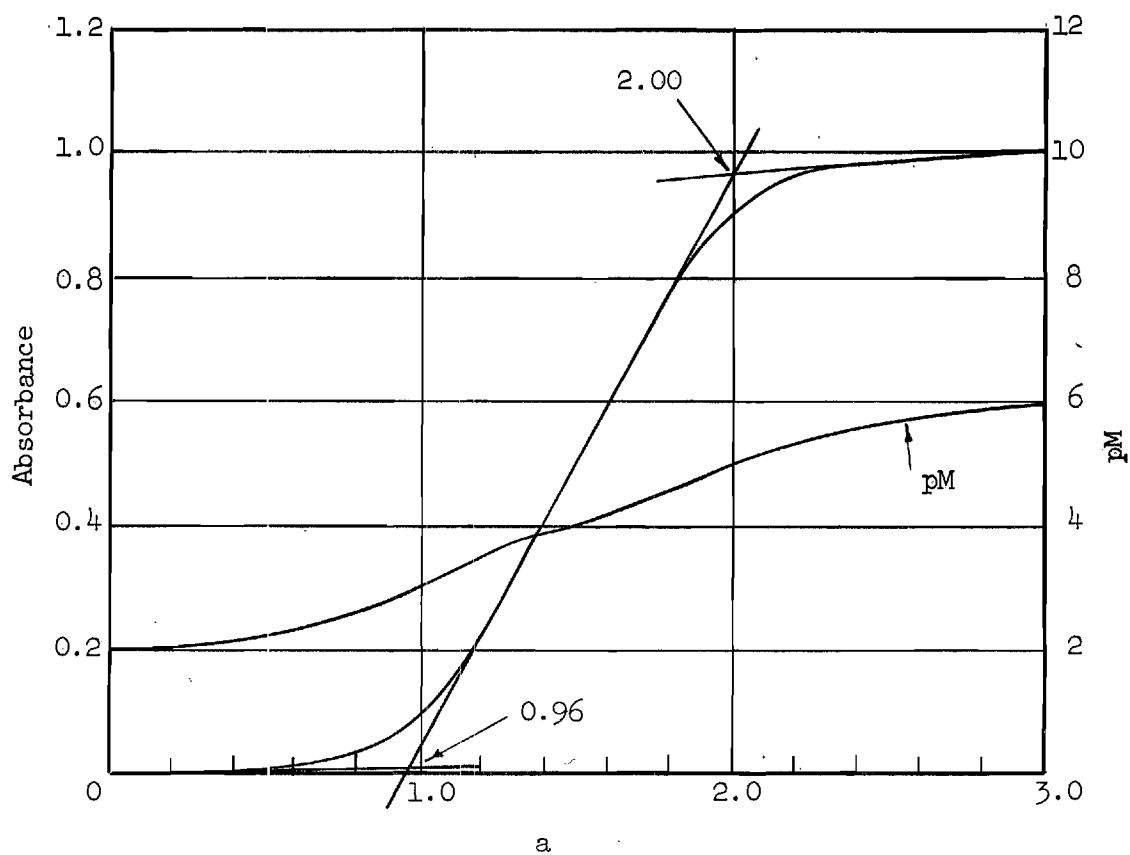


Figure 3. Photometric and pM Titration Curves for the Consecutive Determination of Two Metals.

$$K_M = 10^6, K_N = 10^4, \varrho = 100, c_M = c_N = 10^{-2},$$

$$k_M = k_N = k_Y = 0, k_{NY} = 100$$

### Historical Background and Review

Widespread interest in the application of photometric titrations has occurred only within the last fifteen years. Detailed aspects of this development are available in several reviews (30, 31, 32, 33) and in a book by Headridge (34).

Instrumental development and application of photometric titrations to various systems have developed together. In general instruments have been constructed along two lines. Phototitrators have been constructed from basic components either by individuals as their needs demanded or more recently by large manufacturers on a commercial basis. On the other hand, spectrophotometers, such as the Beckman instruments and others, have been modified in ways so as to enable the performance of the titration in the cell compartment. Instruments have been built which record the first and second derivatives of the titration curve. The main disadvantage of a modified spectrophotometer has been pointed out by Flaschka and Sawyer (35). This is the requirement that the titration cell must be housed in a light tight compartment. This will limit the convenience of the photometric titration.

Probably the first and simplest approach to a photometric titration was achieved by Tingle (36). With a hand spectroscope, he observed the color change of an indicator during the titration of a highly colored alkaloidal solution. Muller and Partridge are generally credited with the first photometric titration (37). They constructed a phototitrator which performed automatically. The burette valve was actuated at the end point by an electrical signal caused by the large change in the photo cell current when the indicator changed color. These investigators

recognized that the use of monochromatic light was important. The method saved time and labor and in many cases was more precise than a visual titration. For example, it could be applied to permanganate, dichromate and iodometric titrations with a much higher precision than possible by a visual estimation. Extension to precipitation titrations by measurement of the reflected light from turbid solutions was predicted.

Goddu and Hume (25) were the first to modify a spectrophotometer and apply it to photometric titrations. In a series of studies they investigated acid-base titrations and evaluated the method with regard to selectivity.

Other investigators have applied the method to redox titrations to improve the detection of the end point using systems which are difficult for the eye to detect because of dragging end points or background colors. A large area encompassing precipitation reactions has been studied by Bobtelsky (38). Organic reactions have been used for the basis of several photometric titrations. Both inorganic and organic reactions have been carried out in non-aqueous solvents to further extend the application of this method. In addition several successful determinations are based on the use of UV radiation. A more fundamental use of photometric titrations is the determination of combining ratios of complex and metal ion. The method originated from the work of Yoe and Jones (39). In addition it is possible to obtain stability constants from the titration curve especially for complexes of moderate stability since it is important that some dissociation occur at the end point in order to apply this method. The applications introduced above are available in more detail in the book by Headridge (34).

Since 1960, research has followed similar lines. Acid-base titrations, especially weak organic compounds have been studied extensively and usually in non-aqueous solvents (41,42). Both step and slope indication has been employed. Very recently a study of the titration of carbon dioxide, bicarbonate and carbonate was reported based on the UV absorption of the carbonate ion (43). Uranium and plutonium have been titrated using redox reactions as the basis of the analysis (44,45). A method for determining mixtures of ferrous and ferric iron based on a redox titration was developed (46). A titration based on the reaction between 1,3-dimethylvioluric acid and alkaline earths and alkali metal ions has been studied (47). Another inorganic non-chelometric titration reported is the determination of fluoride using thorium nitrate as the titrant (48). In the miscellaneous category an end point based on the luminescence accompanying certain acid-base titrations has been studied (49). A differential end point technique applicable to acid-base and chelometric titrations was developed recently (50).

The end point in complexometric titrations has been located by this method in many kinds of determinations but the major portion of them are based on the reaction of EDTA with a metal ion. The value of combining the selectivity gained by the use of chelons as titrants and photometric end point detection in metal ion analysis has been appreciated but not fully exploited on a practical scale. Headridge has summarized complexometric titrations that have been devised up to about 1960 (34). Since that time a thorough investigation of all the possibilities has not been made. Some of the studies which have been made will be briefly summarized now: Iron has been titrated in the presence

of aluminum (51), micro amounts of copper, nickel, lead, zinc and uranium have been titrated with 1,nitroso-2,naphthol in N,N-dimethylformamide (52), the sum of iron, cobalt and copper with EDTA using a metalfluore-chromic indicator has been done on an automatic derivative recording apparatus (53), calcium in blood serum has been titrated with EDTA (54), small amounts of rare earths have been titrated with EDTA and arsenazo indicator (55) and calcium and magnesium have been titrated with EDTA (56).

## CHAPTER III

## EQUIPMENT AND CHEMICALS

Photometric Titrator

The instrument used for this research was the photometric titrator designed and constructed by Flaschka and Sawyer (57). Most photometric titrators reported in the literature have been modified commercial filter photometers or spectrophotometers. These modifications are often difficult to make and furthermore hamper the application of the instrument for its intended use. But the greatest disadvantage is that the titration cell must be housed in a light tight compartment. Thus, the problem becomes one of building a cell so that it can be used with the instrument thus limiting the size and shape of the vessel. The cell must be large enough so that the entire beam passes through it and it must be small enough to fit into the compartment. It is most convenient if the titration cell can be used in the open so that a range of sizes of vessels can be used. In addition the operator can examine the cell and its contents in order to detect such effects as turbidity, presence of dust particles and the position of the stirrer.

The design of the apparatus is not as critical as for a general purpose photometer but certain important requirements must be fulfilled. High electrical and mechanical stability are necessary so that no fluctuations or displacements occur during the titration. No provision is available for rechecking the zero line with a reference solution so

high optical stability must be maintained during the titration. The position of the titration cell is not critical as long as it remains unchanged during the titration. The design of the titration cells is not critical either. The faces of the vessels need only be approximately plane and parallel. The exact length of the light path as well as the optical purity of the faces are of no moment.

#### Components of the Photometric Titrator

A schematic diagram of the phototitrator is shown in Figure 4. The light source, a G.E. Bulb, type 425, is connected through a variable resistor to a 6 volt lead storage battery. The bulb draws only a small current which guarantees a negligible voltage drop. A diaphragm, which has a wedge-shaped opening, is placed in the light path to enable control of the light intensity optically. A condensing lens next produces a parallel beam of light. These components are mounted in a box at one end of the base of the titrator. The titration vessel is held in place by a clamp which is in turn held securely by two springs to the light detector compartment. This compartment, at the opposite end of the base of the titrator, is constructed so that an interference filter can be inserted between the titration cell and the photodetector. Interference filters are used to provide better monochromaticity. The light is then focussed on the light detector by another lens. The photodetector is a solid state device consisting of a symmetrically diffused NPN silicon junction mounted in the focal plane of a small lens. This device, (a Texas Instrument.Co.; 1N2175, photoduodiode) is 12 mm in length and 2 mm in diameter; the photosensitive surface is only a fraction of 1 mm<sup>2</sup>

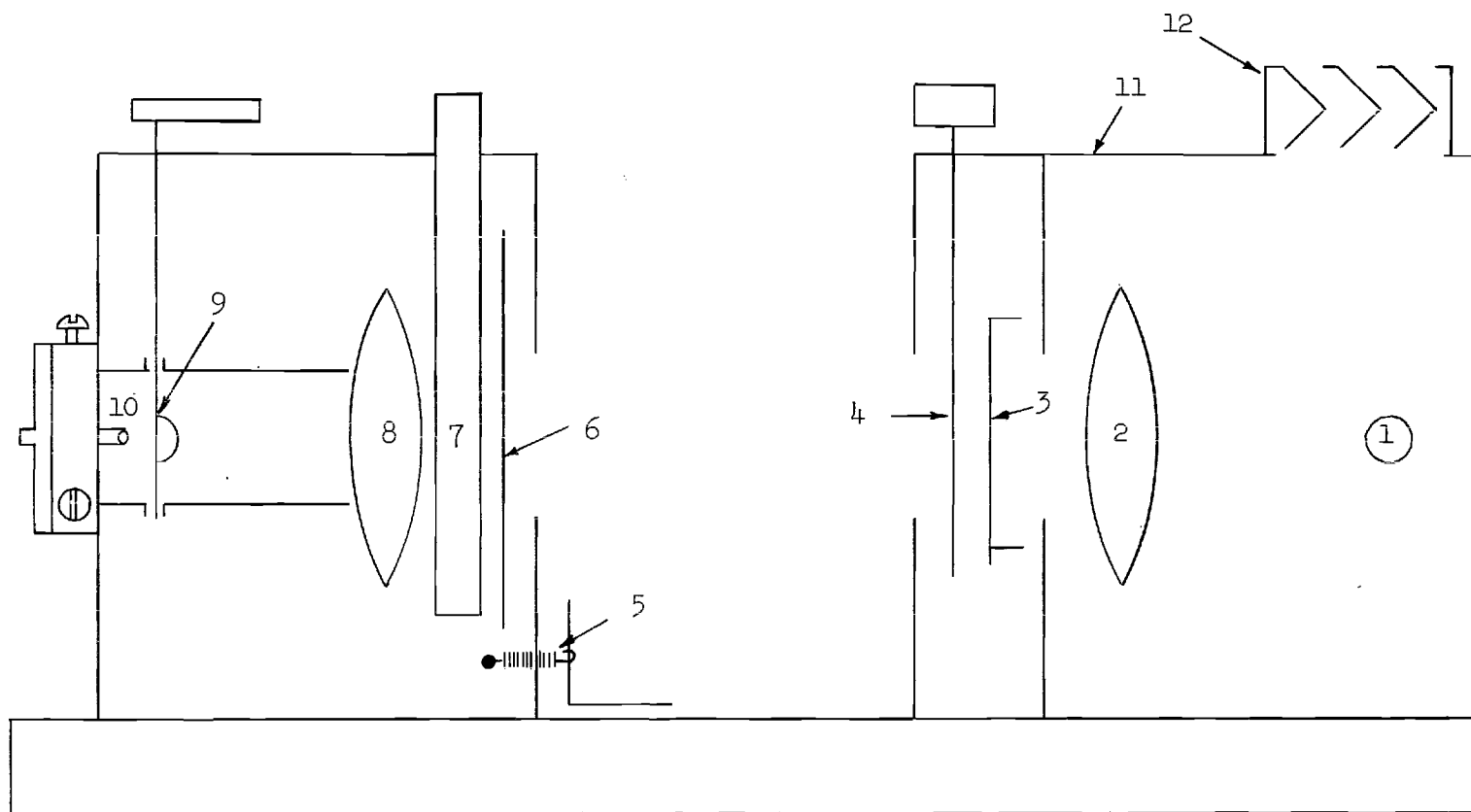


Figure 4. Diagram of the Phototitrator.

- |                 |                |                        |                          |
|-----------------|----------------|------------------------|--------------------------|
| 1. Light source | 4. Shutter     | 7. Interference filter | 10. Photodiode           |
| 2. Lens         | 5. Cell holder | 8. Lens                | 11. Light source housing |
| 3. Diaphragm    | 6. Diaphragm   | 9. Shutter             | 12. Air vent             |

in area. Sensitivity, as well as spectral response characteristics are very satisfactory for the present purposes. The photodetector is connected to a galvanometer (a Rubicon Instruments Co. device) with a sensitivity of  $7 \times 10^{10}$  amp/mm. Compensation for dark current is obtained by a zero-adjusting circuit. A zero-suppressor circuit is also included to enable scale expansion.

The advantage that the titration cell is open to the ambient light is the result of the use of the very small photodiode. In order for light to strike the diode it must pass through the focussing lens and therefore pass within a very small angular range. In addition the stray light must pass through the interference filter. The arrangement is so effective that the motion of a high powered flash-light about the apparatus could not be detected. The entire instrument is painted a flat black both inside and out. All external wiring was made of shielded cable to avoid spurious response by the galvanometer.

#### Titration Cells. Stirring.

The cells were constructed of plate glass cut into rectangular pieces and bonded with epoxy resin. Cell volumes of approximately 100 to 200 mls and light paths of 1.5 to 3 cm were constructed and proved to be satisfactory for most titrations in the macro scale. Cells were also constructed of Pyrex glass so that titrations could be made at elevated temperatures. Heating was accomplished by a spiral wire inserted into a U-shaped Pyrex glass tube.

The stirrer is a glass rod with a small propellor at the lower end and driven by a 6 v dc motor. The direction of rotation and pitch

of the propellor are such that the motion of the stirred liquid is from bottom to top. This prevents the formation of air bubbles which could interfere with the titration.

### Other Instruments

#### Spectrophotometers

All spectral curves were made with a Cary Model 14 Recording spectrophotometer with the kind permission of the Coca-Cola Company. This aid is gratefully acknowledged.

#### pH Meter

All pH measurements were made with a Leeds and Northrup pH meter. The device was calibrated with potassium acid tartrate (saturated solution, 25°C, pH 3.57).

#### Automatic Burette

A Sargent Automatic Constant Rate Burette Model C was used to deliver the titrant with an uncertainty of  $\pm 0.002$  ml.

#### Glassware

The usual volumetric ware such as calibrated volumetric flasks, calibrated pipettes, calibrated burettes, flasks and beakers was used as required.

### Chemicals

#### Disodium Ethylenediamine Tetraacetate, Dihydrate (EDTA)

J. T. Baker Chemical Company "Baker Analyzed" Reagent EDTA was dissolved in de-ionized water. A few pellets of sodium hydroxide were required to hasten and aid the dissolution. The solution was prepared

to be approximately 0.1 M and standardized against a standard copper solution.

Ethyleneglycol-bis(aminoethyl)-tetraacetic acid (EGTA)

The G. F. Smith Chemical Company EGTA was used to prepare approximately 0.1M solutions of the chelon. Dissolution was aided by the addition of a few pellets of sodium hydroxide. Turbid solutions were filtered. The EGTA solutions were standardized against calcium chloride solutions prepared from J. T. Baker reagent grade calcium carbonate. The indicator Calcon was used to detect the end point.

Triethylenetetramine, Disulfate (Trien)

The trien solutions were prepared by dissolving the salt in de-ionized water with the aid of a few pellets of sodium hydroxide. Turbid solutions were filtered. The approximately 0.1 M solutions of trien were standardized against standard copper solutions and the end point detected photometrically.

Eriochrome Black T Indicator Powder (Erio T)

One gram of the solid Erio-T was thoroughly ground with 200 gm of reagent grade sodium chloride. J. T. Baker Reagent Grade Erio-T and sodium chloride were used. The indicator powder was stored in tightly stoppered polyethylene bottle.

Murexide Indicator Powder

The J. T. Baker reagent was ground with sodium chloride in the same proportions as the Erio-T indicator. The powder was stored similarly.

Pyrocatechol Violet Indicator (PCV)

J. T. Baker Reagent Grade powder was used. Approximately 50 mg of the dye was dissolved in 50 ml of water and stored in a polyethylene bottle. The solution is stable for more than two months.

### Calcon Indicator Powder

The powder was prepared in the same manner as the Erio-T powder.

### L-Ascorbic Acid

Eastman Organic Chemicals reagent was used.

### Triethanolamine

J. T. Baker Reagent Grade material was used to prepare approximately 20 per cent (v/v) aqueous solution for masking reagent.

### Potassium Cyanide

J. T. Baker Reagent Grade solid was used for masking.

### Bases

DuPont concentrated ammonium hydroxide was used. J. T. Baker Reagent Grade sodium hydroxide pellets were used to prepare solutions.

### Acids

DuPont concentrated hydrochloric, nitric and sulfuric acids were used to prepare solutions.

### Copper Nitrate Solution

J. T. Baker Reagent Grade copper wire was cleaned and dried and accurately weighed to give exactly 0.1000 M solutions. The wire was dissolved in nitric acid, the solution carefully warmed to dispel oxides of nitrogen and diluted to the mark. This solution was used to standardize the EDTA and Trien solutions.

### Calcium Chloride Solution

J. T. Baker Reagent Grade calcium carbonate was accurately weighed and dissolved with hydrochloric acid to prepare standard solutions. The solution was carefully warmed to dispel excess carbon dioxide then diluted to the mark after cooling to room temperature. This solution was used to standardize the EGTA solution.

### Other Metal Salt Solutions

J. T. Baker reagent grade metal salts were used to prepare the aqueous solutions. If the salt undergoes hydrolysis a few drops of nitric acid was added.

### Hydrogen Peroxide

J. T. Baker Reagent Grade 30 per cent hydrogen peroxide was used for an oxidizing agent.

### Tartaric Acid

J. T. Baker Reagent Grade solid tartaric acid was used.

## Buffer Solutions

### Buffer pH 10

J. T. Baker Reagent Grade ammonium chloride and DePont ammonium hydroxide were used to prepare the buffer. Ammonium chloride (70 gm) and ammonium hydroxide (570 ml) were combined and diluted to one liter. The solution was stored to be used as a stock solution.

### Buffer pH 5

J. T. Baker sodium acetate and DuPont hydrochloric acid was used. Sodium acetate (27.3 gm) and hydrochloric acid (60 ml of 1 N) were combined and diluted to one liter.

## Standardization Procedures

### EDTA Standardization

An aliquot of the copper solution was pipetted into a flask and buffer of pH 10 was added until a deep blue color formed and no turbidity observed. This was diluted with deionized water. Murexide indicator

was added and the solution titrated with EDTA until the color changed from yellow (green) to deep violet.

#### EGTA Standardization

An aliquot of the standard calcium chloride solution was pipetted into a flask and diluted with de-ionized water. This was followed by the addition of sodium hydroxide solution and Calcon powder. The solution was titrated until the red color changed to blue.

#### Trien Standardization

An aliquot of the standard copper nitrate solution was pipetted into a photometric titration cell. The solution was diluted and buffered with ammonium acetate. This solution was used to set 100 per cent transmittance. The solution was titrated with trien. Transmittance values were recorded, converted to absorbance and plotted versus the volume of trien added on linear graph paper. The end point was located by extrapolation.

### Standardization of Metal Ion Solutions

#### Cobalt and Nickel

An aliquot of the metal ion solution was pipetted into a flask and buffer pH 10 added. Powdered murexide was used as the indicator. The solution was titrated with EDTA standard solution until the color of the solution changed to a deep violet.

#### Magnesium, Cadmium and Zinc

The same procedure as used for copper, etc., was used for these metals except that Erio T was the indicator. The titration was terminated when the solution changed to a deep blue.

## CHAPTER IV

OPERATION OF THE PHOTOMETRIC TITRATOR  
AND THE TITRATION PROCEDUREObtaining and Recording of Data

The output of the photodiode is an electrical current which results when the transmitted light strikes the photo-sensitive portion of the photodiode. This output is displayed on the galvanometer. The current is proportional to the intensity of the transmitted light. The procedure for establishing the transmittance scale for a photometric titration is the same as used for normal spectrophotometric measurements. The zero per cent transmittance point is adjusted with the shutter closed and the 100 per cent transmittance point is adjusted with water (or blank solution) in the light beam. Now the galvanometer can indicate transmittance readings between zero and 100 per cent T.

One way to obtain the titration curve is to place the titration vessel filled with water (or blank) in the light beam, adjust the zero point with the shutter closed and then, with the shutter open, adjust 100 per cent T with the diaphragms. The water is removed from the titration vessel and replaced with the solution to be titrated. It is also possible to add an aliquot of the unknown solution to the blank solution which already contains the buffer, masking agents and any other auxiliary reagents required for the titration. The titration is started and the transmittance readings are recorded after each increment of titrant is added.

Since the absorbance, not the transmittance, is related linearly to the volume of titrant, the results may be treated in two ways. The per cent T is first transformed to absorbance by the use of tables of logarithms (it is convenient to prepare a table which contains the conversions already calculated) and the latter is plotted on linear graph paper, or per cent T is plotted directly on semi-logarithmic paper. The latter procedure is simpler.

#### Considerations for Obtaining Higher Precision

The course which a titration curve may follow, in general, is of two kinds: the absorbance will either increase or decrease during the titration. Furthermore, if the changes in absorbance (transmittance) cover a large portion of the scale (preferably the entire scale) the instrument is being used to obtain the highest precision possible.

For the case when the transmittance decreases during the titration (absorbance increases) and the solution has a high initial absorbance, higher precision can be obtained by using the solution to be titrated as the reference solution (57). The precision of the measurement is thereby increased by a factor of  $100/T_1$ , where  $T_1$  stands for the per cent transmittance of the solution with water used as a 100 per cent T reference. The following problem will illustrate the advantage of this modification. Assume that the transmittance is adjusted to 100 per cent with water and zero per cent T with the shutter closed. When the sample is placed in the light beam the reading is 50 per cent T. Assume next that during the titration the transmittance decreases to a final value of 30 per cent T. Only 20 of the 100 divisions on the

scale have been used. Now the 100 per cent T point is adjusted with the starting solution instead of water. This requires that the light intensity be increased by means of the diaphragms or electrically through a variable resistor. In this example the light intensity must be doubled. With regard to water as the reference, the 100 per cent T point is outside the galvanometer scale to the right, viz., at 200 S.D. (scale divisions). Thus the scale reads from 50 per cent T on the right to zero per cent T on the left. The scale range which will now be used in this titration will be from 100 S.D. to 60 S.D. or 40 S.D.

When using one-cycle semi-logarithmic paper, however, the only differences in the plots of these two titration curves is a parallel shift of one curve with respect to the other in the direction of the ordinate. The actual span on the ordinate is the same for each curve, because the change in absorbance units for the particular titration is the same regardless of the method of plotting results or instrumental adjustment. For the example, the absorbance change  $\Delta A$ , is

$$\Delta A = -\log(0.50) + \log(0.20) = 0.30 - 0.70 = -0.40$$

which is the same ordinate distance in length on semi-logarithmic paper whether the plot is from 50 to 30 S.D. or from 100 to 60 S.D. However, the higher precision gained in the galvanometer scale reading is nullified by the closer spacing of the lines on the graph paper. Thus the transmittance readings must be converted to absorbances and the plot drawn on linear graph paper so that an appropriately higher precision scale can be chosen.

If during the titration the transmittance increases, the attainment of higher precision must be handled differently. Obviously adjusting 100 per cent T with the solution to be titrated would result in the galvanometer pointer moving off scale at some time during the titration. Assume that the solution again shows 50 per cent T when measured using water as the reference solution (100 per cent T) and that during the titration the transmittance increases to 70 per cent. The suggestion that, instead, the starting solution should be used to adjust the zero per cent T point by electrical adjustments will give an incorrect titration curve. This can be shown in a general manner (58). Confusion can be avoided if one keeps in mind that measurements are made using a real galvanometer scale divided into 100 scale divisions. Expansion of the scale will result in different values being attached to the S.D. It is helpful, also, to imagine that the scale extends off to the right and left sides of the real scale. For example, in the first problem the 100 per cent T point was another 100 S.D. to the right, i.e., at 200 S.D. When S.D. are referred to in the discussion they may not necessarily refer to the numbers or the markings on the real galvanometer scale. Also the relationship between S.D. and transmittance values should be kept in mind.

Assume that the zero point for a titration system is at M S.D. Adjustment of 100 per cent T is made and this corresponds to N S.D. When the sample is introduced into the light beam, the reading is P S.D. The per cent transmittance corresponding to the reading P S.D., with respect to the total scale is given by the relation

$$(N-M) : 100 = (P-M) : \% T$$

which yields

$$\%T = 100(P-M)/(N-M)$$

Hence the absorbance is given by

$$A = -\log\left(\frac{\%T}{100}\right) = -\log\left(\frac{P-M}{N-M}\right) = \log(N-M) - \log(P-M)$$

Consider first what occurs if zero transmittance corresponds to the real zero point on the galvanometer scale i.e.,  $M=0$ . The expression for absorbance simplifies to

$$A = \log N - \log P$$

Thus the absorbance is directly proportional to the logarithm of the reading from the galvanometer scale and the procedure of plotting  $\log P$  on linear paper or  $P$  on logarithmic paper will yield the correct titration curve.  $P$  must, of course, occur on the readable portion of the galvanometer scale.  $\log N$  remains constant during the titration so that addition or subtraction of this value will shift the curve up or down but will not influence the end point. By subtracting  $\log P$  from 2 it is insured that the titration curve starts at the zero point of the ordinate.

If the galvanometer zero does not correspond to zero light intensity, then  $M \neq 0$ . This would be the situation first suggested, i.e., setting zero on the galvanometer with the unknown solution. The value of  $\log(N-M)$  is still a constant but it would no longer be correct to plot  $\log P$ . Instead  $\log(P-M)$  must be plotted. This requires that the value of  $M$  (in S.D.) be known. In practice  $M$  can be determined by

setting the galvanometer zero with the shutter closed and then introducing the solution into the light beam. The galvanometer will now read M scale divisions, so that if the galvanometer is now adjusted to zero again electrically, it is necessary to add the value of M to each reading during the titration to obtain the correct curve. The electrical adjustment may be performed with an adjustable voltage connected to the terminals of the galvanometer to allow the entire scale to be shifted an arbitrary amount in either direction. Regardless of the value of M it is possible to subtract  $\log (P-M)$  from any arbitrary constant in order that the titration curve starts at the zero point of the ordinate. If the zero is shifted to -100 S.D. ( $= M$ ) and the initial solution is used to set 100 S.D., the logarithms of  $P - 100$  are subtracted from 2.301 ( $= \log 200$ ) in order to start the curve at the zero point of the ordinate.

There are two situations in which M is not set equal to zero. First, such a setting may be used in order to achieve increased precision in the measurement when transmittance decreases during the titration. Second, it may be necessary to set M less than zero so that the galvanometer readings do not go beyond the readable scale of the galvanometer during a titration where the transmittance increases.

When the transmittance decreases during the titration a greater increase in precision can be obtained by displacing the zero point. (i.e., the galvanometer setting with no light reaching the photodiode). Consider a hypothetical titration during which the transmittance decreases from 50 per cent T to 40 per cent T (water is used to set 100,

per cent T). Using the solution to be titrated to set 100 per cent T the precision can be doubled. The transmittance will now decrease from 100 S.D. to 80 S.D. However, the precision can be increased again. First the 100 per cent T is established with solution to be titrated. By moving the galvanometer needle through the application of an additional voltage the 100 S.D. setting is shifted to the zero S.D. setting. Thus the zero point is shifted 100 S.D. to the left. Then with the same solution in the cell the scale is expanded by increasing the intensity of the light so that the galvanometer needle is set at 100 S.D. The galvanometer deflection during the titration is now from 100 to 60 S.D. The precision with which the galvanometer can be read has been quadrupled.

For a system where the transmittance increases during the titration, the zero point (i.e., the galvanometer setting with no light reaching the photodiode) may be adjusted to -100 S.D. First, zero is set by not allowing any light to reach the photodiode. Then 100 S.D. setting is adjusted by increasing the light intensity; this is done without using a reference solution. The 100 S.D. setting is then displaced to the left by applying the appropriate voltage in order to compensate the voltage which gives rise to the 100 S.D. setting. Thus the galvanometer zero is shifted to -100 S.D. The solution to be titrated is placed in the cell and by adjusting the light intensity the galvanometer needle is set on zero. During the titration the galvanometer needle will deflect upwards. If large changes in absorbance occur the pointer may leave the galvanometer scale. This can be avoided by decreasing the sensitivity through selection of a less negative value of M.

Several pre-titrations may be necessary to determine this. This inconvenience may be circumvented by operating with a "sectioned" titration curve (58). Whenever the pointer reaches 100 S.D. a resetting to the zero point of the galvanometer is performed by changing the light intensity. This procedure may also be used when the pointer reaches the zero point of the galvanometer scale during a titration in which the transmittance decreases.

## CHAPTER V

## THE CONSECUTIVE TITRATION OF CALCIUM AND MAGNESIUM

Introduction and Review

The analysis of solutions containing mixtures of calcium and magnesium is possible using gravimetric procedures or a combination of a gravimetric procedure and titration. The latter method should really be classified as a separation. Calcium can be separated from magnesium by precipitation as calcium oxalate. But even this procedure must be preceded by a separation of all metal ions except magnesium and the alkali metals. Calcium oxalate can be precipitated homogeneously, dried or ignited and weighed as the oxalate, carbonate or oxide. Numerous sources of error exist. Magnesium oxalate is both occluded and postprecipitated. If the sodium ion concentration is high sodium oxalate is coprecipitated. If the magnesium to calcium ratio is high the separation is very unsatisfactory. Small amounts of calcium escape precipitation and must be recovered from the magnesium pyrophosphate if magnesium is determined in this way. The classical permanganometric or cerimetric procedure depends on the precipitation of calcium oxalate and hence some of the errors which occur in the gravimetric procedures still exist. After the calcium is removed the magnesium can be precipitated and ignited to the pyrophosphate or it can be precipitated with oxine and titrated with a standard solution of potassium bromate-potassium bromide.

The introduction of EDTA simplifies the analysis of Ca and Mg mixtures greatly. The "classical" complexometric determination of calcium and magnesium is based on the use of two aliquots. In the first aliquot calcium is titrated at a pH greater than 12 where magnesium precipitates as the hydroxide. In the second aliquot the sum of the two metals is determined at pH 10. The magnesium content is determined by difference. This procedure is a significant improvement over the methods previously available. However, certain disadvantages and limitations persist and many papers have been published describing attempts to overcome them.

The method of masking magnesium by hydroxide precipitation has some disadvantages. The precipitate will include some calcium, thus causing an error which will become intolerably high when a certain Mg:Ca ratio is exceeded. This error may be significantly reduced by adding an excess of EDTA over the amount of calcium present and then precipitating the magnesium as hydroxide. The excess EDTA is then back-titrated in an aliquot of the clear supernate (59). The procedure should be strictly classified as separation and not as masking. Lott and Cheng (60) were able to decrease the co-precipitation of calcium considerably by the addition of polyvinyl alcohol. Burg and Conaghan (61) reported the same effect with acetylacetone.

Still another problem arises when the hydroxide masking procedure is used. The precipitate adsorbs the indicator. This problem has been studied in detail by Belcher and coworkers (62). Again the addition of polyvinyl alcohol or acetylacetone is an effective remedy.

Despite these improvements the precipitate still was considered as a potential source of trouble and its exclusion seemed desirable. Tichomirova and Simackova (63) performed the titration of calcium at a high pH and prevented the precipitation of magnesium by adding tartrate. For large quantities of magnesium considerable amounts of tartrate are needed to prevent precipitation. When applying this method using EDTA as the titrant high results are obtained for calcium according to Burg and Conaghan and this indicates that some of the magnesium is being cotitrated (61).

The introduction of EGTA (ethyleneglycol-bis(aminoethyl)-tetraacetic acid) as a titrant for calcium greatly improved the situation. The titration of calcium could be performed at a pH where magnesium remains in solution without the addition of a masking agent. The logarithms of the stability constants of the calcium and magnesium complexes are 11.0 and 5.4 respectively (64). The difference of 5.6 units is sufficient for the selective titration of calcium in the presence of magnesium. Excellent results have been obtained using a potentiometric end-point with the mercury drop electrode on the macro- (65) as well as on the ultramicro scale (66). An indirect end-point using the zinc-Zincon system was developed, which permitted a visual titration (67). Unfortunately, this indicator system is very sensitive to changes in pH and the ammonia concentration thus causing difficulties in its application to practical analysis. Both methods are further restricted because certain important masking agents, in particular cyanide, cannot be used.

Burg and Conaghan proposed a combination of the old and new methods (61). These investigators titrated calcium at a high pH with EGTA (using Calcon as the indicator) in the presence of tartrate to prevent the precipitation of magnesium. No magnesium was co-titrated under these conditions because of the favorable ratio of the stability constants. Unfortunately, it was impossible to proceed with an EDTA titration of magnesium (using Erio-T indicator) after lowering the pH because the end-point was sluggish. Therefore, they titrated the sum of calcium and magnesium in another aliquot and calculated the magnesium content by difference. The use of aliquots is inconvenient and imposes a limitation on the procedure when only small samples are available for analysis. Another difficulty arises in adjusting the pH to the high value of 13 when a composite sample is to be used and ammonium salts have been introduced during any previous analytical operations. These salts would have to be removed before the calcium titration.

Because of the complications that occur when calcium is titrated in the presence of magnesium hydroxide it seemed worthwhile to investigate whether or not the selective titration of calcium at a lower pH is possible. The pH should not be higher than about 10 so that magnesium is not precipitated and errors due to occlusion, coprecipitation and large excess of masking agents do not occur. In addition the determination of magnesium after the calcium by using a different titrant and/or indicator seemed to be possible.

## Experimental

### Apparatus

All titrations were performed with the photometric titrator described in Chapter III. Plate glass titration cells with light paths of 1.5 and 3 cm and capacities of 100 to 200 ml were used. The usual volumetric glass ware was used to prepare solutions. The titrant was delivered with the Sargent Automatic Burette. The absorbance curves were made with a Cary Model 14 Recording Spectrophotometer.

### Reagents

All reagent solutions were prepared by dissolving the appropriate chemicals in de-ionized water. Standard solutions were prepared in the manner described in Chapter IV.

## Results and Discussion

An inspection of Table 1 will show why EGTA is a good choice as a titrant for calcium in the presence of magnesium. The difference between the logarithms of the stability constants is 5.6. In order to selectively titrate one metal in the presence of a second metal the difference should be about 6. If an indicator is used for a visual detection of the end point the difference should be about 8. Thus EGTA, theoretically, is a good titrant but an instrumental detection of the end point is necessary.

Performing the titration at pH 10 prevents the precipitation of magnesium hydroxide. Also, the pH is maintained at 10 so that the  $\alpha$  factor of EGTA is low; the value of the  $\alpha$  factor at pH 10 is 0.1 (63).

The choice of a step indicator for this titration was made on the basis of a series of titrations of calcium chloride solutions at

Table 1. Logarithms of Stability Constants (64)

Chelon				
Metal ion	EGTA	EDTA	Erio T <sup>*</sup>	Murexide <sup>*</sup>
Mg	5.4	8.7	5.44	-
Ca	11.0	10.7	3.84	4.0
Sr	8.5	8.7		
Ba	8.4	7.9		

\* Apparent stability constants at pH 10 (68).

pH 10 (ammonia-ammonium chloride buffer) with EGTA. The indicators used were murexide, Erio T, calmagite and calcon. The titration curves obtained using these indicators were compared. Erio T, calmagite and calcon were unsatisfactory as step indicators. The titration curves showed too much curvature; extrapolation was difficult and even impossible in some cases because the curves showed no straight portion on which to base an extrapolation. This is due to the low stability of the calcium-indicator complexes. In addition, magnesium forms stronger complexes with these indicators than calcium and would therefore seriously interfere with calcium end point. The photometric titration curve for calcium using murexide as the indicator was very satisfactory. An example of this curve is shown in Fig. 5, Curve A (No Mg). The change in absorbance as calcium-murexide is transformed to free murexide and calcium-EGTA is sufficiently large so as to provide adequate sensitivity. No curvature occurs at the end point. Extrapolation from points immediately before and after the end point is easily accomplished. The color transition is very unsuitable for the eye (salmon-red to orange-yellow) but the phototitrator detects the change satisfactorily.

The addition of ascorbic acid to prevent the oxidation of the uncomplexed murexide is imperative. Before the end point a very slight drift in the galvanometer needle could be detected if no ascorbic acid was present. After the end point, however, a very pronounced drift occurs in the galvanometer needle. Oxidation of the murexide while it is in the metal complex does not occur to a great extent. After the end point, when the murexide has been freed from the metal complex, it

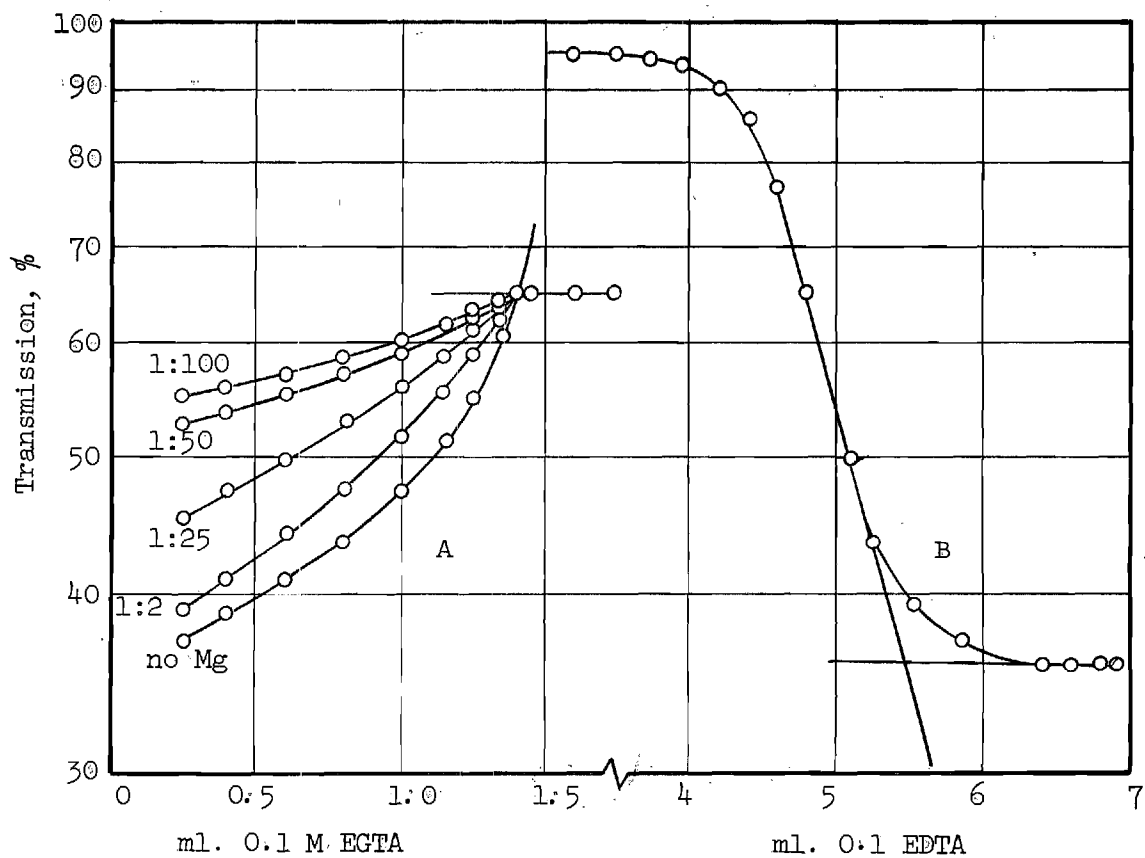


Figure 5. Typical Calcium and Magnesium Titration Curves.

Curve A - Calcium titration curve  
Ca:Mg Ratio indicated at the start of the curve.

Curve B - Magnesium titration curve.

is rapidly oxidized. In the presence of ascorbic acid this decomposition is prevented. A time study showed that if a spatula tip of ascorbic acid is added to the solution to be titrated the murexide indicator is stable for at least eight to ten minutes. If the titration is to be prolonged more ascorbic acid must be added.

The spectral curves of the free murexide and the calcium-murexide complex are shown in Fig. 6, Curves I and II. The solutions used to make the spectral curves were prepared in the following manner: two samples of murexide of identical weight were put into volumetric flasks, buffer of pH 10, and ascorbic acid were then added. To one sample calcium chloride solution in excess of the murexide was added. The solutions were diluted to the mark and the absorbance curves were taken. From these curves the  $\Delta$ -curve was determined, Fig. 6, Curve A. The largest difference in absorbance between free murexide and calcium-murexide occurs at 490 m $\mu$ . Murexide has been used for indicating the end point for calcium titrations above pH 12 where complexes of different composition and color exist (31) but it has never been used at pH 10.

Theoretically, magnesium will not interfere with the titration of calcium at pH 10 using EGTA as the titrant and murexide indicator. That the magnesium did not interfere was verified experimentally. Solutions of known calcium concentration were titrated in the presence of increasing amounts of magnesium. The results of some of these titrations are presented in Table 2. Calcium can be determined even when the magnesium to calcium ratio is 130/1.

The titration curves in Fig. 5, Curve A, show the effect of increasing magnesium concentration; as the magnesium concentration increases

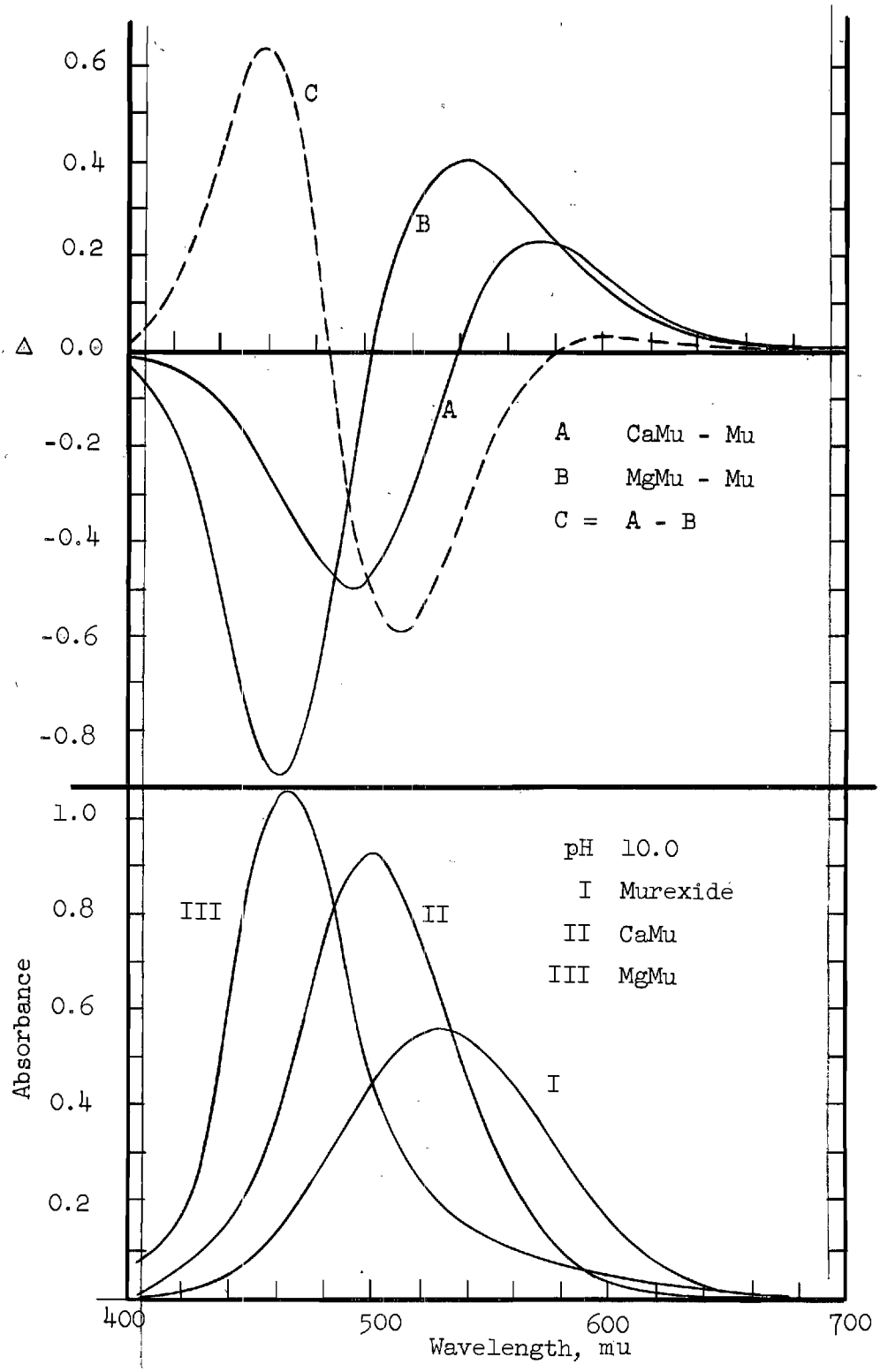


Figure 6. Δ-Curves and Spectral Curves.

Table 2. Representative Results for the Titration of Calcium  
in the Presence of a Large Excess of Magnesium

CaCl <sub>2</sub> (0.1 M)		Mg:Ca ratio	Mg(NO <sub>3</sub> ) <sub>2</sub> (0.1 M)	
Taken (ml)	Found (ml)		Taken (ml)	Found (ml)
1.13	1.15	22:1	25	not determined
1.24	1.17	40:1	50	"
1.00	1.04	100:1	100	"
1.51	1.55	132:1	200(0.2M)	"

(1:2, 1:25, etc.) the slope of the line before the end point decreases. These titration curves were obtained by repeating the photometric titration procedure for titrating calcium on successive solutions containing increasing amounts of magnesium. Although the slope decreases, the extrapolation is not difficult to make and the end point can still be easily located. The data can be plotted on linear graph paper also, in order to increase the precision in locating the end point. The curves were obtained without increasing the sensitivity of the instrument.

When the magnesium concentration was large a turbidity formed while preparing the solution to be titrated. This turbidity, which is due to magnesium hydroxide, can be avoided if the solution is prepared cautiously. The procedure is carried out in the following manner: aliquots of calcium and magnesium solutions are pipetted into the titration cell which contains about 100 ml of water, ascorbic acid is added and the pH of the solution is measured with a pH meter. The pH is adjusted to 10 by the dropwise addition of a dilute sodium hydroxide solution. The solution is stirred vigorously while adding the sodium hydroxide to avoid local precipitation of magnesium hydroxide. Similarly when the buffer 10 is added the solution is stirred vigorously. This solution is then used to set 100 per cent transmittance. Murexide is added and the solution titrated.

Magnesium also forms a weak complex with murexide at pH 10. The spectral curve of the magnesium murexide complex is shown in Fig. 6 (below) Curve III. If the magnesium concentration is high then the color change which occurs at the calcium end point will be from the color of calcium-

murexide to that of magnesium-murexide instead of the color of free murexide. For the photo-titrator this is not a serious problem. An isosbestic point can be found at about 505  $\mu$  for magnesium murexide and free murexide. At this wavelength, then, the response the photo-titrator is the same regardless if the color change is to magnesium murexide or to free murexide. This fact is evident from the  $\Delta$ -curve Fig. 6 (above), Curve B, also. This curve is obtained by subtracting the absorbance curve of the free murexide from the curve of the magnesium murexide complex. The optimum wavelength for the titration, 505  $\mu$ , can also be found from the  $\Delta$ -curve, Fig. 6 (above), Curve C.

Despite the fact that the magnesium murexide complex is weak a large excess of magnesium might cause a shift in the equilibrium



(omitting charges for simplicity) towards the right to an extent that no useful end point could be obtained. The titration curves show that even with Mg:Ca ratios of 130:1, the break in the titration curve is still sufficiently pronounced to permit a sound extrapolation towards the end point.

The new method for analyzing for calcium in the presence of magnesium was further evaluated by the analysis of a National Bureau of Standards sample of "Burned Magnesite No. 104." The following procedure was used: an accurately weighed sample of the burned magnesite was dissolved with hydrochloric acid and diluted to 250 ml in a volumetric flask. A 25.00 ml aliquot was taken with a pipette and first treated to mask the iron. To do so the aliquot was diluted to about

100 mls and tartaric acid added. The solution becomes yellow due to the formation of the ferric-tartrate complex. A large excess of tartrate must be avoided. The solution is neutralized with sodium hydroxide until the solution changes to a brown color. Ten ml of buffer 10 is added. Next 0.1 gm of potassium cyanide is added to convert the ferric iron to the ferricyanide. The solution becomes deep yellow. About 0.1 gm of ascorbic acid is added and the solution is heated almost to boiling. The ferricyanide was reduced to ferrocyanide and the solution changed to almost colorless. A slight turbidity formed which was filtered, washed and discarded. The filtrate was transferred to the titration cell. Ascorbic acid and five mls of 10 per cent triethanolamine solution to mask aluminum and manganese was added. The solution prepared in this way finally was used to set 100 per cent transmittance. About 0.1 gm of murexide powder was added and the solution titrated with 0.09731 M EGTA. A determination in triplicate gave the following results:

	mls EGTA	% CaO
I	1.28	3.34
II	1.26	3.29
III	1.27	3.31
Avg.	1.27	3.31
National Bureau of Standards Certified Value		3.35

The titration of magnesium in the same solution after the calcium determination will be considered next. Whether or not EGTA can be used as the titrant can be decided from theoretical considerations. The stability constant of the Magnesium-EGTA complex is low ( $\log K=5.4$ ).

If a solution of magnesium at a concentration of  $10^{-3}$  M is assumed, a  $KC_m$  value of about 100 results which is satisfactory if a self indicating system is used for detecting the end point. Since magnesium, magnesium-EGTA and EGTA are all colorless this method is not feasible at least not in the visible range. Another possibility is the use of the indicator Erio T for step indication and EGTA as the titrant. The requirement for step indication is that the  $\log(K_{MY}/K_{MI}) \approx 4$  where  $K_{MY}$  and  $K_{MI}$  are the apparent constants for the metal-complex and metal-indicator complex. For erio T and EGTA then one would calculate

$$\log(5.4/5.4) = 0$$

Thus EGTA would not be a satisfactory titrant.

The classical procedure for the EDTA titration of magnesium uses Erio T as the indicator. The  $\log$  of  $K_{MgY}/K_{MgI}$  is 3.3 which is a borderline case but Erio-T is a very satisfactory indicator for magnesium titrations. The classical method can be applied here after the titration of the calcium using murexide indicator. The phototitrator will be necessary because of the background color due to the reagents used in the calcium determination. The optimum wavelength for the titration can be deduced from the  $\Delta$ -curves or from the spectral curves of magnesium-Erio T and free Erio T (69). The optimum wavelength is 620  $m\mu$  and fortunately a 622  $m\mu$  interference filter was available.

After the titration of calcium, free murexide and excess EGTA will be present when the magnesium is titrated. A study of the effects due to the presence of these reagents was conducted. A series of

titrations of magnesium in the presence of murexide and excess EGTA was made. The excess of EGTA is due to the addition of the titrant beyond the end point in order to provide a basis for the extrapolation. Representative titration curves are shown in Fig. 7. Curve A is the titration curve of magnesium in the presence of an amount of murexide equivalent to that used in the calcium determination. No effect could be detected on the titration curve. Murexide does not absorb at 622 m $\mu$ . Curve B shows the effect of EGTA on the titration curve for magnesium. The solution contains a large excess of EGTA; more than four times that which would be present when titrating past the calcium equivalence point. The slope of the titration curve before the end point is decreased indicating that some of the magnesium is combined with EGTA.

The results of a series of titrations of mixtures of calcium and magnesium are presented in Table 3. A typical set of titration curves are shown in Fig. 5, Curves A and B. The curves are conveniently plotted on logarithmic paper using the ordinate for the galvanometer readings and the abscissa for the volume of titrant. The results were satisfactory so that it was not necessary to increase the sensitivity of the instrument. The magnesium curves show no interference because of the excess of EGTA.

In general, those metal ions which interfere in the visual determination of calcium and magnesium will interfere with the photometric titration. The same methods of masking can be applied with the exception of masking by precipitation.

The effects of the masking reagents on the calcium and magnesium titrations were evaluated by repeating the calcium and magnesium

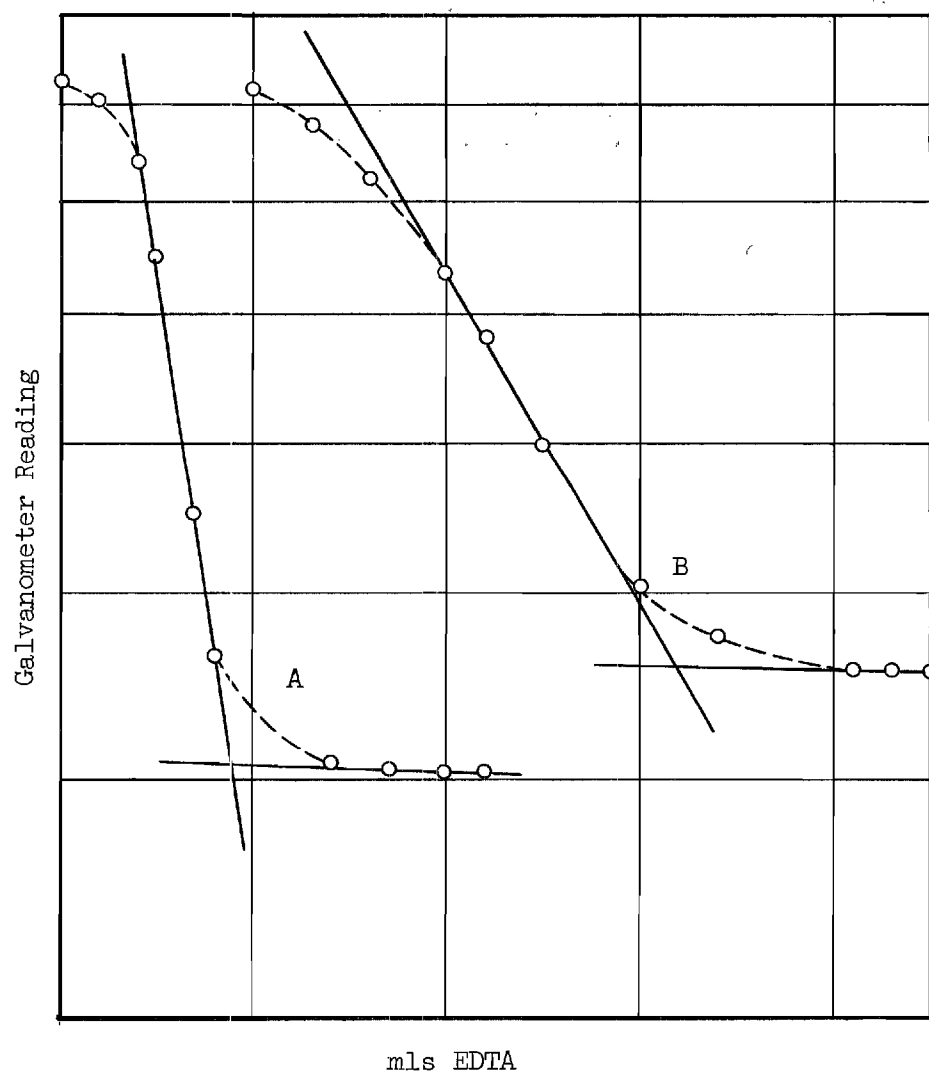


Figure 7. Titration Curves of Magnesium in the Presence of Excess Murexide and Excess EGTA.

Table 3. Representative Results for the Titration of Calcium and Magnesium

CaCl <sub>2</sub> (0.1 M)		Mg(NO <sub>3</sub> ) <sub>2</sub> (0.1 M)	
Taken (ml)	Found (ml)	Taken (ml)	Found (ml)
2.95	2.95		
3.11	3.10		
5.37	5.39		
9.74	9.72	none	
2.95	2.96		
5.23	5.22		
9.45	9.50		
3.60	3.65	6.02	6.02
4.29	4.29	3.66	3.61
6.43	6.42	4.38	4.41
2.24	2.26	25.66	25.67
2.14	2.16	2.26	2.23
2.29	2.30	4.36	4.34
3.44	3.40	2.26	2.30
1.05	1.05	4.11	4.12
		3.07	3.06
		0.94	0.98
none		3.07	3.06
		2.78	2.79
		4.38	4.41

titrations in the presence of the masking reagents. Predictably, potassium cyanide (0.5 gm) and triethanolamine (10 mls of a 25 per cent solution) have no effect on the titration of either calcium or magnesium. Tartaric acid was found to be detrimental when present in excess of a certain amount. If the tartrate concentration is greater than approximately three times the molar concentration of calcium, a time effect is observed. This is due to the displacement of calcium from the calcium-murexide indicator complex by tartrate and subsequent formation of a calcium-tartrate complex. When no tartrate is present the solution prepared for the normal calcium titration is stable as manifested by the motionless galvanometer needle. The addition of tartrate has no apparent effect until it is present in threefold excess then the galvanometer needle begins to drift upward indicating the release of murexide. Thus when using tartaric acid -- especially for the iron masking procedure -- only enough tartaric acid must be added to complex the iron and then provide only a slight excess so that the calcium titration is not hampered.

Calcium and magnesium could be successfully titrated in the presence of nickel, zinc, copper, cadmium and mercury when potassium cyanide was used as masking reagent. Titrations were done with metal ion concentrations up to twice the calcium concentration. No special precautions are required as to the amount of cyanide added since the excess has no effect on the calcium or magnesium results. Aluminum can be masked with triethanolamine. Calcium and magnesium can be titrated in the presence of masked aluminum up to an aluminum concentration equal to the calcium concentration. Iron is masked by converting it to the

ferrocyanide complex. This procedure is given in detail under the "Burned Magnesite" analysis. For iron concentrations equal to the calcium concentration the tartrate causes the time effect described previously.

The amount of tartrate required to complex this amount of iron is released when the ferrocyanide complex is formed. The tartrate will then remove the calcium from the calcium-murexide complex by forming the calcium-tartrate complex. The amount of tartrate required in the iron-masking procedure is estimated by the intensity of the yellow color of the ferric-tartrate complex. For smaller amounts of iron this masking procedure is satisfactory since the amount of tartrate required is less than the critical amount for the replacement of calcium from the murexide complex.

Manganese seriously interferes if its concentration is greater than about  $5 \times 10^{-4}$  M. Below this amount manganese can be completely masked with triethanolamine. With larger amounts of manganese upon addition of the triethanolamine the solution becomes turbid and dark green in color. Furthermore the manganese(III)-triethanolamine complex oxidizes the Erio T indicator. This effect can be eliminated by the use of hydroxylamine which reduces the manganese(III) but the manganese(II) is then cotitrated by the EGTA.

Strontium and barium are serious interferences. They will be cotitrated with calcium, thus, only the sum of calcium, barium and strontium can be determined. In addition the reaction between EGTA and the indicator complexes of barium and strontium is slow and the titration must proceed slowly until the reactions come to equilibrium.

Increasing the temperature does not aid the rate significantly. Hence, strontium and barium have to be separated, before the calcium titration.

The possibility of determining calcium in the presence of barium received some attention. The logarithms of the stability constants of the CDTA (cyclohexanediaminetetraacetic acid) complexes of calcium and barium are 12.3 and 8.0 respectively. Using the step indicator, Calcon, it would be possible to titrate calcium in the presence of barium at pH 12. The most appropriate wavelength would be 622 m $\mu$ . Calcium can be successfully titrated in the presence of barium if the barium concentration is equal to or less than the calcium concentration. The titration curve is the typical step-indicating type and is very similar to the magnesium photometric titration curve in Fig. 5. The results of some titrations are presented in Table 4. However, when the barium concentration is greater than the calcium concentration a serious time effect occurs and the titration reaction occurs very slowly. The rate is faster in dilute solution but not significantly so. Most seriously, this time effect occurs in the vicinity of the end point. When the barium is present in large amounts it reacts with the CDTA before the calcium. The exchange reaction between the barium-CDTA and the calcium-Calcon complex is slow. This is demonstrated by adding a large excess of a solution of barium-CDTA to a solution of calcium-Calcon complex and observing the slow change in transmittance. Heating the solution to 90°C helps somewhat when the barium concentration is about three times the calcium concentration. At higher concentrations the reaction is slow even at 90°C. Since this approach would not be helpful in the calcium-magnesium consecutive titration no further experiments were attempted. The CDTA

Table 4. Representative Results for the Titration of Calcium in the Presence of Barium

CaCl <sub>2</sub> (0.1 M)		BaCl <sub>2</sub> (0.1 M)
Taken (ml)	Found (ml)	Taken (ml)
3.00	3.02	0.00
3.54	3.55	0.00
1.17	1.17	1.00
3.55	3.51	3.00
3.51	3.53 (90°C)	6.00
3.48	3.51 (90°C)	9.00
3.86	3.88	3.00
1.37	1.40	3.00
1.34	1.37	1.00

would also cotitrate magnesium and strontium because the stability constants of these two metal complexes are both about  $10^{10}$  (70).

The only anions that would be commonly found in this type of analysis which interfere in the calcium and magnesium titration with EGTA and EDTA respectively are sulfate and phosphate. Both would precipitate calcium if present in high enough concentration.

It is not necessary to keep the solutions free of carbon dioxide in order to prevent the precipitation of calcium carbonate. The precipitate will disappear during the course of the titration. Only the points close to the end point are required to establish the end point. However, it is important that the titration proceed slowly because the dissolution of the calcium carbonate is a relatively slow process. No false results are obtained when working with solutions which are initially turbid if the titration rate is reduced appropriately.

The titration procedure which was used for the analysis of mixtures of calcium and magnesium is now summarized. Exactly measured volumes of the metal ion solutions were pipetted into the titration cell and de-ionized water was added to bring the volume up to about 150 mls. If the solution was too acidic sodium hydroxide was added dropwise until the pH was about 10 as measured with a pH meter. The concentration of calcium or magnesium in the titration cell was about  $10^{-2}$  to  $10^{-3}$  M. Between 5 and 10 mls of buffer pH 10 was added. A 508 m $\mu$  interference filter was inserted in the filter holder. The cell was positioned in the phototitrator and 100 per cent T was adjusted with this solution. A spatula tip of ascorbic acid was added to prevent the air oxidation of the indicators. Murexide powder was then added and the calcium was

titrated with standard EGTA solution. The transmittance was recorded and plotted on semi-logarithmic paper. After the calcium end point was found, the 622  $\mu$  filter was inserted in place of the 508  $\mu$  filter and Erio T indicator was added. The transmittance was adjusted to about 95 per cent (instead of 100 per cent to provide room for changes due to dilution) and the magnesium was titrated with EDTA. The end points were found by extrapolation through the recorded points.

### Conclusions

Of the chelometric methods available, then, none is completely satisfactory for determining calcium in the presence of magnesium because a pH greater than 12 must be used to mask the magnesium as magnesium hydroxide. Methods modified to determine calcium in the presence of magnesium are of limited use because of restrictions on the conditions, i.e., the pH, presence of masking agents and end point detection method.

The chelometric titration with a photometric end point can be used to determine calcium in the presence of large amounts of magnesium when EGTA is used as a selective titrant and at a pH of 10 where insoluble magnesium hydroxide does not precipitate. A step indicator, murexide, is used because visual indication is impossible because of the unfavorable color transition. Ascorbic acid must be present to prevent the oxidation of the indicator.

Furthermore, magnesium can be determined (with EDTA as the titrant and Erio T as the step indicator) in the same solution. The photometric end point again avoids problems arising when the end point is detected visually.

The presence of many other metal ions can be tolerated because effective masking agents can be employed which when used in excess do not hamper either the calcium or the magnesium end point. Manganese is an exception, however, since only very small amounts can be tolerated. Phosphate and sulfate will interfere because they precipitate the calcium. Tartrate interferes if present in three-fold excess of the calcium, but since it is usually purposely added its amount can be controlled if the calcium concentration is known approximately. Barium and strontium are serious interferences since they will be cotitrated with calcium.

## CHAPTER VI

THE TITRATION OF CADMIUM IN THE PRESENCE OF ZINC  
AND OTHER METALSIntroduction

The chelometric titration of cadmium in the presence of zinc to a visual end point cannot be done and only the sum of cadmium and zinc can be determined. Methods based on the instrumental detection of the end point are available, however, which enable the selective titration of cadmium, e.g., amperometry. Sweetser and Bricker have developed an EDTA titration of cadmium in the presence of zinc using a photometric end point (71). The titration is performed in a strongly alkaline solution so that the zinc is transformed into the unreactive zincate ion. The cadmium is kept in solution by the addition of a small amount of cyanide. The titration is performed at 236 m $\mu$ . The use of this very short wavelength, the high alkalinity and the fact that the amount of cyanide used is critical are serious disadvantages of this procedure.

The use of the photometric end point in the visible range of the spectrum for a cadmium analysis does not seem feasible at first. Cadmium and zinc, of course, are both colorless in aqueous solutions. Most chelons and the corresponding cadmium and zinc chelonates are colorless in aqueous solution also. The method of end point indication depends on the addition of some auxiliary colored or color forming substance. A comparison of the stability constants of various chelons with zinc and cadmium indicates possibilities for a selective titration. The use

of a slope indicator also has been considered for indicating the end point in a selective titration of cadmium. The development of these considerations for a practical analysis will be discussed on the following pages.

## Experimental

### Apparatus

All titrations were performed with the phototitrator described in Chapter III. Titration cells of both 100 and 200 ml capacities were used. The usual calibrated volumetric glassware was used to prepare and store solutions. Spectral curves were made with a Cary Model 14 Recording Spectrophotometer.

### Reagents

All of the reagents required for the experiments described in this chapter were prepared and standardized according to procedures which have been described in Chapter IV.

## Results and Discussion

The numerical values of the stability constants of the cadmium-chelonates are always close to those of the corresponding zinc-chelonates with only one remarkable exception, namely EGTA (ethyleneglycol-bis-(aminoethyl)-tetraacetic acid). The logarithms of the absolute stability constants of a number of the chelonates of EGTA are tabulated in Table 5. The difference between the logs of the cadmium-EGTA stability constant and the zinc-EGTA stability constant is 3.9 log units. This difference is insufficient for a visual titration using a metallochromic indicator and it is even a borderline case for a photometric

Table 5. Logarithms of the Absolute and Apparent Stability Constants of the EGTA Complexes of Some Metal Ions  $\beta$  Factors for 0.1 M and 1 M Total Ammonia ( $[\text{NH}_3]$  +  $[\text{NH}_4^+]$ ) (10).

Metal Ion	$\log K_{\text{abs}}$	$\log \beta$ (pH 10, Total $\text{NH}_3$ 0.1M)	$\log K_{\text{app}}$	$\log \beta$ (pH 10, Total $\text{NH}_3$ 1M)	$\log K_{\text{app}}$
Ba <sup>+2</sup>	8.4	-	8.4	-	8.4
Ca <sup>+2</sup>	11.0	-	11.0	-	11.0
Cd <sup>+2</sup>	16.7	3.1	13.6	6.8	9.9
Hg <sup>+2</sup>	23.2	15.6	7.6	19.0	4.2
Mg <sup>+2</sup>	5.4	-	5.4	-	5.4
Sr <sup>+2</sup>	8.5	-	8.5	-	8.5
Zn <sup>+2</sup>	12.8	4.7	8.1	8.7	4.1
Cu <sup>+2</sup>	17.8	8.3	9.5	12.2	5.6
Mn <sup>+2</sup>	12.3	-	12.3	-	12.3
Co <sup>+2</sup>	12.3	2.0	10.3	5.4	6.9
Ni <sup>+2</sup>	13.6	3.9	9.7	8.4	5.2
Pb <sup>+2</sup>	14.6	-	14.6	-	14.6

titration using a metallochrome indicator. Furthermore, a visual indication would be impossible since no indicators are known which will selectively react with cadmium.

In order to estimate the feasibility of a titration using EGTA the apparent stability constants were compared. The apparent constants were calculated using the data in Table 5 which is a tabulation of the  $\beta$  factors for a number of metal ions in ammoniacal solution for a total concentration of ammonia ( $[\text{NH}_3] + [\text{NH}_4^+]$ ) of 0.1 M and 1 M at pH 10. The difference between the apparent stability constants in 0.1 M total ammonia is increased to 5.5 log units. The difference is more favorable but the end point detecting mechanism was still to be chosen. A self indicating mechanism within the visible range of the spectrum was not possible since all of the species involved in the titration reaction are colorless. A possibility may exist in the ultraviolet region but this aspect was not pursued.

Because of the difference of 5.5 log units in the apparent stability constants of the cadmium and zinc EGTA chelonates the possibility of placing a self-indicating system between the cadmium and zinc was considered. The requirements which must be fulfilled are that a metal ion must have an apparent stability constant with a value such that the ratio  $K_{\text{CdY}}/K_{\text{MY}}$  is satisfactory for a photometric end point and that a satisfactory change in absorbance occurs when the metal ion is titrated with EGTA after the cadmium. An example of the slope indicating mechanism has been mentioned previously; the use of copper as a slope indicator for the EDTA titration of bismuth has been successful (72). Copper is especially suited for this purpose because of the

relatively large difference between the extinction coefficients of the free copper ion or its amino complex and any chelon complex. An inspection of Table 5 reveals that a comparison of the absolute constants would result in the following arrangement in decreasing order:  $Cu \geq Cd > Zn$ . However, comparison of the apparent constants at pH 10 in 0.1 M total ammonia shows a different order:  $Cd > Cu \geq Zn$ . This very favorable arrangement is due to the  $\beta$  factors.

Theoretical considerations in Chapter II have shown that for an extrapolative procedure,  $Q(=K_m/K_n)$  should be of the order  $10^1$  or  $10^2$  or greater in order to satisfactorily titrate two metals in succession. For the system cadmium plus copper, the value of  $Q$  is about  $10^4$ . Therefore, cadmium is titrated before copper with EGTA in the presence of ammonia at pH 10.

These theoretical deductions were verified experimentally by titrating solutions with known amounts of cadmium using copper as the slope indicator. In order to determine the proper interference filter to use the spectral curves of copper-tetramine and copper-EGTA at pH 10 and total concentration of ammonia of 0.1 M were made. These spectral curves are shown in Fig. 8. The  $\Delta$  curve was also plotted and optimum wave length was determined to be in the range of 700 or 750  $\mu$ . A 742  $\mu$  filter was chosen.

A series of titrations were done of solutions containing known amounts of cadmium ion, copper ion and buffer 10. Some of the results are given in Table 6. A typical example of a titration curve is shown in Fig. 9. A very sharp break occurs at the end point and by means of extrapolation the exact end point is easily determined. The occurrence

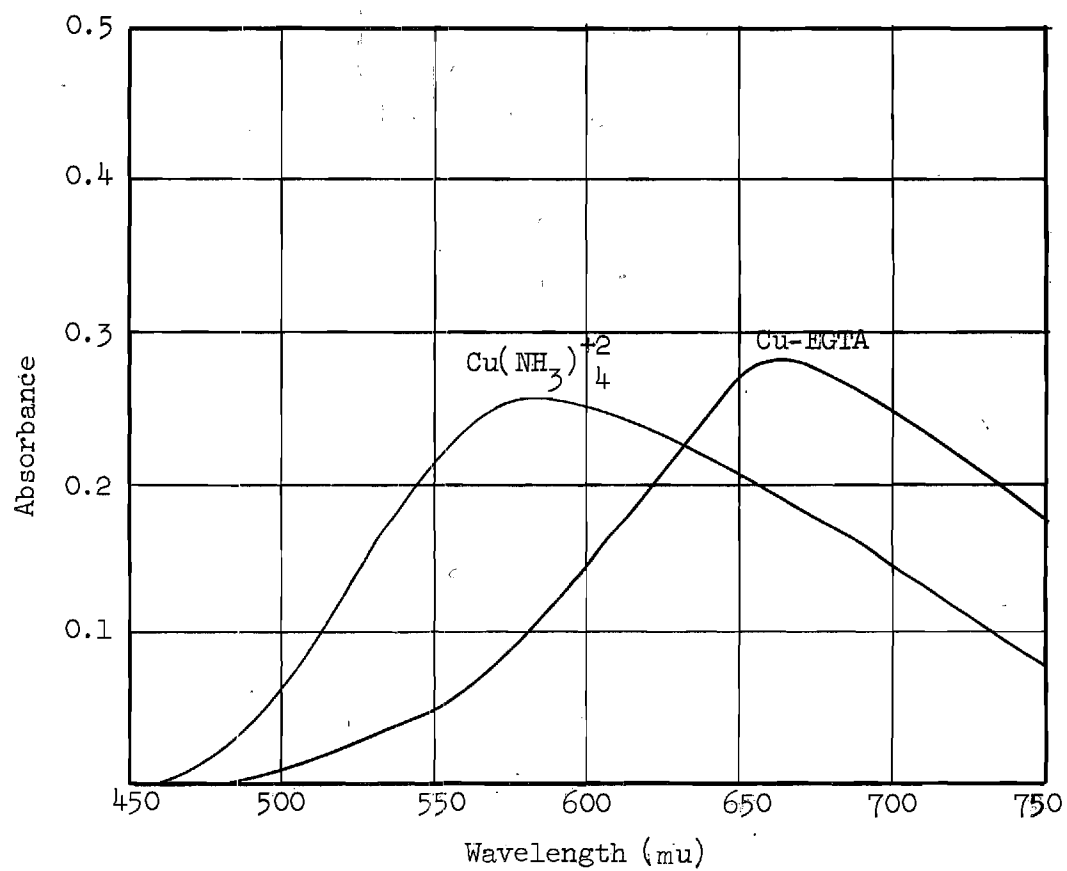


Figure 8. Spectral Curves of Copper in Ammonia Buffer and in Presence of EGTA.

Table 6. Representative Results for the Consecutive Titration of Copper and Cadmium

Cadmium mls		Copper mls	
Taken	Found	Taken	Found
2.58	2.57	5.00	5.01
5.00	4.98	6.70	6.72
7.87	7.89	8.99	9.00
9.90	9.95	10.00	10.02
10.00	10.00	5.00	5.03

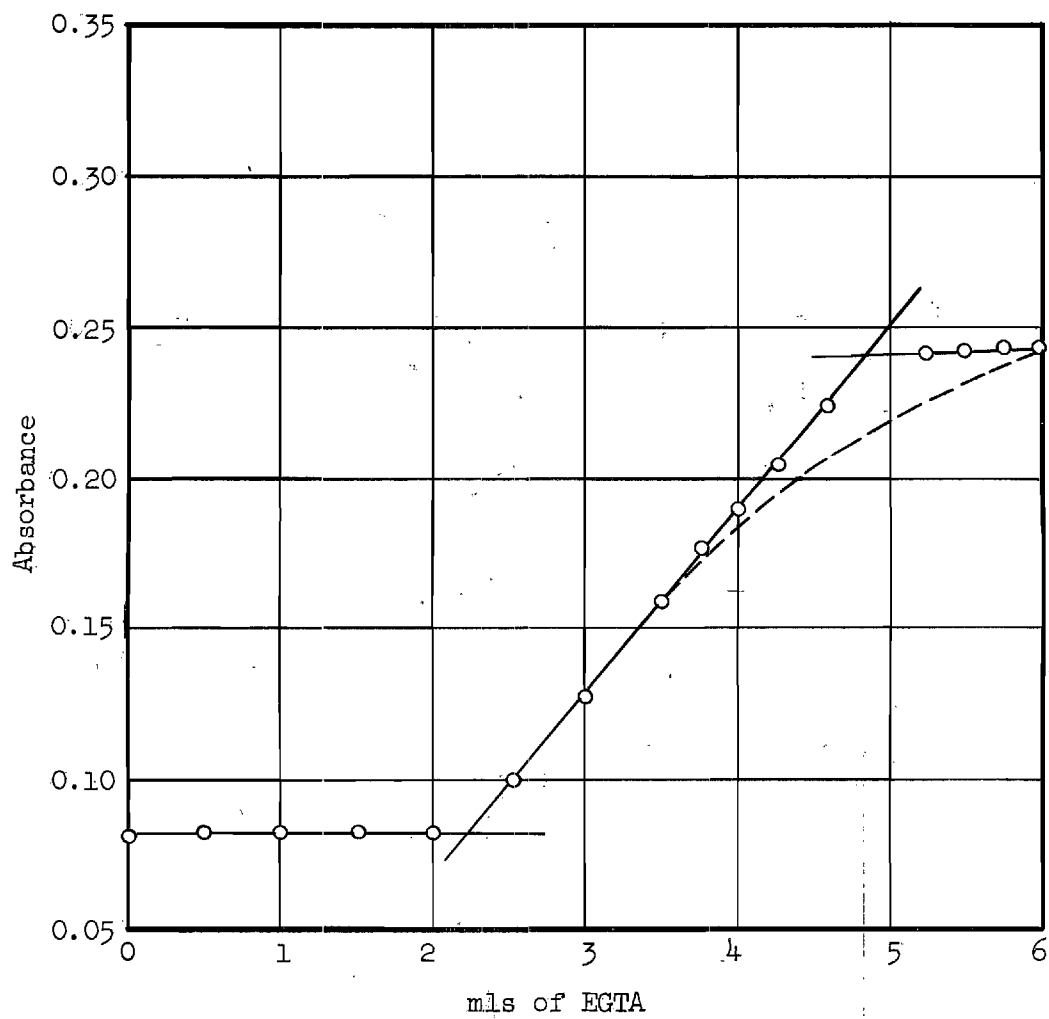


Figure 9. A Typical Cadmium Titration Curve.

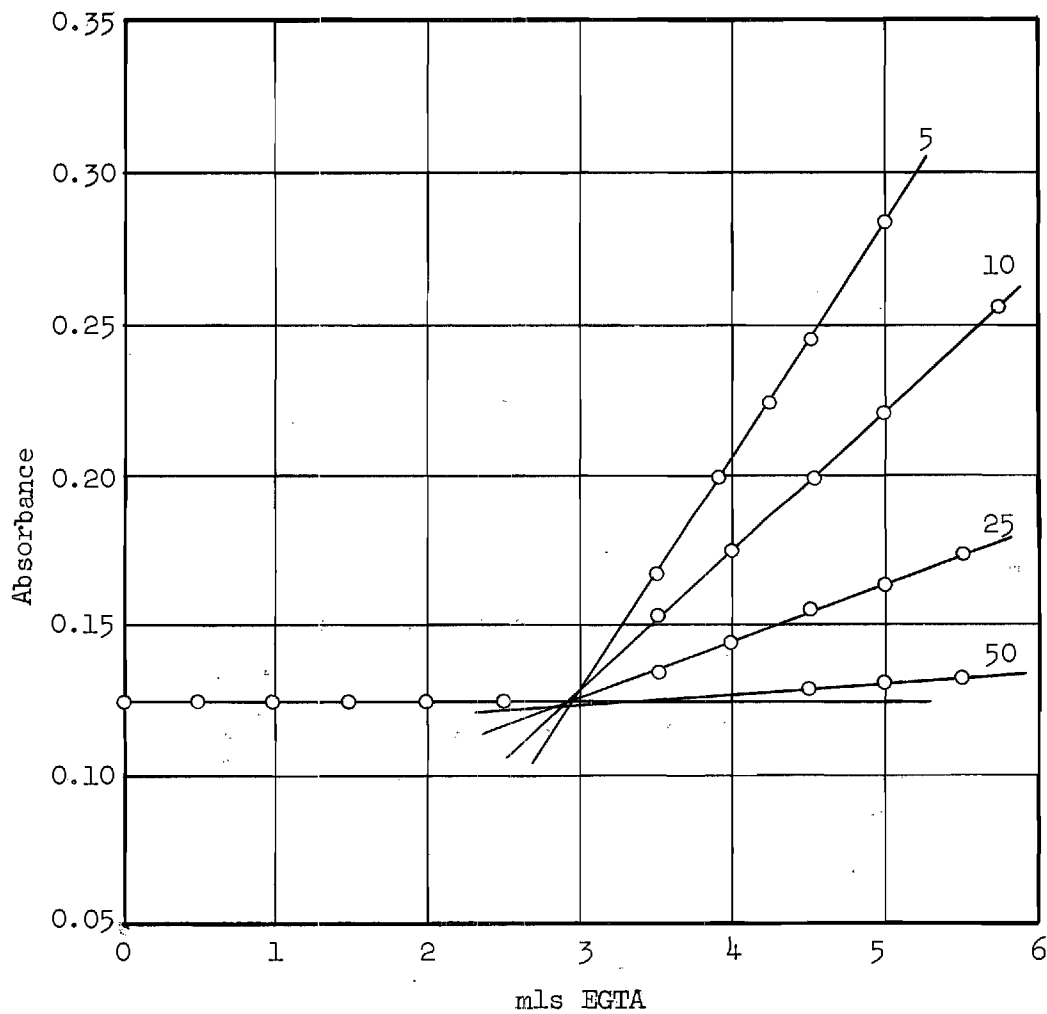
of the sharp break verifies that the difference between the apparent stability constants of the cadmium-EGTA and copper-EGTA complexes is large enough. It is possible to continue the titration beyond the cadmium end point and determine the copper (see solid line in Fig. 9) concentration. The break at the second end point is sharp also.

The effect of the presence of zinc on the analysis of cadmium solutions was evaluated next. A series of solutions containing known amounts of cadmium, copper, zinc and buffer 10 were titrated with standard EGTA solution. The results of some of these titrations are presented in Table 7. A typical titration curve which is obtained from this series is shown in Fig. 9 (dotted line). The presence of zinc does not hamper the location of the cadmium end point. Very satisfactory results are obtained even when the ratio of zinc to cadmium is 500:1. However, the increased zinc concentration causes a curvature in the titration curve around the vicinity of the copper end point. This curvature is due to the small difference between the apparent stability constants of copper-EGTA and zinc-EGTA. The value can be calculated from the apparent constants given in Table 5;  $9.5 - 8.1 = 1.4$ . This value is lower than the theoretically deduced limit of about 2. Hence, the zinc is partially titrated with the copper. Although this factor makes location of the copper end point more uncertain it does not at all hamper the location of the cadmium end point.

The apparent slope of the curve after the cadmium end point is dependent on ammonia concentration. The effect of increasing the ammonia concentration while all other concentrations are kept constant is shown in Fig. 10. The effect occurs both in the presence and in the absence

Table 7. Titration of Cadmium with 0.1 M EGTA in the Presence of Zinc

Cadmium (0.1 M, 3 cm cell)		Zinc (ml 0.1 M)	Cd:Zn Ratio
Taken (ml)	Found (ml)		
1.00	1.00	none	none
4.00	4.01	none	none
4.00	4.02	5	1:1.25
4.00	3.97	25	1:6.25
5.00	4.98	100	1:2.20
9.90	9.94	25	1:2.80
10.00	10.03	100	1:10
Cadmium ( $5 \times 10^{-3}$ M, 10cm cell)		Zinc (ml 0.1 M)	Cd:Zn Ratio
Taken (ml)	Found (ml)		
2.03	2.06	none	none
2.03	2.00	10	1:100
1.01	1.04	15	1:300
3.56	3.64	50	1:260
2.03	2.08	50(0.2M)	1:500
10.00	10.00	25	1:50



Note: Numbers on the curves indicate the number of milliliters of ammonia-ammonium chloride buffer pH 10 which were added to a solution  $1 \times 10^{-3}$  M in copper.

Figure 10. Dependence of the Slope of the Cadmium Titration Curve on the Ammonia Concentration.

of zinc. The slope of the line corresponding to the titration of copper decreases because of the increase in the value of the  $\beta$  factor as the ammonia concentration is increased. The value of the  $\beta$  factor increases from a value of 8.3 in a solution 0.1 M total ammonia to 12.2 in a solution 1 M in total ammonia at pH 10 for the copper ion. Hence, the  $KC_m$  value for copper is reduced to about  $10^1$  corresponding to a solution which is about  $10^{-3}$  M in total copper ion. Thus a large curvature would be expected theoretically since even in the most ideal case the lowest value for  $KC_m$  tolerable is about 50. Again for a practical application one need only adjust the concentration of ammonia in the solution to about 0.1 M total ammonia since an uncertainty of plus or minus a few milliliters of buffer will not seriously affect the location of the end point. On the other hand extremely concentrated solutions of ammonia will make location of the end point impossible.

The effect of using a lower pH can be explained in terms of the  $\alpha$  and  $\beta$  factors. As the pH is lowered the value of the  $\beta$  factor for ammonia and any one specified metal ion decreases. For all of the metals listed in Table 5 at pH 5 the  $\beta$  factors are either 0 or less than 0.1. Thus, at pH 5 the  $\beta$  factor is no longer significant but the  $\alpha$  factor for EGTA is. The  $\alpha$  factor for EGTA at pH 5 is 8.3 (73). The apparent stability constants at pH 5, arranged in decreasing order, for copper, cadmium and zinc are respectively 9.5, 8.4 and 4.5. The order of titration of cadmium and copper is reversed and the copper is titrated first. This of course negates the use of copper as a slope indicator.

The effect of the presence of other metal ions on the titration of cadmium using copper as the slope indicator was evaluated by titrating

cadmium solutions, containing copper, zinc and the foreign metal ion present at concentrations equal to the cadmium and up to twice the concentration of the cadmium. In summary form those metal ions which did not cotitrate with the cadmium are iron(II), Co(II), Ni(II), Al(III), Hg(II) and Mg(II). Manganese(II) causes a time effect. Lead(II) is cotitrated with cadmium as is calcium. The alkali metals do not interfere.

Since the apparent stability constants of lead and calcium are sufficiently greater than the apparent constant for copper-EGTA they are cotitrated with cadmium. This was verified experimentally. Only the sum of cadmium plus lead (or calcium) is obtained from the first end point.

The apparent stability constants of the EGTA complexes of cobalt (II) and nickel (II) are of the same order as the copper (II) stability constant (see Table 5). Thus, they are cotitrated with copper. The cotitration is not detrimental if only the cadmium end point is desired. Of course only the sum of copper and cobalt (or nickel) will be obtained at the second end point. The cotitration of these ions also tends to decrease the slope of the line after the end point. This decrease is not serious, however, and the end point can still be located.

The use of masking agents to increase selectivity is hampered by the fact that many of the masking agents will also mask cadmium under the optimum conditions of the titration. Tartaric acid must be used in order to mask some of the metal ions against hydroxyl ion in order to prevent hydrolysis. Hydrolysis must be prevented because the turbidity due to the precipitation of insoluble hydroxides will interfere with

light beam. The presence of tartrate was determined not to be detrimental to the cadmium titration by several titrations of cadmium in the presence of tartrate.

The problem of interferences is not so serious because the separation of zinc and cadmium from most other elements can be readily effected by ion exchange methods (74). On the other hand, some multi-components mixtures can still be resolved by chelometric titration using aliquots, different masking agents, different titrants and visual indicators. Up till now only the sum of zinc and cadmium could be conveniently determined chelometrically. With the photometric end point, however, the cadmium may be selectively analyzed.

The following examples will illustrate the principle of this approach.

Consider, first, a solution containing lead, cadmium, zinc and copper. A series of experiments were attempted in which the lead was masked with EDTA. The following experiment is typical of those conducted. To the solution containing lead, cadmium, zinc and copper was added tartaric acid to prevent hydrolysis of the lead. The solution was neutralized with sodium hydroxide and then buffer of pH 10 was added. Potassium cyanide was added to mask the copper, cadmium, and zinc against the EDTA. The lead was then titrated with EDTA using Erio. T to a visual end point. Formaldehyde was added to selectively demask the zinc and cadmium. This solution was placed in a titration cell and photometrically titrated with EGTA in order to determine the cadmium using the copper already present as slope indicator. However a drift in the galvanometer needle was observed which lasted for over

a half hour. The drift was due to the slow release of copper from the copper-cyanide complex by the excess formaldehyde. Attempts to destroy the cyanide complexes by other means were unsuccessful. The procedure was therefore modified further.

After demasking the zinc and cadmium with formaldehyde the solution was titrated with EDTA using Erio T to a visual end point. The sum of zinc and cadmium was obtained with this titration. A second aliquot was taken and the sum of cadmium and lead was obtained by using the photometric procedure. The solution was titrated with EGTA and the copper already present acted as the slope indicator. The third aliquot was titrated with EDTA at pH 6 using PAN as the visual indicator. This titration provided the sum of all four metals. The results of a particular titration are shown in Table 8. The results are satisfactory with the exception of copper. The copper content is obtained by taking the difference between two large numbers hence the uncertainty in the result is greater.

The general procedure one may follow when titrating cadmium will now be presented. The sample containing zinc and cadmium is dissolved and an aliquot is taken and pipetted into the titration cell. De-ionized water is then added to dilute the solution to about 100 mls and 10 mls of buffer pH 10 added. If copper is not already present in the sample the required amount of copper nitrate solution is added. About 5 to 10 mls of buffer pH 10 is then added. The cell is positioned in the titrator and 100 per cent transmittance set with this solution. The cadmium is titrated with a standard EGTA solution. A 742  $\mu$  interference filter is used. The transmittance readings are recorded and plotted on

Table 8. The Analysis of a Mixture of Zinc, Cadmium,  
Lead and Copper

A. Titration Data						
Aliquot Number	Metals Titrated			mls EDTA Required		
1a	Pb			3.80		
1b	Zn + Cd			6.48		
2	Cd + Pb			4.88		
3	Zn + Cd + Pb + Cu			12.54		

B. Calculations						
Metal Ion Determined	Calculation			mls EDTA		
	mls EDTA for Aliquot Number	mls EDTA - for Aliquot Number	mls EDTA or for Metal Ion Shown	Found	Re- quired	
Pb	-	-	-	3.80	3.82	
Cd	2	-	1a	1.08	1.05	
Zn	2	-	Cd	5.40	5.45	
Cu	3	-	(Cd+Zn+Pb)	2.26	2.18	

semi-logarithmic paper. For very dilute solutions the titration cell may be turned lengthwise thus increasing the light path to about 10 cm.

#### Conclusions and Recommendations

Cadmium can be titrated with EGTA using copper as the slope indicator at 742 m $\mu$ . The solution is buffered at pH 10 with an ammonia-ammonium chloride buffer. The formation of ammonia complexes of cadmium and copper causes the apparent stability constant of the copper-EGTA complex to be less than the cadmium-EGTA complex. Thus cadmium is titrated before copper. The ammonia concentration must be controlled (but within wide limits) so that the slope of the copper titration curve is not decreased too much. Cadmium can be titrated in the presence of large amounts of zinc. Satisfactory results are obtained when the cadmium to zinc ratio is 1:500. Cadmium can be titrated in the presence of iron(II), cobalt(II), nickel(II), aluminum(III), mercury(II) and magnesium. The alkali metals do not interfere. Lead(II) and calcium are cotitrated with cadmium. Other metal ions interfere by being cotitrated or by causing kinetic problems. However, since the method is so satisfactory for analyzing cadmium in the presence of zinc and since the separation of zinc and cadmium from almost all interfering ions by an ion exchange procedure is easily carried out the problems of interfering metal ions is not a serious one. The investigation of the application of better masking reagents is a possibility for further research. Certain mixtures of metal ions can be analyzed by means of masking and titrating several aliquots. The solution of a mixture cadmium, zinc, copper and lead was successfully carried out in this way.

## CHAPTER VII

## THE CONSECUTIVE TITRATION OF COPPER AND NICKEL

Introduction

The chelometric analysis of copper and nickel is usually difficult to carry out without first separating the elements. When separated, the determination of nickel or copper is easily performed with EDTA as the titrant and murexide as the visual indicator.

Sweetser and Bricker have used EDTA in a method for determining nickel when no copper is present and they have established the end point photometrically (75). They used the same procedure to determine copper when nickel is absent. Burtner has described an ultraviolet photometric titration of nickel using EDTA as the titrant (76). However, copper will interfere. The same procedure can be used to determine copper in the absence of nickel.

Flaschka and Soliman have used triethylenetetramine (trien) to selectively titrate copper in the presence of a large number of metal ions (77). The end point is established photometrically with the copper-trien complex acting as a self-indicating system. Many common metals did not interfere at the pH at which the titration was performed. Those metals which did interfere could be masked.

The method of Flaschka and Soliman is concerned only with the selective titration of copper. Since they found that copper could be titrated in the presence of nickel it seemed worthwhile to extend the method and try to analyze for nickel in the same solution. A number of

possibilities as to how this can be accomplished exist and these have been investigated to determine whether or not a basis for the consecutive titration can be found.

### Experimental

#### Apparatus

The phototitrator used for these experiments was described in Chapter III. Solutions were prepared and stored in the usual volumetric glassware. Calibrated pipettes, burettes and volumetric flasks were used when necessary. The Sargent Model C Automatic Burette was used to deliver the titrant. All spectral curves were made with a Cary Model 14 Recording Spectrophotometer.

#### Reagents

All reagents were prepared and standardized when necessary according to the procedures described in Chapter IV. De-ionized water was used in the preparation of all solutions.

### Results and Discussion

Flaschka and Soliman have described a selective titration for copper using trien as the titrant (77). In particular they could eliminate the interference by nickel by performing the titration at pH 5 using an acetate buffer. This method is possible because at pH 5 the stability of the nickel-trien complex is low. The absolute constants for a number of metals with trien are tabulated in Table 9. The Table also contains the  $\beta$  factors and the apparent stability constants at pH 10. The value of  $Q (=K_{Cu}/K_{Ni})$  at pH 10 is  $10^2$  which is the theoretical limit for a successive titration. Flaschka and Soliman could only observe the sum of copper and nickel at pH 10. At pH 5 the value of  $Q$  is increased

Table 9. Logarithms of the Absolute and Apparent Stability Constants of Several Metals with Trien at pH 10.

Metal ion	log $K_{abs}$	log $\beta$ Factor, pH 10		log $K_{app}$	
		0.1 M Total $NH_3$	1 M Total $NH_3$	0.1 M Total $NH_3$	1 M Total $NH_3$
$Cd^{+2}$	10.8	3.1	6.8	7.7	4.0
$Co^{+2}$	11.0	2.0	5.4	9.0	5.6
$Cu^{+2}$	20.4	8.3	12.2	12.1	8.2
$Fe^{+2}$	7.8	-	-	-	-
$Hg^{+2}$	25.3	15.6	19.0	9.7	6.3
$Mn^{+2}$	4.9	-	-	-	-
$Ni^{+2}$	14.0	3.9	8.4	5.6	5.6
$Zn^{+2}$	12.1	4.7	8.7	7.4	3.4
$Pb^{+2}$	10.4	-	-	-	-

to about  $10^6$ . Thus it is possible to titrate the copper in the presence of nickel. Even at pH 7 the value of  $Q$  is about  $10^5$  and a selective titration can still be performed.

The use of a chelon such as trien (triethylenetetramine), a polyamine, has a distinct advantage. Because coordination to a metal ion can occur only through nitrogen atoms those metal ions that have a low affinity for nitrogen will form only weak complexes. Because of this fact trien is more selective in its reactions. Trien forms 1:1 complexes of high stability generally only with copper, silver, mercury, cadmium, zinc, cobalt and nickel. Almost all other metal ions will not interfere in a titration reaction (they will not be cotitrated) when trien is used as the titrant.

The photometric end point is based on a self-indicating mechanism. As the copper-aquo complex (or any other copper complex which may form in the presence of the buffer or other auxiliary reagent) is converted to the copper-trien complex the absorbance of the solution increases at 565 m $\mu$ . These considerations were verified by titrating a series of copper solutions at pH 5 and pH 7, in the presence of tartrate ion, with trien. A typical titration curve for copper alone is shown in Fig. 11, Curve A. The end point break is very sharp and very little curvature occurs as would be expected since the  $KC_M$  value for copper is very favorable. Assuming that the copper concentration is  $10^{-3}$  M, one can calculate that the  $KC_M$  value is about  $10^7$ .

Flaschka and Soliman (77) also found that in highly alkaline solutions in the presence of tartrate the order of titration is reversed; the nickel is titrated first and then the copper. At 660 m $\mu$  the titration

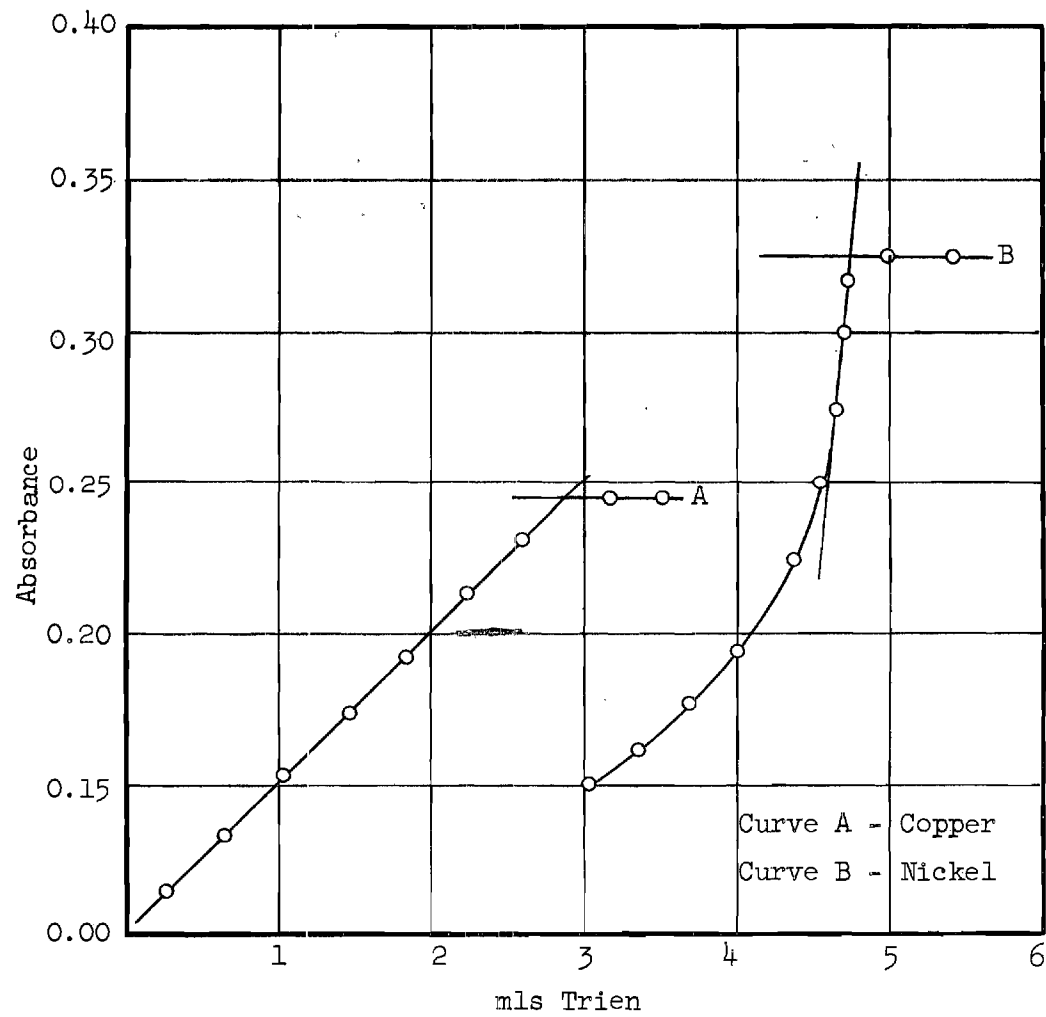


Figure 11. Typical Titration Curves of Copper and Nickel with Trien.

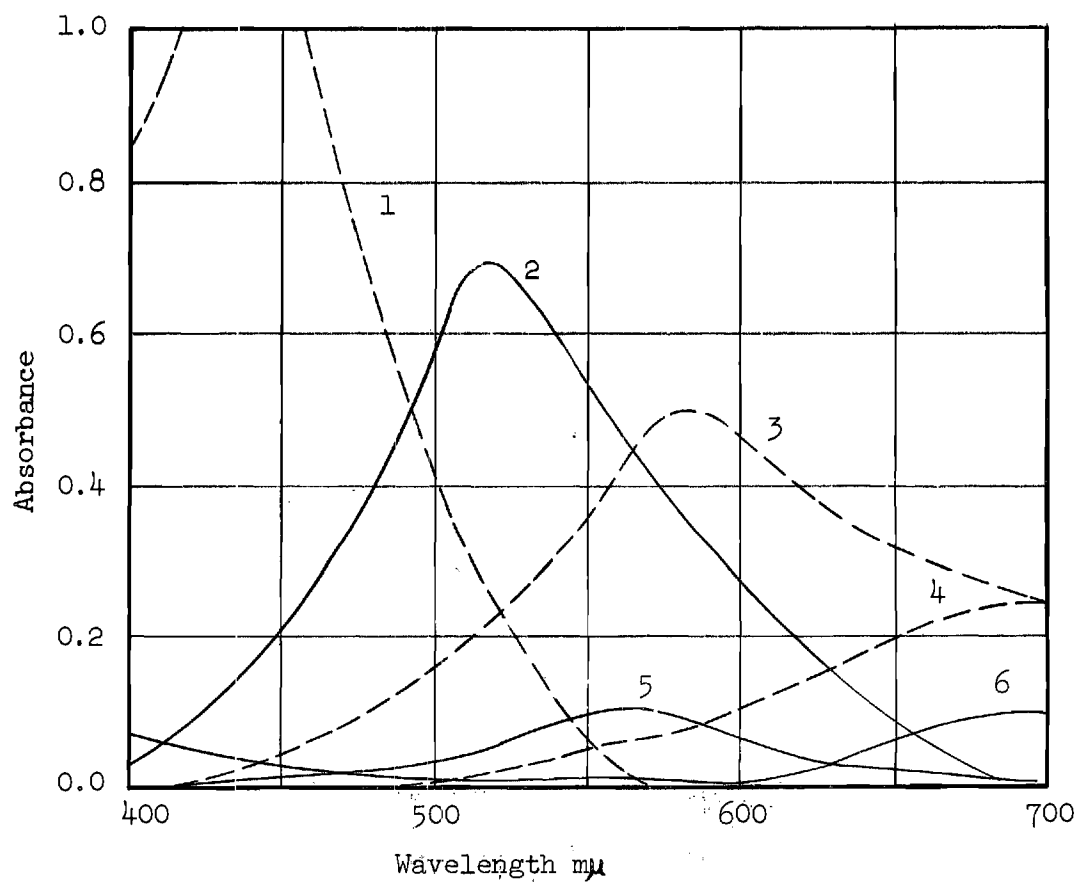
curve shows a double break. A disadvantage of this modification is the slow reaction of nickel with trien. The existence of this kinetic problem was verified and more experiments were performed in an attempt to overcome it. The titrations were performed at a pH greater than 12 using sodium hydroxide to adjust the pH. The solutions were heated up to 70°C by means of a heating spiral in a glass tube placed in the titration cell. Performing the titration at this temperature increased the rate but not significantly. The titration required at least a half hour to complete and the end points determined were in error by several per cent. This approach was discontinued.

The possibility of titrating the nickel after the copper has been titrated was considered next. The advantage of this approach is that the copper would be masked as the trien complex and should not interfere with reactions in which the nickel might take part. Nickel is commonly titrated with EDTA using murexide as a visual indicator. The solution is buffered at pH 10 using an ammonia-ammonium chloride buffer. Of course a phototitrator is unnecessary to locate the end point when nickel is titrated in this manner. However, if this method is used to analyze for nickel in the presence of copper-trien the unaided eye would be unsuitable for detecting the end point. Copper trien exhibits a deep blue color which would hamper the detection of the color change due to the transformation of nickel-murexide to nickel-EDTA. The phototitrator is necessary if nickel is to be titrated in the same solution with copper-trien.

The value of the apparent stability constant of the nickel-trien complex at pH 10 ( $\log K_{app} = 11.8$ ) indicates that trien may be substituted

for EDTA as the titrant. This is convenient for the titration procedure since there would be no need to change or refill the burette. The requirement that  $\log (K_{NiT}/K_{NiMu})$  be greater than 4 is not fulfilled however. In a solution where the total ammonia concentration is 0.01 M the log of the ratio of the apparent constant for nickel-trien to the apparent constant for nickel-murexide at pH 10 is only 2.5. Thus the ammonia concentration must be adjusted carefully in order to prevent the interference of ammonia with the indicator reaction. The concentration of ammonia required was determined experimentally. A series of solutions containing known concentrations of nickel and varying amounts of ammonia-ammonium chloride buffer was titrated with trien, using murexide as indicator. A satisfactory end point is obtained when 5 to 10 ml of the buffer are used in 200 mls of solution and when the nickel concentration is of the order of  $10^{-3}$  M. Greater amounts of ammonia cause the break to be too small and smaller amounts of ammonia do not adequately buffer the solution.

The appropriate wavelength was chosen on the basis of the spectral curves shown in Fig. 12. A 591 m $\mu$  interference filter was chosen and it need not be changed since the absorbance change occurring during both titrations is sufficient at this wave length. Table 10 shows some of the results for the consecutive titration of copper and nickel. Fig. 11 shows the typical self-indicating type of curve for the copper titration (Curve A) and a typical step-indicating type curve for the nickel titration (Curve B). Both breaks are sharp and the end point is easily established by extrapolation.



- Curve 1 - Nickel-murexide pH 10  
 2 - Murexide pH 10  
 3 - Copper-trien pH 7  
 4 - Copper-tartrate pH 7  
 5 - Ni-tartrate pH 10  
 6 - Ni-trien pH 10

Figure 12. Spectral Curves of Copper and Nickel Complexes.

Table 10. Representative Results for the Successive Titration of Copper and Nickel with Trien

Copper ml		Foreign Metal ions Present ml 0.1 M	Nickel ml	
Found	Taken		Found	Taken
1.23	1.21	none	6.25	6.16
2.36	2.36	"	2.99	3.02
2.43	2.42	"	1.77	1.76
4.85	4.87	"	4.86	4.78
15.63	15.61	"	2.19	2.14
4.86	4.88	Bi 5	7.90	7.93
5.62	5.62	Al 10	3.21	3.25
10.00	10.02	Pb 10	2.25	2.22
6.75	6.73	Ag 5	8.90	8.94
5.00	5.04	Tartaric acid	10.00	10.06
7.82	7.81	Ca 10, Mg 10	5.00	4.98

The possibility of an exchange reaction was considered. The reaction could occur in the following manner between copper-trien and nickel-murexide



However, no effects could be detected because of this exchange.

The effects of interfering ions were evaluated by performing the titration of copper and nickel at pH 5 and 7 and pH 10 respectively in the presence of tartaric acid. Those ions which were found to interfere in the copper titration as described by Flaschka and Soliman interfered in the consecutive titration of copper and nickel (77). By performing the titration at a pH of 5 the following ions did not interfere in the copper portion of the titration: zinc, lead, cadmium, bismuth, iron(III), silver, nickel, cobalt(II) and aluminum. However, several of these elements interfered with the nickel titration at pH 10. First, no interference was observed when the following ions were present during the nickel titration: manganese(II), iron(III), aluminum, bismuth, lead and silver. However, zinc and cadmium both interfered because they were cctitrated. The titration curves were unusable because of the curvature. Cobalt interfered because it was slowly air oxidized to cobalt(III) and was stabilized in the presence of trien.\* This slow reaction manifests itself as a slow drift on the galvanometer. Attempts to preoxidized the cobalt or to mask it were unsuccessful.

On the basis of the considerations just discussed the following procedure can be used for analyzing mixtures of copper and nickel.

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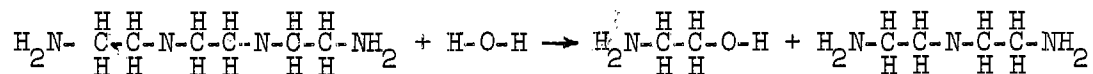
\* See below p. 122.

An aliquot of the solution which contains copper and nickel is pipetted into the titration cell and diluted to about 100 mls with de-ionized water. Ammonium acetate is then added to buffer the solution at pH 7. This solution is used to set 100 per cent transmittance. A 591 m $\mu$  interference filter is inserted into the filter holder. The copper is then titrated with standard trien solution. The transmittance readings can be recorded and plotted immediately on semi-logarithmic graph paper. After the copper end point is reached ammonia-ammonium chloride buffer and a spatula tip of ascorbic acid is added. Powdered murexide is added and the nickel titrated with trien. Again the points are plotted on the same graph paper used for the copper titration and the end point is found by extrapolation.

Although the trien used for these analyses was believed to be pure enough for titration purposes a portion of the stock was recrystallized. The recrystallized trien was used to prepare a standard solution and its behavior was compared to a standard solution prepared from the unrecrystallized material. The trien was purified by recrystallization from water, washing with alcohol, drying and storing it in a well stoppered bottle. The titration curves obtained with both kinds of trien were identical in shape and gave the same end points within experimental error.

Solutions of trien were stored for a long period of time and their titer checked periodically. After a week a filmy solid formed in the trien solution. The solid was filtered off and the filtrate collected in a dry bottle. No change in the titer was detected. Titrations made monthly over a three month period showed no change in titer but a slight

curvature was detected in the titration curves in the vicinity of the end point. The trien was hydrolyzed into other poly amines and alcohols



The overall stoichiometry of the reaction of copper with the hydrolysis products of trien is the same as with pure trien. All of the products of the hydrolysis of one molecule of trien could react with a single copper ion. The stability constants of the copper complexes with the products of hydrolysis are less than those of copper-trien and hence an increase in curvature at the end point would be expected.

#### Conclusions and Recommendations

Copper and nickel can be analyzed in the same solution by means of the photometric end point. Trien is used as the titrant and a 591 mμ interference filter is used to obtain the appropriate wavelength of light. At pH 7 the copper is titrated first. The copper-trien is a self-indicating complex. The stability of this complex is high and a very sharp break occurs at the end point of the photometric titration curve. Nickel is titrated next after the pH of the solution is increased to 10 and buffered with an ammonia-ammonium chloride buffer. Murexide is used as the step indicator. Again a very sharp break can be obtained and the end point can be easily located. The following metals do not interfere: manganese(II), iron(III), aluminum, bismuth, lead and silver. Zinc and cadmium do not interfere with the copper titration but are cotitrated with nickel. Cobalt(II) interferes because of the slow conversion of cobalt(II)-trien to cobalt(III)-trien due to air oxidation.

The method is hampered by the interference of cadmium and zinc. Further investigation with respect to masking these metals would improve the situation. Similarly, a procedure which could eliminate the cobalt interference should be investigated.

## CHAPTER VIII

## A SELECTIVE TITRATION OF COBALT

Introduction

Only a few titrimetric procedures for the analysis of solutions containing cobalt are available. For example, cobalt can be titrated with potassium cyanide in the presence of potassium chlorate using the disappearance of the turbidity due to silver iodide to detect the end point. The potassium chlorate oxidizes the cobalt(II) to cobalt(III). The cobalt(III) is titrated with cyanide and forms a stable cyanide complex (78). However, the method cannot be used in the presence of nickel, copper zinc or manganese. Cobalt(II) can also be titrated with potassium ferricyanide; the end point can be established potentiometrically (79).

Practically all chelometric determinations of cobalt are based on an EDTA titration. Both direct and indirect methods are used. Most of the methods depend on a separation of cobalt from nearly all other elements.

A particular chelometric determination of cobalt, using it in its trivalent state, has been described by Kinnunen and Wennerstrand (80). Cobalt in an ammoniacal solution is oxidized with hydrogen peroxide in the presence of EDTA so that the cobalt(III) is stabilized as a complex. The solution is acidified to pH 2 and the excess EDTA is back titrated with a standard thorium solution using xylenol orange as the indicator. But only small amounts of cobalt can be titrated in

this manner. The color of the cobalt(III)-EDTA complex is an intense red and this obscures the end point. The cobalt(III)-EDTA complex is highly stable; its absolute stability constant is about  $10^{41}$  (81). This fact can be useful for analytical purposes.

## Experimental

### Apparatus

The phototitrator used for the titrations described in this chapter was described in detail in Chapter III. A Sargent Model C Automatic Burette was used to deliver the titrant. The usual volumetric glassware was used. All spectral curves were recorded on a Cary Model 14 Spectrophotometer.

### Reagents

The reagents used in the following experiments were prepared and standardized according to procedures described in Chapter III. All solutions were prepared with de-ionized water.

## Results and Discussion

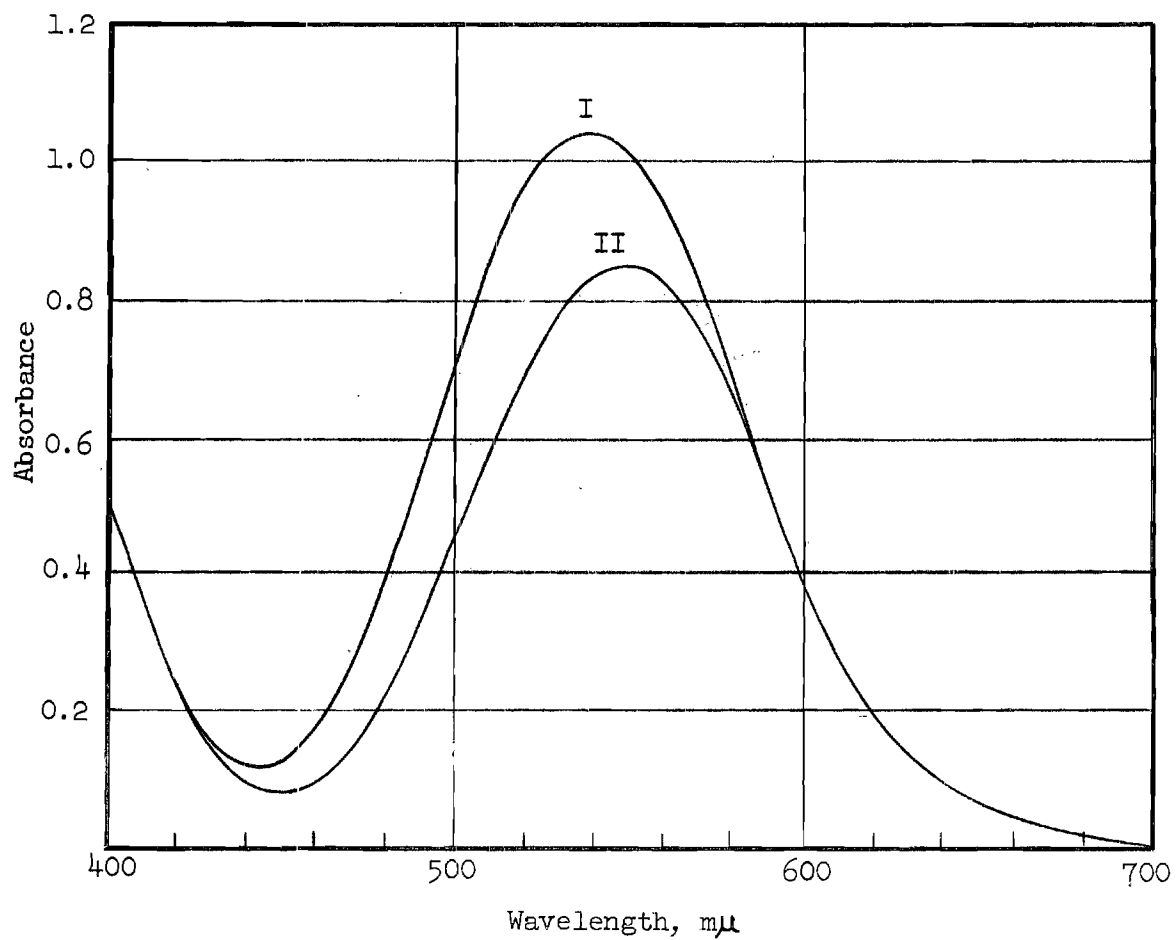
A selective titration of cobalt(II) was first thought to be possible by using trien (triethylene tetramine) as the titrant. The photometric titration was to have been based on the self-indicating type mechanism; the cobalt(II)-trien complex absorbs at a different wavelength than the cobalt(II)-aquo complex. Titrations were performed but this direct approach was not successful. In the presence of trien cobalt(II) is oxidized to cobalt(III) by oxygen from the air dissolved in the water. The cobalt(III) is stabilized by the formation of the cobalt(III)-trien complex. Although this reaction proceeds only slowly it hampers the photometric titration. The cobalt(III)-trien complex is reddish brown

in color and is strongly absorbing at the optimum wavelength for the titration. A serious drift occurs on the galvanometer because of this reaction.

The titration was performed in the presence of several reducing agents (ascorbic acid, sodium sulfite, hydroxylamine) but the cobalt could not be kept in the reduced state. An attempt was made to titrate cobalt(III) in the form of the green cobalt(III)-carbonato complex. Titration curves were obtained but the end points were in error and the readings on the galvanometer were difficult to obtain because of erratic behavior. No further experiments were attempted with trien.

Attention was directed next to the use of the cobalt(III)-EDTA complex. Because of the intense red color of the solution of this complex, visual indication of the end point is limited to the titration of dilute solutions. The spectral curve of the cobalt(III)-EDTA complex is shown in Figure 13. The phototitrator is an excellent substitute for the eye in such cases. The stability constant of this complex has been determined and is remarkably high ( $\log K_{\text{abs}} = 40.7$ ) (81). A direct titration does not seem to be feasible. However, a back titration in the manner of Kinnunen and Wennerstrand (80) using a photometric end point is possible.

The large value of the stability constant means that a back titration at a very low pH is possible. A very selective titration can be performed because the EDTA complexes of many other metals form only to a slight extent or not at all at low pH values. Table 11 is a tabulation of the absolute stability complexes of many common metal ions with EDTA. The apparent stability constants have been calculated both at



Curve I -  $\text{Co}(\text{H}_2\text{O})\text{Y}^-$   
II -  $\text{CoY}^-$

Figure 13. Spectral Curves of Cobalt(III) - EDTA at pH 1.8.

Table 11. Logarithms of the Absolute and Apparent Stability Constants of Some Common EDTA Complexes

Metal ion	$\log K_{\text{abs}}$	$\log K_{\text{app}}$ (pH 1.0)	$\log K_{\text{app}}$ (pH 0.5)
Al <sup>+3</sup>	16.1	-	-
Ba <sup>+2</sup>	17.8	0.6	-
Ca <sup>+2</sup>	10.7	-	-
Cd <sup>+2</sup>	16.5	-	-
Co <sup>+2</sup>	16.3	-	-
Co <sup>+3</sup>	40.7	23.5	21.6
Cu <sup>+2</sup>	18.8	1.6	-
Fe <sup>+2</sup>	14.3	-	-
Fe <sup>+3</sup>	25.1	7.9	6.0
Hg <sup>+2</sup>	21.8	4.6	2.7
Mg <sup>+2</sup>	8.7	-	-
Mn <sup>+2</sup>	14.0	-	-
Ni <sup>+2</sup>	18.6	1.4	-
Pb <sup>+2</sup>	18.0	0.8	-
Th <sup>+4</sup>	23.2	6.0	2.0
Zn <sup>+2</sup>	16.5	-	-

pH 1.0 and pH 0.5 and are also tabulated in Table 11. The fact that most of these complexes are so weak is due to a competition between the metal ion and the hydronium ions for the EDTA. At low pH values most of the EDTA is present in the free protonated forms. Table 12 lists the values of  $\log \alpha$  at several low pH values. These values can be used to calculate the apparent stability constant. According to Table 11 only a few metals ions have significantly large stability constants at pH 1.0.

Because the procedure is based on the back titration of the excess EDTA (i.e., all EDTA which is not combined with cobalt(III)) the metal ion employed as a back titrant will need to satisfy certain requirements. First the apparent stability constant of the metal-ion EDTA complex must be high enough so that it is not significantly dissociated at the pH of the titration. Second, it should be capable of displacing metal ions which still form EDTA complexes at the pH used in order that all the excess EDTA is titrated. Kinnunen and Wennerstrand used thorium as a back titrant for the excess EDTA (80). However, bismuth was chosen as a back titrant for this investigation because it was readily available and it forms a very stable EDTA complex even at low pH values.

Bismuth can be titrated with EDTA to a visual end point using pyrocatechol violet (PCV). The analytical uses of PCV have been reviewed by Suk and Malat (82). Especially important is the fact that PCV is an excellent indicator to use when the pH is low. PCV undergoes very sharp color changes at pH 2 when it is converted from the metallized form to free form. PCV, as are most metallochrome indicators, is also an acid-base indicator and thus the color changes which it undergoes as a metallochrome indicator depend on the pH of the solution. Spectral curves of

Table 12. Logarithms of  $\alpha$  Factors for EDTA at Low pH Values

pH.	log $\alpha$ EDTA
4.0	8.5
3.5	9.6
3.0	10.7
2.5	12.0
2.0	13.5
1.5	15.3
1.0	17.2
0.5	19.1
0.0	21.2

PCV at various pH values are shown in Fig. 14. In an acidic solution PCV is very stable and no precautions against its decomposition need be taken. PCV forms complexes with many metal ions but at low pH values it is rather selective, forming complexes only with the trivalent ions. PCV forms both 1:1 and 2:1 (metal:indicator) complexes with many metals including bismuth. The 1:1 bismuth complex is red and the 2:1 complex is blue. At a pH less than 1.5 however only the red complex with bismuth forms (82).

In order to evaluate the method a series of titrations were performed on solutions containing known amounts of cobalt(II). The titration procedure involved an oxidation step so that the cobalt(II)-EDTA is converted into the cobalt(III)-EDTA complex.

The choice of wavelength was made from the spectral curves of free PCV and the bismuth-PCV complex as shown in Fig. 14. The choice of wavelength depends on the pH to be used for the titration. The most satisfactory wavelength occurs at 620  $m\mu$ . The pH can be lowered considerably and still a large difference exists between the absorbances of free PCV and bismuth-PCV complex. The cobalt(III)-EDTA complex does not absorb appreciably at this wavelength and thus adds only a moderate and constant background. The pH of the solution should never go higher than 2 and if it is necessary to lower the pH to at least 0.5 the absorbance change is still satisfactorily large.

The procedure for the oxidation of the cobalt involves several steps and errors may occur in each of them. The cobalt will not be oxidized completely at a low pH. Several solutions were treated in the following manner: a known quantity of cobalt was placed in the titration

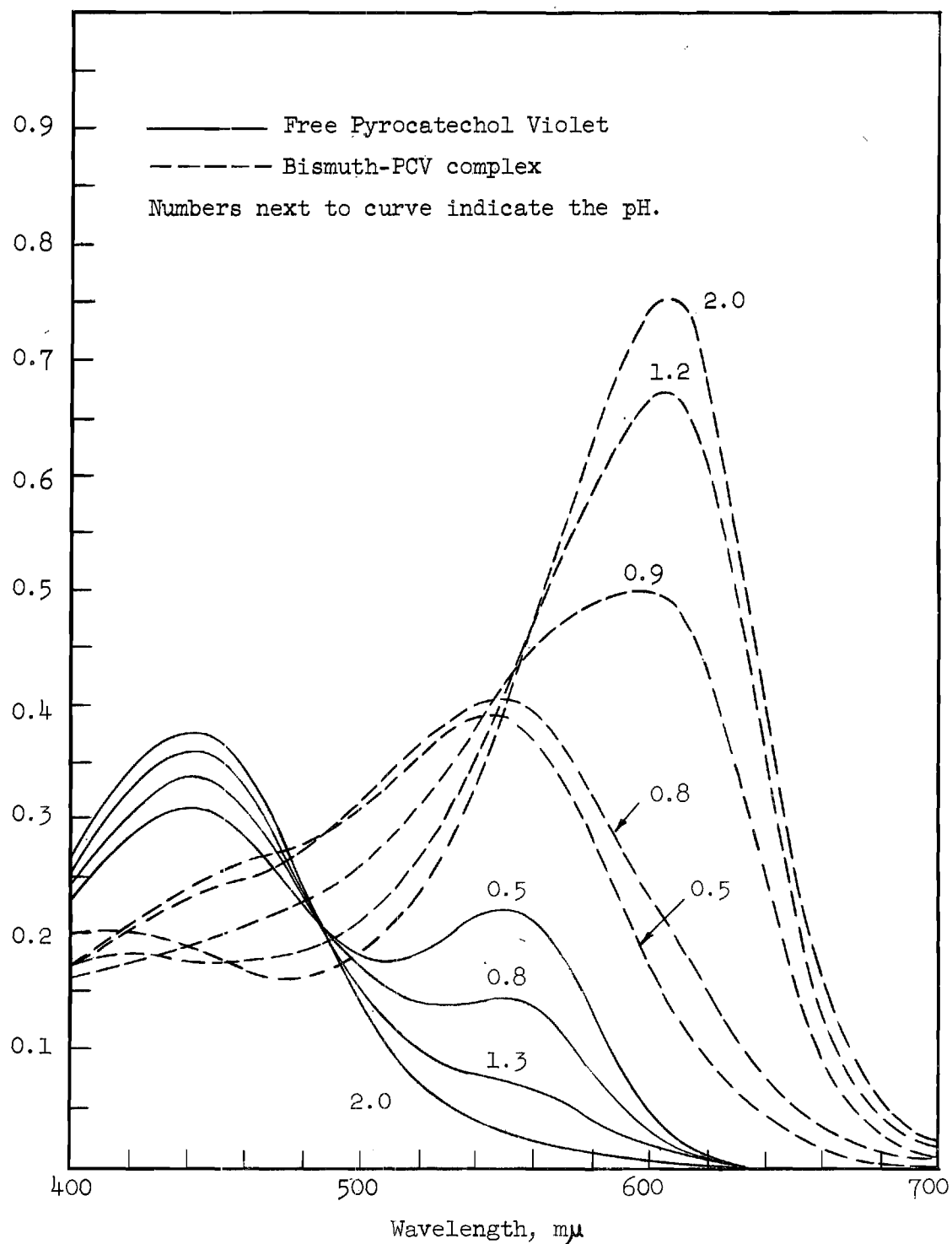


Figure 14. Spectral Curves of Pyrocatechol Violet and Bismuth-PCV Complex at Various pH Values.

cell. An excess of EDTA over the cobalt was added and the pH was adjusted to a value of 2 using a pH meter and adding dropwise dilute nitric acid solution. Hydrogen peroxide (5 drops of 30 per cent solution) was then added. The solution was diluted and the excess EDTA back titrated with standard bismuth solution. One should avoid the use of solutions containing chloride ion since bismuth will form insoluble bismuth oxychloride. Thus nitric acid and ammonium nitrate (for a buffer) must be used for adjusting the pH or for buffering solutions. The quantity of EDTA titrated was always higher than the calculated quantity added in excess. When the same procedure was repeated but the oxidation performed at pH 10, the correct amount of excess EDTA was determined. At the low pH a portion of the cobalt is uncomplexed, and either is not oxidized or is oxidized and immediately reduced by water before complexation with EDTA can occur. At pH 10 all of the cobalt is complexed with EDTA and is oxidized by the hydrogen peroxide completely.

If the excess of EDTA present is not enough to complex all metal ions present another error can occur. During a series of titrations of solutions containing both cobalt and zinc the quantity of excess EDTA determined by the back titration with standard bismuth was found to be too high. Again this indicated that not all of the cobalt was being oxidized. The importance of adding enough EDTA to complex all of the metal ions present can be explained on the basis of the equilibrium



If some free metal,  $\text{M}^{n+}$ , is present in the solution it will partially replace the cobalt(II) from the EDTA complex. With the exception of

the alkali metals, all metals will replace the cobalt to a certain extent. How far the equilibrium is shifted to the right depends on the ratio of the stability constants of the EDTA complex and on the concentration of metal M. Even with a metal such as magnesium, which has a low stability constant, the shift was sufficient enough to cause low results for cobalt if a portion of the magnesium remains uncomplexed. The experiments were repeated but an excess of EDTA over all the interfering metals present was used. The correct results for cobalt were obtained.

Kinnunen and Wennerstrand (80) performed the cobalt oxidation in an ammoniacal medium. This procedure was followed initially but a study of the quantity of hydrogen peroxide needed for oxidizing the cobalt revealed that a portion of the oxidant was lost. The study was made because a minimum amount of hydrogen peroxide should be used because of the formation of bubbles and their detrimental affect on the light beam. If too much hydrogen peroxide is used some time must be spent in removing all of the bubbles. In ammoniacal medium an inordinate amount of hydrogen peroxide was required to obtain the correct results for cobalt, otherwise cobalt results were too low. This indicated incomplete oxidation. A portion of the hydrogen peroxide was lost due to the oxidation of ammonia to nitrogen with a large amount of gas bubbles being generated. The solution was therefore adjusted to pH 10 with sodium hydroxide: no buffering agent being added. Identical experiments performed with sodium hydroxide instead of ammonia-ammonium nitrate buffer gave the correct results for cobalt. A smaller amount of the oxidant suffices for the complete oxidation of cobalt than was needed in ammoniacal medium, and barely

any bubbles are produced. In addition the rate of oxidation seemed to be enhanced. At pH 10 the oxidation proceeds very rapidly. This is easily observed because the solution turns to a deep blue upon the addition of a drop or two of 30 per cent hydrogen peroxide. If the pH is slightly lower, 9 for example, the oxidation proceeds more slowly. This kinetic aspect was not studied in detail since at pH 10 the reaction is rapid and the correct results were obtained.

No interference due to the oxidation of the free EDTA by the moderate amount of unreacted hydrogen peroxide at pH 10 was observed. A solution was titrated after standing for 15 minutes and no error was found in the analysis indicating that no EDTA was destroyed. However, a solution which was titrated after standing for 18 hours indicated that a significant portion of the EDTA was destroyed by the excess hydrogen peroxide.

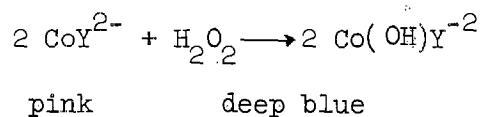
After the oxidation of the cobalt(II)-EDTA complex to the cobalt(III)-EDTA complex the pH of the solution was decreased to 1. Nitric acid was added dropwise while the pH of the solution was measured with a pH meter. The solution was then titrated with standard bismuth solution. During the initial experiments a drift in the galvanometer needle was observed as the titration was begun. However, the drift did not always occur and when it did occur the rate of drift varied greatly. The effect was traced back to the nitric acid. Oxides of nitrogen in the nitric acid will react with and destroy the PCV and thus cause the galvanometer needle to drift.

The drift was avoided if an excess of hydrogen peroxide was added; one or two drops over the amount required to oxidize the cobalt. The

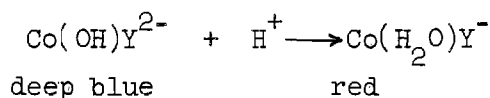
excess hydrogen peroxide reacted with the oxides of nitrogen and their interference was removed. Urea will also destroy the nitrogen oxides, thus, a spatula tip was added to the solution just before addition of the indicator.

A series of experiments were performed to determine whether or not the acidity of the solution had any effect on the cobalt(III)-EDTA complex or the excess EDTA. Three solutions were prepared and oxidized in an identical manner. Then the pH of the first solution was adjusted to 1.0 and titrated immediately. The pH of the second solution was adjusted to about zero and this solution was set aside for one hour. The third solution was adjusted to pH zero and then brought back to 1.0 with sodium hydroxide and immediately titrated with standard bismuth solution. The results were the same for all three titrations indicating that the complex and the excess EDTA are not destroyed at the low pH or at least not within a reasonable time period required to perform the titration.

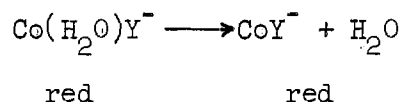
A study of the cobalt(III)-EDTA complex has been made by Schwarzenbach (83). Two red complexes are known to exist which hardly can be distinguished by the eye but which the phototitrator can readily distinguish (see Fig. 13). In alkaline medium the oxidation of the cobalt(II)-EDTA complex by hydrogen peroxide proceeds, according to Schwarzenbach, in the following manner



On acidification a proton is attached and this process is accompanied by a color change to red



The complex containing one molecule of coordinated water is not stable and it dissociates in a rather slow process according to the equation



Fortunately at the wavelength which the titration is performed the two cobalt complexes have the same extinction coefficient and this slow decomposition does not interfere with the titration (see Figure 13).

The pH of the solution containing the cobalt(III)-EDTA complex to be titrated can vary between certain values depending on the constituents in the solution. The pH should be no greater than 2 in order to prevent the hydrolysis of bismuth, iron, thorium and zirconium. The pH used may be as low as 0.5 in order to insure that some of the more stable EDTA complexes other than those of the cobalt(III) and bismuth are completely dissociated.

The effect on the titration curve due to changes of pH was studied. Identical aliquots of a bismuth solution were taken and the pH of each was adjusted to 2.0, 1.5, 1.0 and 0.5 respectively. The pH was adjusted with nitric acid and measured with a pH meter. The titration with EDTA was performed at 622 m $\mu$ . The results of these titrations are shown in Fig. 15. As the pH is lowered the break becomes smaller. However, the end point is established without difficulty.

After accounting for the sources of error the method was evaluated by titrating solutions obtaining known amounts of cobalt. The procedure

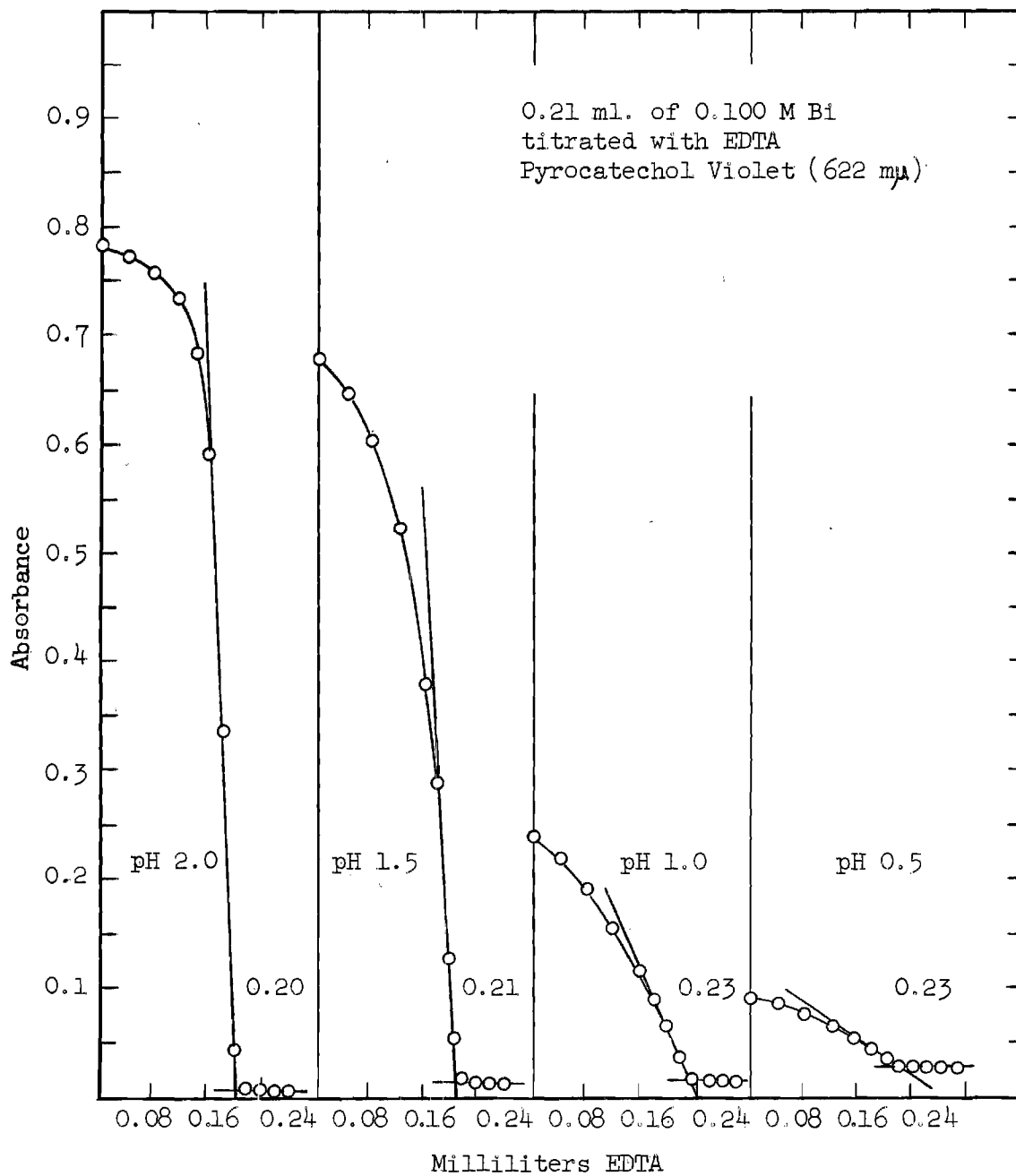


Figure 15. Titration of Bismuth with EDTA and Pyrocatechol Violet Step Indicator.

involved the following steps: an aliquot of standard cobalt solution was pipetted into a beaker. An excess of EDTA was then added and the solution was then adjusted with a dilute sodium hydroxide solution which was added dropwise while the pH was measured with a pH meter. After reaching pH 10 the solution was well stirred and 3 to 5 drops of 30 per cent hydrogen peroxide was added. The pink solution immediately became deep blue. Next nitric acid was added dropwise to lower the pH below 2. About 200 mg of urea was then added and the solution was quantitatively transferred to the titration cell. Twenty drops of a 10 per cent aqueous solution of PCV was added. The solution was titrated with standard bismuth solution. The transmittance readings were both recorded and immediately plotted on semi-logarithmic paper. The end point was established by extrapolation. The results of a series of titrations are presented in Table 13. In general, the curves were identical in appearance to those shown in Fig. 15.

A study of the effect of the presence of other metal ions was made. The titrations were conducted in the manner described for the solutions containing only cobalt except that the excess EDTA added was enough to complex all metal ions present and provide some uncomplexed EDTA. The following metals did not interfere in the back titration: lead, cadmium, zinc, aluminum, magnesium, calcium and barium. The results of some of these titrations are presented in Table 14. No auxiliary masking agents were required when these ions were present. In the presence of aluminum, however, the pH had to be less than 1 otherwise a time effect was observed.

Titration in the presence of nickel and copper were difficult to carry out using this back titration method. A serious time effect was

Table 13. Representative Results for the Back Titration of Cobalt

Titration at pH	0.1000 M EDTA	
	ml Required	ml Taken
0.5	5.11	5.14
0.6	4.49	4.47
1.0	9.25	9.21
1.0	18.42	18.50
1.0	4.48	4.51
1.0	2.68	2.66
1.0	5.59	5.60
1.0	3.30	3.29
1.0	5.07	5.08
1.5	23.40	23.56
2.0	7.78	7.79

Table 14. Representative Results for Back Titration of Cobalt in the Presence of Foreign Metals

O.1 M Solution of Foreign Metal Ion added ml	Titration at pH	0.1000 M EDTA, ml	
		ml Required	ml Taken
Th <sup>+4</sup> , 5(20ml 0.1 M Na <sub>2</sub> SO <sub>4</sub> for masking)	0.5	5.24	5.20
Mn <sup>+2</sup> , 5	0.6	4.60	4.63
Mn <sup>+2</sup> , 5	0.6	4.17	4.17
Mn <sup>+2</sup> , 5	0.7	5.15	5.14
UO <sup>+2</sup> , 5	0.6	5.63	5.66
WO <sub>4</sub> <sup>-2</sup> , 5	0.6	5.67	5.60
Ca <sup>+2</sup> 5, Mg <sup>+2</sup> 5	0.6	4.26	4.26
Mg <sup>+2</sup> 12	1.0	5.56	5.63
Al <sup>+3</sup> 20	0.6	5.32	5.34
Pb <sup>+2</sup> 12	1.0	4.41	4.43
Cu <sub>4</sub> <sup>+2</sup>	1.0	2.68	2.67
Cu <sup>+2</sup> 10	1.5	13.39	13.35
Cu <sup>+2</sup> 15	1.5	5.79	5.78
Cu <sup>+2</sup> 15	0.6	4.60	4.65
Ni <sup>+2</sup> 5	0.6	4.58	4.59
Ni <sup>+2</sup> 15	0.6	8.56	8.57
Ni <sup>+2</sup> 10, Cu <sup>+2</sup> 5	0.6	7.10	7.08
Ni <sup>+2</sup> 9, Zn <sup>+2</sup> 5, Pb <sup>+2</sup> 8, Cu <sup>+2</sup> 5 Mg <sup>+2</sup> 5, Ca <sup>+2</sup> 5	0.6	8.89	8.90
Ni <sup>+2</sup> + Co <sup>+2</sup> (0 C)	2.0	18.12	18.15
Co <sup>+2</sup> (room temperature)	2.0	8.71	8.70

observed. A study of the titration reaction revealed that both nickel and copper were slowly replaced from their EDTA complexes by bismuth. The rate was not aided by changing the pH. Thus for those metals which were slowly replaced the back titration procedure was further modified. After the addition of excess EDTA, oxidation and acidification, instead of titrating the excess EDTA, an excess of bismuth over the amount of EDTA added was provided. The replacement reaction now occurs rapidly; the bismuth combining with all of the EDTA except that combined with cobalt(III). The excess of bismuth is now back titrated with a standard EDTA solution at the same wavelength used previously. Nickel and copper do not interfere if the "double" back titration procedure is used. The results of a series of titrations using this modified method are presented in Table 14.

Several other common metal ions interfered with the titration and a series of studies were made in order to eliminate the interference.

When a solution of manganese alone was treated with an excess of EDTA and the solution was made alkaline a yellow turbidity formed. Upon addition of hydrogen peroxide a vigorous reaction occurred and manganese dioxide precipitated. Upon acidification the pink color of the manganese(III)-EDTA complex appeared. Excess bismuth was added and the excess back titrated with EDTA. The experimental value for the excess EDTA determined was always low indicating that not all of the EDTA in the manganese(III) complex had been replaced. In addition a slight time effect was observed during the titration indicating that the replacement is occurring slowly. This interference, due to the formation of the manganese(III)-EDTA complex, can be eliminated by reducing the manganese(III) with ascorbic

acid. Thus after the oxidation step and subsequent acidification of the solution with nitric acid a spatula tip of ascorbic acid is added to the solution. Titrations of cobalt in the presence of manganese can be performed successfully using this modification. A series of titrations were performed to determine whether or not the ascorbic acid would reduce the cobalt(III). A solution of cobalt(III)-EDTA at pH 1.0 with 200 mg of ascorbic acid present at the end of 1 hour was titrated and the correct amount of cobalt was found indicating no reduction of Co.

If mixtures of chromium(III) and cobalt are analyzed according to the normal procedure the results obtained for cobalt are too high indicating that some of the chromium is being co-titrated. Chromium forms its EDTA complex only very slowly so that it is precipitated during the alkalization step. Some of the chromium is oxidized to chromate when hydrogen peroxide is added to the alkaline solution. When the solution is acidified the precipitated chromium(III) hydroxide redissolves. Any dichromate present per se would not interfere. However, in the presence of left over hydrogen peroxide the dichromate is reduced to chromium(III) which in statu nascendi rapidly complexes with the EDTA.

Thus, if a solution containing chromium(III), cobalt(II) and EDTA is boiled at pH 3-4 the deep violet of the chromium(III)-EDTA complex appears. The excess EDTA can be titrated with bismuth solution. This titration gives the chromium alone since the cobalt is in the divalent state and is readily replaced by bismuth. In a second aliquot the sum of cobalt and chromium can be obtained if the procedure is slightly modified. First the sample solution is boiled with excess

EDTA to hasten the complexation of the chromium, the solution is cooled and made alkaline. Then the cobalt is oxidized with hydrogen peroxide. The titration is performed at pH 1 and the sum of cobalt and chromium is obtained. The cobalt is determined by difference.

Thorium forms a highly stable EDTA complex and will be cotitrated unless it is masked by the addition of sodium sulfate. The titration must be performed at pH 0.5 in order to prevent the formation of basic bismuth sulfate which will precipitate at a higher pH.

Other metals which form highly stable EDTA complexes will be cotitrated. For example bismuth, zirconium, indium and gallium all interfere (82). No masking agent is known for these ions. Mercury interferes by producing erratic time effects which could not be eliminated. Although mercury ordinarily is masked with bromide this was impossible under the conditions of the titration since bismuth oxy-bromide precipitated. Silver seriously interfered because it is first precipitated as the oxide during the oxidation step and it also catalyzed the decomposition of the EDTA by the hydrogen peroxide which caused a vigorous reaction.

Iron is known to cause an interference (84). Theoretically, it should be cotitrated since it has a very high stability constant with EDTA. It destroys the indicator, however, thus its presence renders the titration impossible.

At pH 0.5 only a few anions were found to interfere. Citrate and tartrate interfere by masking the bismuth against EDTA. Halides interfere by forming insoluble bismuth oxy-halides. Even at pH 0.5 very small amounts of chloride cause a turbidity. The molybdate anion

interferes because it reacts with the indicator thus masking it against bismuth.

The possibility of determining the sum of cobalt and nickel in a sample by combining this approach with a method for determining nickel at  $0^{\circ}\text{C}$  was investigated (14). The sample solution containing nickel and cobalt was treated in the normal fashion, i.e., oxidation, acidification, etc., but just before back titration with bismuth the solution was cooled to  $0^{\circ}\text{C}$  by the addition of ice to the sample solution in the titration cell. The nickel reacts so slowly at  $0^{\circ}\text{C}$  that none of it is replaced from the EDTA complex during the titration. Thus, the back titration with bismuth provides the basis for obtaining the sum of nickel and cobalt. The solution was then allowed to warm to room temperature so that the bismuth replaced the nickel. The excess of bismuth was titrated with EDTA and the amount of cobalt calculated. Table 14 contains the result of a determination carried out in this manner.

Titration at  $0^{\circ}\text{C}$  was impossible unless water vapor was prevented from condensing on the cold titration cell. This problem was easily overcome by allowing a gentle flow of nitrogen gas to pass over the cell face during the titration. No difficulties were encountered using this modification.

On the basis of the considerations just discussed the following method for selectively analyzing for cobalt will be outlined. The solution containing cobalt and other metal ions is pipetted into a beaker. A measured amount of a standard EDTA solution is added so that all of the metal ions present (with the exception of the alkali metals) are complexed and some EDTA is present in excess. The pH of the solution

is raised to 10 by addition of sodium hydroxide. A pH meter is used to measure the pH while adding the sodium hydroxide. Then 4 to 5 drops of 30 per cent hydrogen peroxide is added to oxidize the cobalt(II). Next nitric acid is added dropwise until the pH is less than about 2. The nature of the interfering ions present will determine the final pH. A spatula tip of urea is added. This solution is quantitatively transferred to the titration cell and the phototitrator is adjusted to about 90 per cent transmittance with this solution. Adjustment to 100 per cent transmittance is avoided so that a safety range is provided if the transmittance is slightly higher at the end point because of dilution. The excess EDTA is then back titrated with a standard bismuth solution.

If nickel and copper are present, instead of titrating with standard bismuth and exactly measured excess of bismuth is added. An excess of bismuth is signaled by the change in color of the indicator. The excess bismuth is then back titrated with standard EDTA solution.

#### Summary

A highly selective method for titrating cobalt has been devised based on the conversion of cobalt(II) to the highly stable cobalt(III)-EDTA complex. The titration is performed at a pH less than 2 where most metal-EDTA complexes are completely or nearly completely dissociated. The cobalt must be oxidized in the presence of an excess of EDTA and the excess EDTA is back titrated with standard bismuth solution. For practically all of the common metals this procedure is satisfactory. Copper and nickel are replaced very slowly from their EDTA complexes, however. In order to overcome this kinetic problem an excess of bismuth solution is added instead of back-titrating with bismuth. The

replacement reaction occurs much more rapidly under this condition. The excess bismuth is now back titrated with a standard EDTA solution. Pyrocatechol violet is used as a step indicator and gives excellent photometric titration curves.

Most metal ions will not interfere either because the pH is too low or they can be masked. The most serious interference which cannot be prevented is due to iron. To use this method then one must first separate iron. Chromium interferes but the method can be modified in such a way so as to enable the determination of both cobalt and chromium.

Nickel and cobalt can be determined in the same solution by performing two titrations. The sum of nickel and cobalt is obtained by titrating the excess EDTA with bismuth at  $0^{\circ}\text{C}$ . An excess of bismuth is then added after the end point and the solution is warmed to room temperature. The bismuth replaces the nickel from its EDTA complex and the remainder of the uncomplexed bismuth is back-titrated with EDTA.

## BIBLIOGRAPHY

1. Hillebrand, W. F. and Lundell, G. E. F., Applied Inorganic Analysis, 2nd ed. New York: John Wiley and Sons, Inc., 1953, p. 1.
2. Lundell, G. E. F., Ind. Eng. Chem. Anal. Ed., 5, 221 (1933).
3. Feigl, F., Chemistry of Specific, Selective and Sensitive Reactions, trans. R. E. Oesper, New York: Academic Press Inc., 1949, p. 18.
4. Morgan, G. T. and Drew, H. D. K., J. Chem. Soc., 117, 1456 (1920).
5. Reilley, C. N., Schmid, R. W. and Sadek, F. S., J. Chem. Ed., 36, 555 (1959).
6. Schwarzenbach, G., Helv. Chim. Acta, 35, 2344 (1952).
7. Flaschka, H. A. and Barnard, A. J. Jr., "Titrations with EDTA and Related Compounds," Comprehensive Analytical Chemistry, C. L. Wilson and D. W. Wilson, eds. Amsterdam: Elsevier Publishing Co., 1960, p. 288.
8. Reilley, *op. cit.*, p. 555.
9. Schwarzenbach, G. Complexometric Titrations, New York: Interscience Publishers Inc., 1957, p. 10.
10. Wanninen, E., Acta Acad. Abonensis, 21, 104 (1960).
11. Flaschka, H. A., EDTA Titrations, New York: Pergamon Press, 1959, p. 28.
12. *Ibid.*, p. 49.
13. Cheng, K. L., Anal. Chem., 33, 783 (1961).
14. Flaschka, H. A., and Puschel, R., Z. anal. Chem., 149, 345 (1956).
15. Flaschka, H. A., EDTA Titrations, p. 55.
16. Flaschka, H. A. and Barnard, A. J. Jr., *op. cit.*, p. 322.
17. Flaschka, H. A., Talanta, 1, 60 (1958).
18. Flaschka, H. A., EDTA Titrations, p. 49.
19. Flaschka, H. A. and Barnard, A. J. Jr., *op. cit.*, p. 315.
20. Ibid., P. 316.

21. Reilley, C. N. and Scribner, W. G., Anal. Chem., 27, 1210 (1955).
22. Goddu, R. F. and Hume, D. N., Anal. Chem., 26, 1740 (1954).
23. Flaschka, H. A. and Sawyer, P. O., Talanta, 9, 249 (1961).
24. Underwood, A. L., Anal. Chem., 26, 782 (1954).
25. Goddu, R. F. and Hume, D. N., Anal. Chem., 26, 1679 (1954).
26. Higuchi T., Rehm, C. and Barnstein C., Anal. Chem., 28, 1506 (1956).
27. Fortuin, J. M. H., Karsten, P. and Kies, H. I., Anal. Chim. Acta, 10, 356 (1954).
28. Ringbom, A. and Wanninen, E., Anal. Chim. Acta, 11, 153 (1954).
29. Flaschka, H. A., Talanta, 8, 381 (1961).
30. Underwood, A. L., J. Chem. Ed., 31, 394 (1954).
31. Headridge, J. B., Talanta, 1, 293 (1958).
32. Osburn, R. H., Elliott, J. H. and Martin, A. F., Ind. Eng. Chem. Anal. Ed., 15, 642 (1943).
33. Goddu, R. F. and Hume, D. N., Anal. Chem., 26, 1740 (1954).
34. Headridge, J. B., Photometric Titrations, New York: Pergamon Press, 1961.
35. Flaschka, H. A. and Sawyer, P. O., Talanta, 8, 521 (1961).
36. Tingle, A., J. Am. Chem. Soc., 40, 873 (1918).
37. Muller, R. H. and Partridge, H. M., Ind. Eng. Chem. Anal. Ed., 20, 423, (1928).
38. Bobtelsky, M., Heterometry, Amsterdam: Elsevier Publishing Co., 1960.
39. Yoe, J. H. and Jones, A. L., Ind. Eng. Chem. Anal. Ed., 16, 111 (1944).
40. Meites, L. and Thomas, H. C., Advanced Analytical Chemistry, New York: McGraw-Hill Book Company, Inc., 1958, p. 287.
41. Connors, K. A. and Higuchi, T., Anal. Chem., 32, 576 (1960).
42. Hummelstedt, L. E. I. and Hume, D. N., Anal. Chem., 32, 576 (1960).
43. Underwood, A. L. and Howe, L. H., Anal. Chem., 34, 1692 (1962).
44. Florence, T. M., Anal. Chim. Acta, 23, 282 (1960).

69. Ibid., p. 31.
70. Holloway, J. H. and Reilley, C. N., Anal. Chem., 32, 249 (1960).
71. Sweetser, P. S. and Bricker, C. E., Anal. Chem., 26, 195 (1954).
72. Underwood, A. L., Anal. Chem., 26, 1322 (1954).
73. Wanninen, op. cit., p. 106.
74. Kraus, K. H. and Moore, G. E., J. Am. Chem. Soc., 75, 1960 (1953).
75. Sweetser, P. S. and Bricker, C. E., Anal. Chem., 25, 253 (1953).
76. Burtner, D. C., Univ. Microfilms (Ann Arbor, Mich.) Publ. No. 8094, 93 pp.; C. A. 48, 9859 (1954).
77. Flaschka, H. A. and Soliman, A., Z. anal. Chem., 158, 254 (1957).
78. Hall, A. J. and Young, R. S., Chem. and Ind., 44, 394 (1946).
79. Tomicek, O. and Freiburger, H., J. Am. Chem. Soc., 57, 801 (1935).
80. Kinnunen, J. and Wennerstrand, B., Chemist-Analyst, 46, 92 (1957).
81. Reilley, C. N., Scribner, W. G. and Temple, C., Anal. Chem., 28, 450 (1956).
82. Schwarzenbach, G., Helv. Chim. Acta, 32, 839 (1949).
83. Flaschka, H. A. and Sadek, F. S., Z. anal. Chem., 149, 345 (1956).

## VITA

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