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THE MICRODETERMINATION OF CADMIUM
AND ZINC BY PHOTOMETRIC TITRATION

A THESIS

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the Faculty of the Graduate Division
by
Frederick Burke Carley


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THE MICRODETERMINATION OF CADMIUM
AND ZINC BY PHOTOMETRIC TITRATION

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CHAPTER I

INTRODUCTION

The purpose of this work has been to establish a chelometric titration with photometric endpoint detection for the determination of cadmium and zinc in the same solution. The method involves the use of an excess of a complex forming organic dye (commonly used as a metallochrome indicator in visual titrations) to make selective endpoint detection possible.

The possibility of selective endpoint detection by the photometric method has been recognized for some time. Little work has been done involving the use of organic dyes in a selective determination since a large excess of dye is practically always necessary to obtain a useful titration curve and the resulting high absorbance of the solution tends to make it difficult to obtain sufficiently accurate absorbance measurements. However, Flaschka and Sawyer (1) have designed an instrument by means of which titrations can be very successfully performed in solutions of the type mentioned above. This instrument also has additional features which make it well suited for use in a practical analysis.

Because of the high absorptivities of most dyes and

their metal complexes the use of dyes is generally applicable in solutions of metal ions which are very dilute (below 10^{-4} molar). Thus a method for the determination of cadmium and zinc using an organic dye would eliminate a difficult separation process. On the other hand cadmium and zinc can be readily separated from most other metal ions by ion exchange methods.

No methods involving the use of dyes for the determination of cadmium and zinc by photometric titration have been reported.

Methods are available for determining the sum of cadmium and zinc by chelometric titration using an indicator to detect the endpoint visually or, when working with very dilute solutions, instrumentally. Thus cadmium and zinc can be evaluated by means of two titrations, one of which is the selective titration of cadmium or zinc in the presence of the other.

Cadmium can be determined in the presence of zinc by instrumental methods, e. g., amperometry.

Sweetser and Bricker have titrated cadmium in the presence of zinc with EDTA using photometric endpoint detection (2). The absorbance is measured at 236 mμ where the cadmium-EDTA complex and EDTA differ in absorbency. The solution must be strongly alkaline so that zinc is present as the unreactive zincate ion. Cadmium is kept in solution by the presence of a small amount of cyanide ion. The short

wave length used, the high alkalinity, and the fact that the amount of cyanide used is critical are serious disadvantages of the method.

Flaschka and Ganchoff have developed a photometric titration for the determination of cadmium in the presence of up to a 500-fold excess of zinc using EGTA as the titrant and copper as the slope indicator at 742 m μ (3). The solution is buffered at pH 10 with ammonia-ammonium chloride buffer and under these conditions cadmium is titrated before the copper. The presence of zinc makes the location of the copper endpoint uncertain but does not affect the location of the cadmium endpoint. The method is very satisfactory for cadmium and can be readily applied to solutions which are as low as 10^{-4} molar in cadmium ion when a 10 cm light path is used. Use of this method for the evaluation of zinc in the presence of cadmium is not quite so advantageous since two titrations are necessary, a different titrant (EDTA) is used for the evaluation of the sum of cadmium and zinc, and the titer of the zinc is obtained from the difference of two titrations.

A method for the determination of cadmium and zinc using DTPA as the titrant and copper as the slope indicator has been reported (4). In a solution which is 0.5 molar in ammonia the effective stability constant of Cd-DTPA is about 3 log units greater than the constants for Cu-DTPA and Zn-DTPA, which are very close together. Thus cadmium

is titrated first in this system. Cadmium is determined and also the sum of copper and zinc by taking absorbance measurements at 700 mμ where the Cu-DTPA complex absorbs more strongly than the Cu-NH₃ complex. The location of the cadmium endpoint as well as the copper-zinc endpoint is uncertain since the titration curve shows a curvature when zinc is present. The results for zinc are more uncertain since they are obtained by subtracting the amount of copper present from the results of the titration.

CHAPTER II

THEORY

Chelometric Titrations

In the photometric titration of metals, complexing agents are frequently used as titrants, indicators, and masking agents. The following discussion will be concerned with the theory of complexometric titrations. The theory of photometric endpoint detection will be discussed later.

Only a one-to-one complex between the metal ion and the titrant will be considered.

In the titration of a metal ion with a chelon the principal reaction which occurs is:

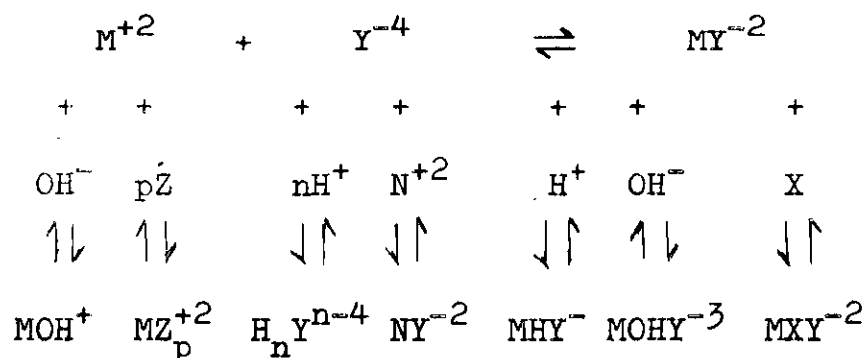


When the metal ion is present in its hydrated form and the chelon is present in its anionic form (with all of its acidic protons removed), the extent of reaction between the metal and the chelon depends only on the equilibrium constant for the reaction written above. The equilibrium constant (K_{MY}) is given by:

$$K_{MY} = \frac{[MY]^*}{[M][Y]} \quad (2)$$

and is called the "absolute stability constant" for the complex MY. Charges are omitted in equation (2), a practice which will be continued. Charges will be considered to be understood when omitted from charged species in the equations to follow.

In most cases equations (1) and (2) do not adequately describe what occurs when a metal is titrated with a chelon. Competing reactions involving hydrogen and hydroxide ions as well as other complex formers and metal ions present must also be considered. The scheme below shows some of the equilibria possibly superimposed in the titration of a metal ion with a chelon.



In this particular case M^{+2} is the hydrated form of the

*This is a concentration constant and is different from the thermodynamic equilibrium constant for which the activities of the species involved are used.

bivalent metal to be titrated, Y^{-4} is the anion of the chelon which is a tetra basic acid, N^{+2} is an interfering metal ion, and Z and X are auxiliary or foreign complex formers.

Effective Constants

In order to determine the extent of the reaction between the metal to be titrated and the chelon, the equilibrium constants for all competing reactions and the concentration of all substances involved must be taken into account. Schwarzenbach (5) introduced the concept of the "apparent stability constant" in order to account for the effect of protonation of the free chelon and the effect of auxiliary complexing agents on the reaction between the metal and the chelon. Ringbom (6, 7) extended this approach to include the effect of competing metals and the formation of hydroxo compounds and mixed complexes. The term "conditional stability constant," which was introduced by Ringbom at the suggestion of I.M. Kolthoff to emphasize the dependence of the constant on the conditions under which it is observed, has the same meaning as the term "apparent stability constant," and the term "effective stability constant," which is also used.

The effective stability constant for the complex MY is defined by the equation

$$K' = \frac{[MY']}{[M'] [Y']} \quad (4)$$

where $[M']$ is the sum of the concentrations of all species present which contain the metal but do not also contain the chelon; $[Y']$ is the sum of the concentrations of all species present containing the chelon but not the metal; and $[MY']$ is the sum of the concentrations of all species present which contain both the metal and the chelon regardless of what ever else is contained in the molecular formulas of the species.

α -Coefficients

The computation of the effective stability constant from the absolute constant under any given set of conditions is greatly facilitated by the use of the α -coefficients which were introduced by Schwarzenbach. The effective and absolute stability constants are related by the equation

$$K' = \frac{\alpha_{MY}}{\alpha_M \alpha_Y} \cdot K_{MY} \quad (5)$$

where the α -coefficients are defined as

$$a) \alpha_M = \frac{[M']}{[M]} \quad b) \alpha_Y = \frac{[Y']}{[Y]} \quad c) \alpha_{MY} = \frac{[MY']}{[MY]} \quad (6)$$

These coefficients are functions only of the concentrations of the interfering components and the corresponding equi-

librium constants and can readily be calculated if the necessary data are available.

The competition of the proton for the chelon is particularly important since chelons are weak polybasic acids. α_Y at any pH can be calculated from the acid dissociation constants of the chelon. However, it is more convenient to use the proton stability constants, which are given for a chelon with four acidic hydrogens by the following equations:

$$\begin{aligned} \text{a) } K_1 &= \frac{1}{K_{4,\text{diss}}} = \frac{[\text{HY}]}{[\text{H}][\text{Y}]} & \text{b) } K_2 &= \frac{1}{K_{3,\text{diss}}} = \frac{[\text{H}_2\text{Y}]}{[\text{H}][\text{HY}]} \\ \text{c) } K_3 &= \frac{1}{K_{2,\text{diss}}} = \frac{[\text{H}_3\text{Y}]}{[\text{H}][\text{H}_2\text{Y}]} & \text{d) } K_4 &= \frac{1}{K_{1,\text{diss}}} = \frac{[\text{H}_4\text{Y}]}{[\text{H}][\text{H}_3\text{Y}]} \end{aligned} \quad (7)$$

In this case $[\text{Y}']$ is given by:

$$[\text{Y}'] = [\text{Y}] + [\text{HY}] + [\text{H}_2\text{Y}] + [\text{H}_3\text{Y}] + [\text{H}_4\text{Y}] \quad (8)$$

By using equations (7) a), b), c), d) to substitute for all protonated forms in equation (8), we obtain

$$\begin{aligned} [\text{Y}'] &= [\text{Y}] + K_1[\text{H}][\text{Y}] + K_1K_2[\text{H}]^2[\text{Y}] + K_1K_2K_3[\text{H}]^3[\text{Y}] \\ &\quad + K_1K_2K_3K_4[\text{H}]^4[\text{Y}] \end{aligned} \quad (9)$$

or

$$[Y'] = [Y] \left[1 + \sum_{i=1}^4 \bar{K}_i [H]^i \right] \text{ where } K_i = \frac{h}{\pi} K_i \quad (10)$$

substitution into 6 b) yields

$$Y = \sum_{i=0}^M \bar{K}_i [H]^i, \quad K_0 = 1 \quad (11)$$

The alpha coefficients for other competing reactions may be calculated in a manner similar to that for the protonation of the chelon.

When more than one side reaction involving the metal, chelon, or metal chelonate is to be considered, it is easy to show that the contributions of the interfering substances can be separated as follows:

$$\alpha_{MY} = \alpha_{MY}(X_1) + \alpha_{MY}(X_2) + \dots + \alpha_{MY}(X_n) + (1-n) \quad (12)$$

$$\alpha_M = \alpha_M(Z_1) + \alpha_M(Z_2) + \dots + \alpha_M(Z_n) + (1-n) \quad (13)$$

$$\alpha_Y = \alpha_Y(H) + \alpha_Y(N_1) + \dots + \alpha_Y(N_n) + (1-n) \quad (14)$$

n is the total number of interfering components.

It is often of interest to know what species containing the metal or the chelon predominate in the solution before reaction. The coefficients defined in equation (6)

are the inverse of the fraction of the "free" substance present. Thus, as the α -coefficient approaches its minimum value of one, the fraction of the metal present in the hydrated form or the chelon present in the unprotonated form approaches unity. The fraction of any other species present is easily obtained. For example, the fraction of the chelon present as H_2Y^{-2} at a particular pH is obtained from equations (7) a), b), and (10) as:

$$\frac{[H_2Y]}{[Y']} = \frac{K_1 K_2 [H]^2}{1 + \sum_{i=1}^4 \bar{K}_i [H]^i} \quad (15)$$

A roughly quantitative idea of the predominating species present in a particular solution can be obtained by inspection of the values of the terms in equations like (8), (12), (13), and (14). Terms in these equations which are negligible compared to the sum indicate that the corresponding species are not present in appreciable amounts.

The values of the effective stability constants involved and the nature and concentrations of the species present greatly influence the outcome of a photometric titration of a metal with a chelon. The results of the foregoing discussion will be used later after some general aspects of photometric titrations are considered.

Basis of a Photometric Titration

In a photometric titration the property of the solution which is of interest is the absorbance (A) which is defined by

$$A = \log \frac{I_0}{I} = \log I_0 - \log I \quad (16)$$

where I_0 and I are intensities of the light incident to the solution and transmitted by the solution, respectively. For monochromatic light, the absorbance of a solution containing one species which absorbs light of the wave length used is given by the Lambert-Beer law as:

$$A = \epsilon bc \quad (17)$$

where ϵ is the molar absorptivity of the specie, b is the light path through the solution in centimeters, and c is the molar concentration of the species. The molar absorptivity is a constant which depends only on the wave length of the light and the identity of the species. When there are more than one absorbing species present, the absorbance of a solution is:

$$A = \sum_{i=1}^h A_i = \sum_{i=1}^h \epsilon_i bc \quad (18)$$

If a reaction involves the appearance or disappearance of one or more colored species, then the possibility

exists that the reaction be made the basis of a photometric titration. Consider the reaction $M + Y \rightarrow MY$ where the product (MY) is colored and the reactants are colorless. If a solution of M is titrated with a solution of Y, the result will be an increase in the absorbance as MY is formed.

After the stoichiometric point is reached there will be no further increase in absorbance if the reaction is complete at this point. Before the stoichiometric point the concentration of MY is directly proportional to the volume of Y added (neglecting the dilution effect). Hence a plot of absorbance against volume of Y added will look similar to curve I in Figure 3.

Dilution by the titrant causes curvature in photometric titration curves. This effect can be corrected for by applying the following:

$$A_{\text{corrected}} = A_{\text{measured}} \frac{V + v}{V} \quad (19)$$

where V is the volume of the solution titrated and v is the volume of titrant added. In practice the titrant is conveniently used in so high a concentration that the volume added is less than one per cent of the volume of the solution and in such a case it is not necessary to apply a correction.

Incompleteness of reaction may cause a curvature in

the titration curve. In the early stages of the titration each increment of Y added will react completely to form MY because of the large excess of M present. As the endpoint is approached the amount of MY produced by each addition of Y will decrease when the amount of M present is insufficient to force the reaction to completion. Immediately after the endpoint the addition of Y will result in the production of a small amount of MY since there is still some unreacted M in the solution. When sufficient Y has been added to force the reaction essentially to completion, further addition of Y will not result in the production of MY.

The endpoint in a photometric titration is usually located graphically. The whole procedure consists in measuring the absorbance (or a related quantity) of a solution after each addition of an increment of titrant, plotting the values obtained on graph paper, and drawing the best two straight lines through the series of points in order to obtain the endpoint as the intersect. When the titration curve has an appreciable amount of curvature around the endpoint, points near the endpoint are not used and the endpoint is "extrapolated" by use of points far from the endpoint.

Types of Indication in Photometric Titrations

Flaschka and Sawyer (8) have devised a new nomenclature for the different type of photometric endpoint detection which indicates both the equilibrium and optical properties of a system.

Self Indication. A system is termed self-indicating when a metal ion initially present in a complex (B complex) is transformed into the titration complex (T complex) of differing absorbance. The T complex must be much more stable than the B complex.

Step Indication. A system where a complex-forming indicator is used is a step-indicating system. For satisfactory indication, the indicator complex must be related in stability to the B and T complexes by $K_B \ll K_I \ll K_T$. The optical properties of all species must be such that there is a difference in slope of the titration curve before and after the endpoint.

Slope Indication. Slope indication refers to the determination of metal via another metal, the latter being part of a self-indicating system. The color change of the self-indicating metal which must be titrated last locates the endpoint for the metal to be determined. The following condition must be met:

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

i.e., the ratio of the stabilities of the T and B complexes of the self-indicating system (subscript s) must be much less than the same ratio for the metal to be determined (subscript d).

Figure 1 contains examples of the three types of

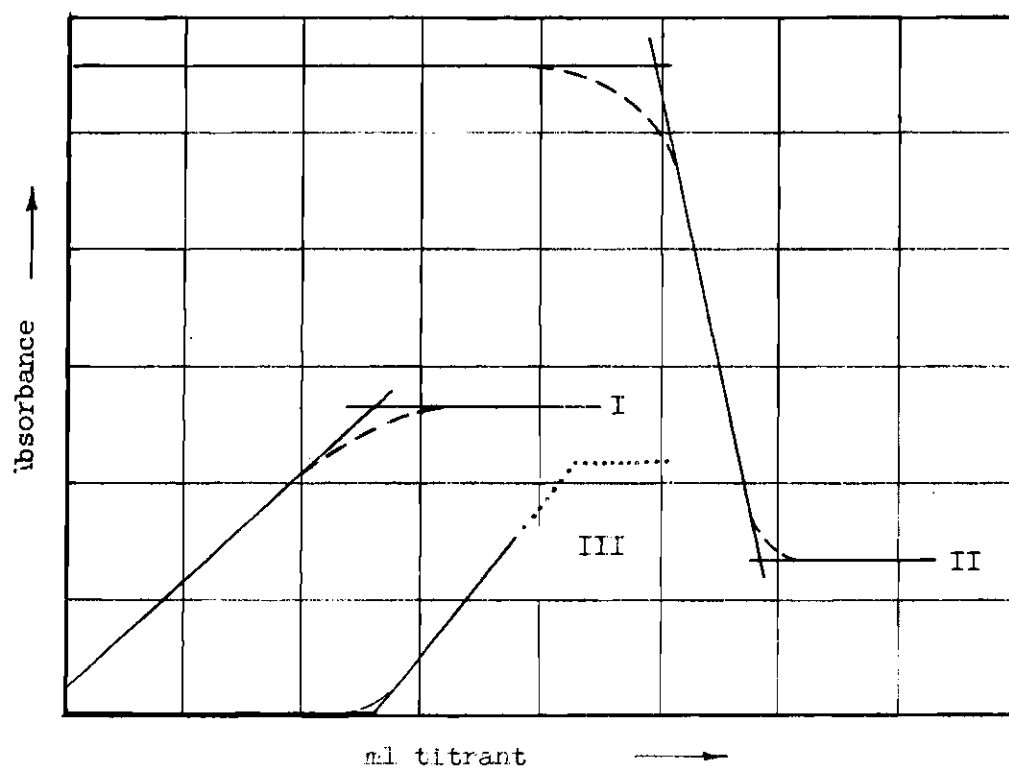


Figure 1. Photometric Titration Curves Obtained with Various Types of Indication.(9)

indication just described. Curve I is a typical curve for a self-indicating system. Curve II is an example of step indication. In this case the free metal ion, the chelon, and the metal chelonate do not absorb at the wave length used. The metal indicator complex absorbs more strongly than the free indicator. The second intersection corresponds to the amount of metal present while the difference between the second and first intersection corresponds to the amount of indicator present. In Curve III the first intersection corresponds to the endpoint for the metal to be determined by the slope-indicating method. Note that the metal from the self-indicating system can also be determined by continuing the titration to the second endpoint (dotted line).

A step-indicating system can be transformed into a self-indicating system by increasing the amount of indicator until it exceeds the amount of metal present. This improves the location of the endpoint in certain cases. Thus, when the metal indicator complex is weak, a good titration curve can be obtained by using a large excess of indicator. The metal is driven into the indicator complex by the large excess of indicator. The metal is driven into the indicator complex by the large excess of indicator. On the other hand the step-indicating curve would show a large degree of curvature due to the weakness of the metal indicator complex.

When two metals are present both may be determined

if enough indicator is added to complex all of the second metal to be titrated provided that the other conditions for indication are met.

Theoretical Photometric Titration Curves

Flaschka (10), Fortuin, Harsten and Kies (11), and Ringbom and Wanninen (12) have done theoretical investigations on photometric titrations for all of the different types of indication. Equations have been derived which relate the absorbance of the system to the degree of titration. Due to the complexity of these equations, it is not possible to obtain from them a mathematical solution to the question: "Where does the extrapolated endpoint lie in relation to the equivalence point?" However, it is possible to plot titration curves theoretically for a given set of conditions, apply the extrapolation technique, and compare the two points mentioned above.

For the purpose of illustrating the dependence of titration curves of a self-indicating system on the equilibrium constants and the concentrations, the following approach is satisfactory.

For the titration reaction $M + Y \rightarrow MY$ assume that the titration curve will be "straight" where the dissociation of the chelate (reverse of above reaction) is less than some small fraction of the total amount of metal present. The concentrations of the species at any point in the titra-

tion before the endpoint are given by

$$[MY'] = aC_M - fC_M, [Y'] = fC_M, \text{ and } [M'] = (1-a)C_M + fC_M$$

where "a" is the fraction of the metal titrated, C_M is the total concentration of metal present, and f is the relative (to C_M) amount of chelonate which dissociates. Substitution into the expression for the effective constants

$$\left(K' = \frac{[MY']}{[M'] [Y']} \right)$$

and solving for the fraction of the metal not titrated

(1-a) yields:

$$(1-a) = \frac{1 - f^2 K' C_M - f}{1 + f K' C_M} \quad (20)$$

The last term in the numerator can be neglected since it is small compared to one. Table 1 shows how the fraction of metal not titrated varies with the product $K C_M$ for some degrees of dissociation of the complex.

Table 1. Fraction of Metal Not Titrated When Dissociation Begins to Occur for Some Values of $K' C_M$.

Ratio of Amount of Chelated to Amount of Metal Present	$K' C_M$				
	10	10^2	10^3	10^4	10^5
0.05	0.6	0.1	*	*	*
0.01	0.9	0.5	0.1	*	*
0.001	0.99	0.9	0.5	0.1	0.01

*Negative value. The amount of free chelon present does not exceed fC_M until after the stoichiometric point is reached.

A similar treatment can be applied to the titration of two (or more) metals. Assume that the effective constants for both metals are high enough that dissociation is negligible and consider only the exchange reaction



in determining the incompleteness of the reaction of either metal at any stage in the titration. The equilibrium constant for the exchange reaction is given by

$$Q = \frac{K'_{NY}}{K'_{MY}} = \frac{[NY'] [M']}{[MY'] [N']} \quad (22)$$

For convenience, let N be the metal which forms the more stable complex so that Q is always greater than one. The following relations can be derived.

$$(1 - a_N) = \frac{1 - f^2 Q R}{1 + f Q R} \quad (23)$$

$$a_M = \frac{1 - f^2 Q R}{1 + f Q R} \quad (24)$$

a_N and a_M are the fractions of N and M titrated, f is the fraction to which the exchange reaction proceeds with respect to the metal present in the smaller amount, and R is the ratio of the amounts of metals present such that $R \leq 1$.

Terms which are small when f is small have been omitted from equations (23) and (24). Table 1 can be used to show the results of equations (23) and (24). Table 1 gives the fraction of N not titrated for values of QR and the fraction of M titrated for values of QR when the exchange reaction starts to show an effect on the titration curve. These results show that for a given system the most favorable titration curve will be obtained when the metals are present in equal amounts.

When considering the effect of both dissociation and exchange on the titration of two metals, the previous discussion shows qualitatively that when the values of $K' C_M$ and QR are both low, the extrapolated endpoint will tend to be higher than the equivalence point for the second metal to be titrated and lower for the metal which is

titrated first.

A high effective constant for the titration complex does not guarantee that a good photometric titration curve can always be obtained. Consider the following titration reaction:



This corresponds to a self-indicating system where MI is the B complex and MY is the T complex. Assume that the color change is due only to a change in concentrations of the species MI and I and that the indicator (I) is in excess of the metal. Now if the complex MI is very stable under the conditions of the titration essentially all the metal present which has not been titrated will be in the form MI and equation (25) will adequately represent what happens during the titration. However, if the complex MI is not very stable, then some of the metal will be present in other forms and the reaction $M + Y \rightleftharpoons MY$, for which there is no color change, will also occur. The ratio of the metal indicator complex to the "free" metal is given by

$$\frac{[MI']}{[M']} = K'_{MI} [I'] \quad (26)$$

This ratio becomes larger as the titration proceeds due to an increase in the concentration of the free indicator (not combined with the metal) which is produced according to

reaction 25. Thus, there will be a larger change in absorbance for each increment of titrant added in the later stages of the titration. The resulting titration curve will be curved rather than straight.

The above problem can usually be remedied by adding a very large excess of indicator so that the change in concentration of indicator will be very small. Equation (26) shows that $[MI]/[I]$ will be practically constant in this case. Increasing the amount of indicator lowers the effective constant for the T complex, and this may sometimes cause difficulty.

CHAPTER III

EQUIPMENT AND CHEMICALS

Photometric Titrator

The photometric titrator used in this work was designed by Flaschka and Sawyer (13, 14). Actually, two instruments were used but, since they are essentially of the same design, the two instruments will be considered as one.

The instrument is very well suited for use in photometric titrations. The titration cell is not housed in a light tight compartment because the design of the instrument otherwise makes this unnecessary. Thus, titration cells of different size may be used in conjunction with the instrument, and stirring, heating (when necessary), and the addition of titrant is easily accomplished without the necessity of removing the titration cell from its position in the light of the instrument. Also, the operator can examine the cell and its contents at any time to detect such effects as turbidity, presence of dust particles, and the position of the stirrer. The instrument has a high degree of electrical and mechanical stability and a provision for effectively "expanding the scale."

Components of the Photometric Titrator

A schematic diagram of the phototitrator is shown in Figure 2. The light source is a G.E. bulb, type 425, powered by a 6-volt lead storage battery. A variable resistor, in circuit with the bulb and battery, controls the output of the light. A condensing lens (1 centimeter in diameter), placed at a distance equal to its focal length away from the light, produces an approximately parallel beam of light which is about 1 centimeter in diameter. A diaphragm which has a wedge-shaped opening is placed in the light path, enabling optical control of the light intensity to be effected. A slot is located in the light detector compartment for insertion of an interference filter in the light beam. A shutter blocks the light beam when the interference filter is not in place. A piece of heat absorbing glass (now shown in figure) is fixed in the light beam. Another condensing lens focuses light from the parallel beam on the photodetector. 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., 1N 2175, Photodiode) has a photosensitive surface of only a fraction of 1 mm². The photodetector is connected to a 13.5 volt mercury battery and a galvanometer, which is made by Rubicon Instruments Co., and has a sensitivity of 7×10^{-10} amps/mm. Two other circuits are connected to the galvanometer. Each of

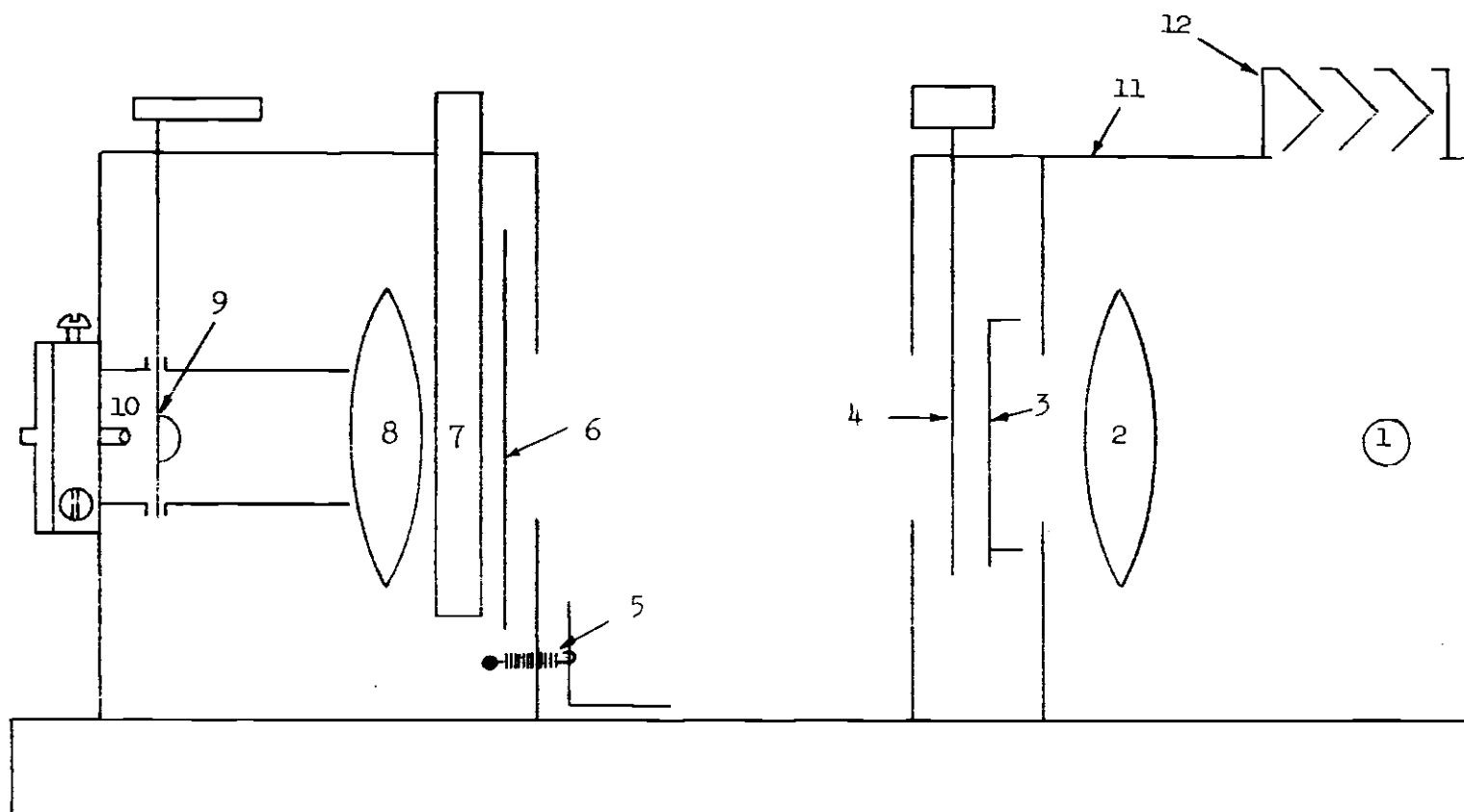


Figure 2. Diagram of the Phototitrator. (15)

- | | | | |
|-----------------|----------------|------------------------|--------------------------|
| 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 |

them may be used to send a current through the galvanometer. One is used as a zero-adjusting circuit and the other is used as a zero-suppressor circuit.

Other Equipment

Titration Cells

A titration cell, which was the bottom section of a 1-cm Corex absorption cell originally used in a Beckman DU spectrophotometer, was used. This cell was placed in a cell holder which had an iris diaphragm at one end and a permanent magnet on the bottom. Another cell with a capacity of about 50 ml and a light path length of 2 cm was also used.

Burettes

A Beckman/Spinco ultramicro burette, Model 153A, with a total capacity of 0.12 ml and a precision of about ± 0.01 ul was used in conjunction with the 1 cm titration cell. The holder for the titration vessel was replaced by a removable steel plate. A glass burette calibrated to deliver up to 0.5 ml was used with the 50 ml cell.

Stirrers

The Beckman/Spinco ultramicro burette was already equipped with a vibrating stirrer. The stirrer was used with the 50 ml cell was a glass rod with a small propellor fashioned from the lower end and was driven by a 6-volt dc motor. The pitch of the propellor and the direction of

rotation were designed to cause a bottom-to-top motion of the stirred liquid.

Spectrophotometer

All spectral curves were made with a Bausch and Lomb Model 505 recording spectrophotometer.

PH Meter

All pH measurements were made with a Leeds and Northrup pH meter. The instrument was standardized by use of a saturated solution of potassium acid tartrate.

Glassware

Ultramicro pipettes, calibrated "to contain," were used with the 1 cm titration cell. Other glassware, including volumetric flasks, flasks, beakers, calibrated burettes, and calibrated pipettes were used as necessary.

Storage Bottles

All solutions used in this work were stored in plastic bottles.

Chemicals

Stock Solutions

Ethyleneglycol-bis(aminoethyl)-tetrascetic acid (EGTA). EGAT from the G. F. Smith Company was used to prepare approximately 0.1M solutions. Dissolution was accomplished by the addition of a few pellets of sodium hydroxide. The resulting solution was filtered and standardized against a calcium chloride solution prepared from J. T.

Baker reagent grade calcium carbonate. Calcon was used as the indicator.

Disodium Ethylenediamine Tetraacetate, Dihydrate
(Disodium Ethylenedinitrilo Tetraacetate, Dihydrate) (EDTA).

J. T. Baker Chemical Company "Baker Analyzed Reagent" EDTA was used to prepare an approximately 0.1M solution. The solution was standardized against a standard copper solution using murexide as the indicator.

Diethylenetriamine Pentaacetic Acid (DTPA). DTPA from the Dow Chemical Company was used to prepare an approximately 0.1M solution. Dissolution was accomplished by the addition of a few pellets of sodium hydroxide. The solution was standardized against a standard copper solution using murexide as the indicator.

Zinc Nitrate Solution. Reagent grade zinc metal was dissolved in nitric acid. The solution was boiled to drive off the excess acid and diluted with deionized water. The solution was prepared to be approximately 0.1M and was standardized against the standard EDTA solution using Erio T as the indicator.

Cadmium Nitrate Solution. Reagent grade mossy cadmium was used. The solution was prepared and standardized in the same manner as the zinc nitrate solution.

Ammonia Buffer pH 10. Reagent grade ammonium chloride (70 gm) and DuPont ammonium hydroxide (570 ml) were combined and diluted to one liter with deionized water.

Working Solutions.

Approximately $2 \times 10^{-3} \text{M}$ solutions of the chelons and $5 \times 10^{-4} \text{M}$ solutions of the metal ions were prepared by quantitative dilution of the standardized stock solutions. Deionized water which had been redistilled using a polyethylene condenser tube was used for all dilutions. The diluted solutions were stored in plastic bottles. Contact time with the volumetric glassware necessary for dilution was kept to a minimum. Working solutions of the buffer were prepared by approximate dilution using redistilled deionized water.

Other Reagents

Copper Nitrate Solution. J. T. Baker reagent grade copper wire was cleaned and dried and accurately weighed. The wire was dissolved in nitric acid and the resulting solution was diluted to the mark after warming to dispel oxides of nitrogen. The solution was prepared to be exactly 0.1000 M and was used to standardize the EDTA and DTPA solutions.

Calmagite Dye Solution. The dye was dissolved in redistilled deionized water to which a drop of ammonia buffer pH 10 had been added to produce an approximately 10^{-3}M solution of the dye.

Murexide Dye Powder. The J. T. Baker reagent was used. The dye was used as the undiluted powder or ground with sodium chloride to give a powder which contained 1 gm of dye per 200 gm of powder.

Bases. DuPont concentrated ammonium hydroxide was used. Reagent grade sodium hydroxide pellets were used to prepare solutions.

Nitric Acid. DuPont concentrated nitric acid was used to prepare solutions.

Special Buffer Solution. An ammonia-ammonium chloride buffer solution of high purity was prepared in the following manner: A beaker containing concentrated ammonium hydroxide was kept in a closed system for 24 hours along with a polyethylene beaker containing redistilled-deionized water to produce a purified ammonia solution. This solution was then mixed with a hydrochloric acid solution prepared in the same manner to give a buffer solution of pH 10.

CHAPTER IV

OPERATION OF THE PHOTOMETRIC TITRATOR

General

The photosensitive component of the photometric titrator, the photodiode, is essentially a variable resistor, the resistance of which is directly proportional to the intensity of the light incident to it. Hence, the number of scale divisions of galvanometer deflection resulting from light incident on the photodiode is a measure of the light transmitted by a solution in the light path of the instrument.

If the light intensity is adjusted to give a scale deflection of 100 S.D. (scale divisions) with water in the titration cell, then the per cent transmittance of any solution placed in the cell is given by the scale reading on the galvanometer. The absorbance of the solution can then be calculated by use of tables of logarithms.

One way to obtain a titration curve is to adjust the zero point (with light off), adjust to 100 S.D. with water in the cell, then introduce the sample into the cell and record the galvanometer reading after each addition of titrant. The titration curve is obtained by converting the readings to absorbance and plotting the values of absorb-

ance and volume of titrant on linear graph paper.

Consideration for Obtaining Higher Precision

The procedure just described is inconvenient in titrations involving solutions with a high initial absorbance. When the absorbances increase during a titration greater precision can be obtained by using the initial solution as a reference (16). The total scale deflection (and thus the precision of measurement) is thereby increased by a factor of $100 T_i$ where T_i stands for the per cent transmittance of the initial solution. Greater precision can also be obtained when the absorbance decreases (transmittance increases) during a titration. However, in this case it is inappropriate to adjust to 100 S.D. with the initial solution since the galvanometer reading will go off scale during the titration.

The use of the zero suppressor circuit greatly facilitates the obtaining of sufficiently accurate galvanometer readings for construction of usable titration curves. Suppose, for example, that the per cent transmittance of a particular solution increases from 40 to 45 during a titration. The usual procedure would give a total deflection of only 5 S.D. If the light is now increased by a factor of 10, the result would be an increase of from 400 S.D. to 450 S.D. during the titration. Normally, the galvanometer pointer will be off the readable scale and thus nothing is gained. However, the zero suppressor circuit can be used

to move the galvanometer zero off scale, to -400 S.D. in this case, and thus a deflection of 0 S.D. to 50 S.D. of the readable scale during the titration can be obtained.

It is not necessary to use the true absorbance values of a solution being titrated in constructing a titration curve. Another valid procedure is to plot the quantity $A' = R - \log (P-M)$ versus volume of titrant where R is an arbitrary constant (and thus need not be used), P is number of scale divisions read with the sample in the titration cell, and M is the number of scale divisions corresponding to zero transmittance. In this work the conversion of the galvanometer readings was accomplished by means of tables relating A' to $(P-M)$ with $R = 2$ ($= \log 100$) for $M = 0$ and $R = 2.301$ ($= \log 200$) for $M = -100$. A' from these tables is equal to the true absorbance when the light intensity is set to give full scale deflection with water.

It is convenient to number the readable galvanometer scale to give directly the value of $P-M$. Thus the scale reads from 0 S.D. to 100 S.D. with $M = 0$ and from 100 S.D. to 200 S.D. with $M = -100$.

When zero suppression is used along with a high light intensity it is quite likely that the galvanometer pointer will go off scale at some point in the titration. When this occurs, it is most convenient to operate with a sectioned titration curve (17). Thus when the reading reaches one end of the scale during the titration, the light is adjusted

to cause the pointer to move to the other end of the scale.

Procedure When Absorbance Increases During a Titration

The following procedure was used when the absorbance increased (transmittance decreased) during a titration: After setting the galvanometer at zero with the shutter closed and zero suppressor off, the shutter was opened and the light adjusted to give a reading of 100 S.D. (or 200 S.D.) with the solution to be titrated in the cell and otherwise ready to be titrated. Titration was commenced and scale readings recorded after each addition of titrant. When zero suppression was used, if the scale reading went below 100 S.D. (off scale), the light was turned up to give a reading of 200 S.D.

Procedure When the Absorbance Decreases During the Titration

When the absorbance decreases (transmittance increased) during a titration, the following procedure was used: After setting the zero point, the light was adjusted to give a reading near 90 S.D. (or 180 S.D.) with the solution in the cell ready for titration except that no metal was present. The metal solutions were then introduced and the titration commenced. Galvanometer readings were recorded after each addition of titrant.

An alternate procedure was sometimes used as follows: The cell was completely prepared for titration and the light adjusted to give a galvanometer reading of about 100 S.D.

(with zero suppression). The titration was commenced and the galvanometer readings recorded after each addition of titrant. Whenever the pointer went off scale, the light was turned down to bring the pointer back to 100 S.D.

CHAPTER V

TITRATION OF CADMIUM AND ZINC USING CALMAGITE

Introduction

Flaschka and Sawyer (18) have developed a method for the determination of submicrogram quantities of calcium and magnesium by photometric titration. In this method an excess of the dye calmagite is added to a solution containing calcium and magnesium so that the amount of dye present is sufficient to complex all of both metals present. The solution is then titrated with a standard solution of EDTA and absorbance measurements are taken at 622 m μ . Evaluation of both metals is possible because the calcium-calmagite complex is so weak that it is not formed to any great extent in this system in contrast to the magnesium calmagite complex and because calcium reacts with the titrant before the magnesium reacts. Thus the self-indicating system magnesium-calmagite-EDTA serves as a slope-indicating system to indicate the amount of calcium present.

Cadmium and zinc form complexes with calmagite of sufficient stability to give a good visual endpoint when either metal is titrated with EDTA (and many other chelons) using calmagite as the indicator. However, the endpoint in the titration of cadmium is poor if a large amount of buffer (ammonia buffer pH 10) is used in the titration and the endpoint becomes progressively poorer as the amount of

ammonia present is increased. On the other hand, zinc still gives a good visual endpoint with calmagite when a relatively large amount of ammonia is present. Thus it may be possible to develop a method for cadmium and zinc similar to the existing method for calcium and magnesium.

Experimental

Apparatus

All titrations were performed with the phototitrator described in Chapter III using the one centimeter titration cell and the Beckman/Spinco ultramicroburette. Ultramicro pipettes calibrated "to contain" were used to deliver solutions. Spectral curves were made with the Bausch and Lomb Model 505 spectrophotometer. The usual calibrated volumetric glassware was used to prepare, standardize, and dilute solutions. Solutions were stored in polyethylene bottles.

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 III.

Results and Discussion

In order to choose an appropriate interference filter for use in the determination of cadmium and zinc, spectral curves were recorded for three portions of a solution containing calmagite at pH 10. One portion contained no metal

and the others contained an excess of cadmium or zinc. Inspection of the spectral curves indicated that the 622 m μ filter which was available would be the most suitable.

It was attempted to establish the self-indicating system, zinc-calmagite-EDTA, which could possibly later serve as a slope indicator for the determination of cadmium. Titrations were performed in solutions containing about 5 μ g of zinc, a total concentration of about 0.1 molar of ammonia buffer-10, and varying amounts of calmagite. EDTA was the titrant used. A curvature was present at the beginning of the titration, as expected, when an insufficient amount of calmagite was present. Approximately a three-fold excess of calmagite was found necessary in order to remove this curvature and thus produce a self-indicating system.

The effect of increasing or decreasing the amount of ammonia present on the amount of calmagite necessary to have a self-indicating system was studied. The total concentration of ammonia was varied from about 0.01 molar to about 0.2 molar. The amount of calmagite necessary was found to be independent of the amount of ammonia present. This verified the expectation that formation of both one-to-one and one-to-two zinc-calmagite complexes was the primary cause of the curvature rather than dissociation of the zinc-dye complex.

The formation of a one-to-two zinc complex to the

practical exclusion of any one-to-one complex or zinc ammonia complexes was expected when somewhat more than two dye molecules were added for each molecule of zinc present from considerations of the stabilities of the one-to-one and one-to-two zinc Erio T complexes. Schwarzenbach (19) gives values for the logarithms of the effective constants for these complexes, the effective constants defined by:

$$K_1(H) = \frac{[ZnD]}{[Zn][D']} \text{ and } K_2(H) = \frac{[ZnD_2]}{[Zn][D']^2}$$

as 11.4 and 17.0, respectively, at pH 10. Considering the effect of ammonia the effective constants become:

$$K_1(H, NH_3) = \frac{K(H)}{\alpha_M(NH_3)} = \frac{[ZnD]}{[Zn'][D']}$$

$$\text{and } K_2(H, NH_3) = \frac{K_2(H)}{\alpha_M(NH_3)} = \frac{[ZnD_2]}{[Zn'][D']}$$

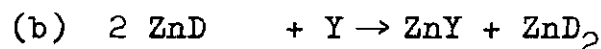
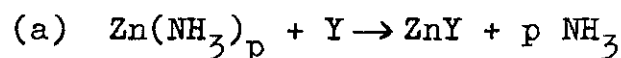
The ratio ZnD_2/ZnD is independent of the ammonia concentration and is given by:

$$\frac{[ZnD_2]}{[ZnD]} = \frac{K_2(H)[D']}{K_1(H)}$$

A simple calculation shows that this ratio is large when the concentration of dye not complexed with metal is of the order of 10^{-4} molar, which corresponds to adding three

molecules of dye for every atom of zinc present when the total concentration of zinc is 10^{-4} molar. Similarly, it can be shown that when the dye is present in sufficient excess dissociation of the one-to-two zinc dye complex is not appreciable when $\alpha_M(\text{NH}_3)$ is less than 10^5 - 10^6 which corresponds to a free ammonia concentration above 0.1 molar.

The following equations are used to show why curvature occurs in certain cases:



If an insufficient excess of dye is present there will be an appreciable amount of ZnD or $\text{Zn}(\text{NH}_3)_p$ present and reactions (a) and (b), for which there is no color change (at least at 622 m μ), will occur in addition to the reaction (c). When a sufficient excess of dye is present, reaction (a) may still occur if the concentration of ammonia is high. This will cause change in slope rather than a curvature provided the excess of dye is large enough since $[\text{ZnD}_2]/\text{Zn}[(\text{NH}_3)_p]$ will be practically constant and reactions (a) and (c) will occur to the same extent throughout the titration.

Solutions of cadmium were titrated with EDTA in the

presence of an excess of calmagite and varying amounts of ammonia buffer-10. The amount of cadmium taken was equivalent to the amount of zinc used previously. The slope of the resulting titration curves was found to be practically the same as for zinc at low ammonia concentrations but when the total ammonia concentration was 0.2 molar or above, the slope of the titration curve was reduced to a small fraction of the maximum value. The slope of the titration curve for zinc was found to be only very slightly lowered at this total concentration of ammonia. It was thus decided to investigate the titration of cadmium and zinc in the same solution using a total ammonia concentration of ammonia of 0.2 molar and an amount of dye which was at least three times the amount of zinc present.

Known amounts of zinc and known amounts of cadmium and zinc were titrated. Ammonia buffer-10 was used in sufficient quantity to give a total ammonia concentration of about 0.2 molar. An amount of calmagite solution was used such that the amount of calmagite was at least three times the amount of zinc present. The amount of zinc used was varied from 0.6 to 30 μg . The amount of cadmium used was varied from 1 to 50 μg . Standard solutions of chelons* were used as titrants.

*DTPA and EGTA, which should give a more favorable value for the exchange reaction constant, were used in addition to EDTA.

Figure 3 shows a representative curve for the titration of cadmium and zinc with DTPA.

The curvature around the cadmium endpoint shown in Figure 3 depends on the equilibrium constant for the exchange reaction, $\text{ZnY} + \text{Cd} \rightleftharpoons \text{CdY} + \text{Zn}$ and also on the rate of the exchange reaction when sufficient time is not allowed for the system to come to equilibrium after each addition of titrant before each measurement is taken. More than ten minutes were required for the system to come to equilibrium in the vicinity of the cadmium endpoint for every chelon used, as evidenced by a slow drift in the galvanometer reading. DTPA was found to give a better curve than EDTA as expected from the stabilities of the zinc and cadmium chelonates of these chelons. Measurements in the vicinity of the cadmium endpoint were taken after waiting about two minutes for the curve shown in Figure 3.

EGTA, which gives a more favorable constant for the exchange reaction, was not as satisfactory as DTPA because its zinc chelonate is not stable enough. The zinc-chelonate of EGTA was found to be about 15 per cent dissociated at the zinc endpoint in this system.

The results obtained were very erratic. The amount of zinc or cadmium found differed as much as 20 per cent from the amount taken. These results were attributed partly to the presence of impurities, primarily calcium, in the water and reagents used. Calcium was included in the titer

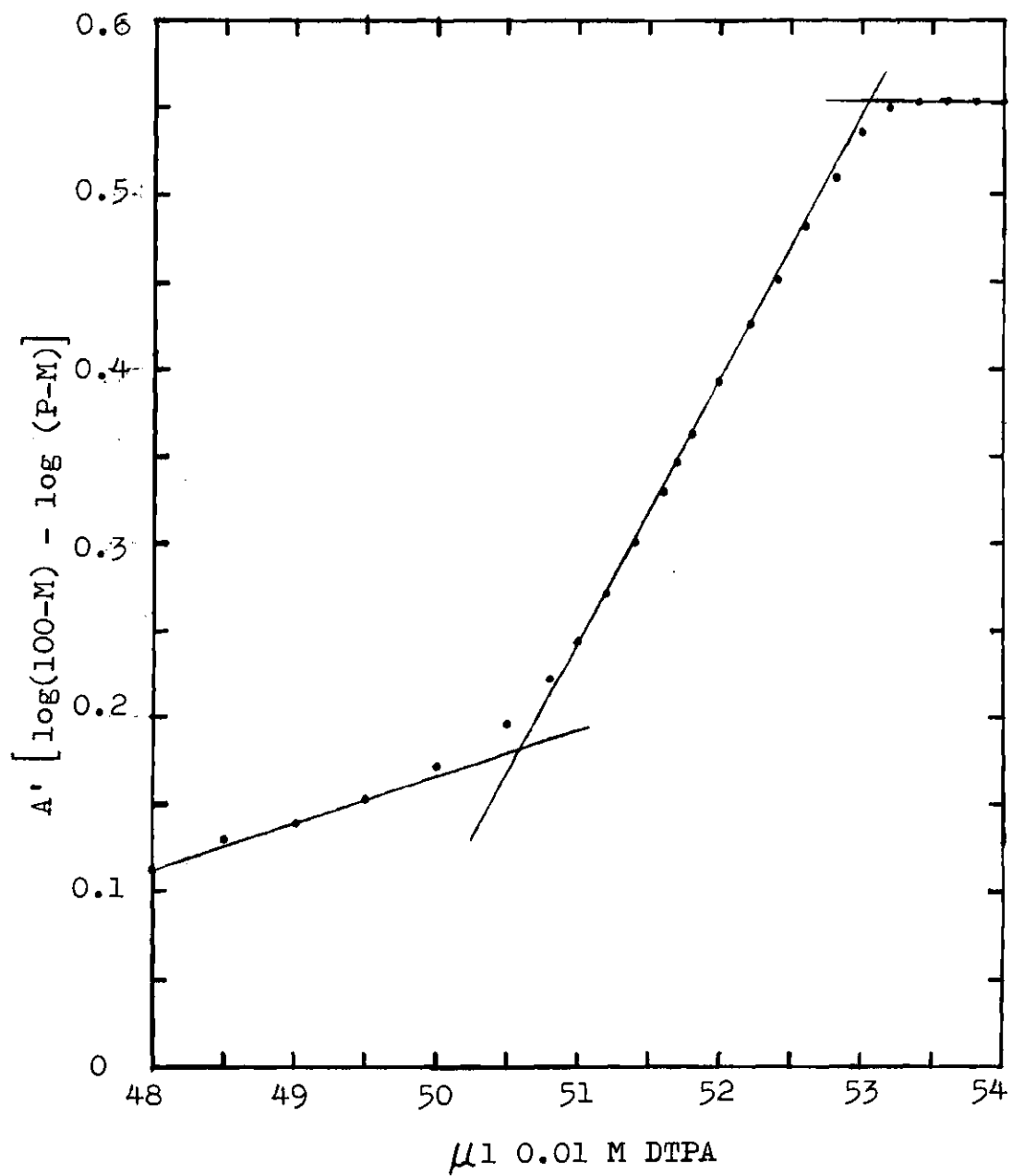


Figure 3. Titration of Cadmium and Zinc Using Calmagite

of the cadmium, as expected, and thus should not affect the titer of the zinc, when cadmium is present. However, the results for zinc were poor also. The poor results for zinc are due mainly to the deviation from linearity near the zinc endpoint shown in Figure 3. It was suspected that this deviation, which was more pronounced in some of the other curves obtained, was due to nonobeyance of the Lambert-Beer Law. However, using the Bausch and Lomb Model 505 spectrophotometer for absorbance measurements did not result in improvement of the titration curve. Most deviations from the Lambert-Beer Law are due to nonmonochromacy of the light used and the light produced by the Bausch and Lomb spectrophotometer has a much higher degree of monochromacy than that produced by the phototitrator.

Attempts were made to obtain a better correlation of the amounts of zinc taken to the amounts found. The zinc endpoints on the titration curves obtained thus far were graphically redetermined by drawing the best straight line through the points very close before the zinc endpoint. An improvement in the results was noted. However, the use of calmagite did not appear to be very suitable for practical application and its use was abandoned in favor of the dye murexide, which seemed to be more promising.

CHAPTER VI

TITRATION OF CADMIUM AND ZINC USING MUREXIDE

Introduction

For most chelons, the stabilities of the zinc and cadmium complexes are not very different from each other. One notable exception is EGTA. The numerical values of the absolute stability constants of the EGTA complexes of cadmium and zinc are 16.7 and 12.8 logarithmic units, respectively (see Table 2). The difference of 3.9 logarithmic units is remarkable. A difference of the same magnitude in the effective stability constants of these chelonates in a system would result in a good photometric titration curve (for the evaluation of both metals in the same solution) provided, of course, that the absorbance properties of the system are suitable and that dissociation of the chelonates is not appreciable under the conditions of the titration.

In contrast to the zinc complexes of many chelons, the zinc-EGTA complex is not stable enough to permit the effective use of dyes which form complexes with zinc of high stability, such as calmagite. In this respect the dye murexide may be suitable since murexide forms complexes with zinc (and many other metals) which are too weak to find application in visual titrations (20).

Table 2. Logarithms of the Absolute and Apparent Stability Constants of the EGTA Complexes of Some Metal Ions and Factors for 0.1 M Total Ammonia (21).

Metal Ion	Log K	Log α_M (pH 10, Total NH_3 0.1 M)	Log K'
Cd	16.7	3.1	13.6
Zn	12.8	4.7	8.1
Cu	17.8	8.3	9.5
Ba	8.4	-	8.4
Ca	11.0	-	11.0
Hg	23.2	15.6	7.6
Mg	5.4	-	5.4
Sr	8.5	-	8.5
Mn	12.3	-	12.3
Co	12.3	2.0	10.3
Ni	13.6	3.9	9.7
Pb	14.6	-	14.6

Experimental

Apparatus

All titrations were performed with the phototitrator described in Chapter III. Interference filters with maximum transmittance at 444 m μ and 456 m μ were used. Titration cells of 1 ml and 50 ml capacity were used along with the necessary volumetric apparatus. Spectral curves were recorded using the Bausch and Lomb Model 505 spectrophotometer.

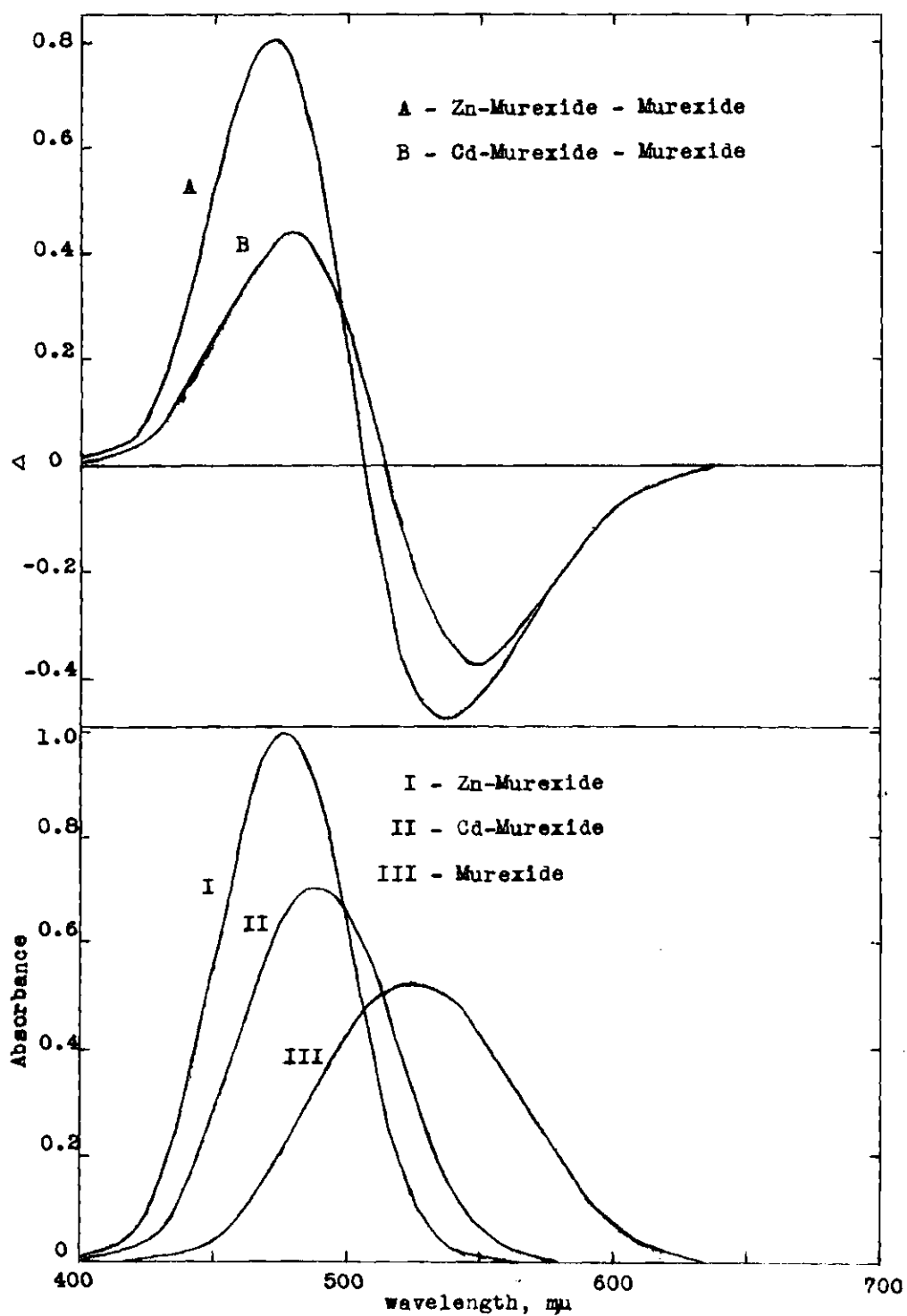
Reagents

All reagents required for the experiments described in this section were prepared and standardized according to procedures described in Chapter III.

Results and Discussion

Spectral curves were recorded for murexide and its zinc and cadmium complexes at pH 10. The resulting curves and the corresponding difference (Δ) curves are shown in Figure 4. The total concentration of murexide was the same in each case. A sufficiently large excess of metal ion was present to insure practically complete reaction of the dye.

The results of Figure 4 can be used to select an appropriate wave length for use in a selective titration of cadmium and zinc, assuming that no change in the nature of the complexes formed occurs when the dye instead of the

Figure 4. Spectral Curves and Δ Curves

metal is in excess.

Use of the region of the spectrum where the uncomplexed dye absorbs most strongly is impractical for two reasons. Solutions of murexide decompose slowly. Thus when absorbance measurements are taken in this spectral region, it will be difficult to obtain good titration curves due to a drift in the galvanometer reading. Moreover, since the zinc and cadmium complexes are weak, a large excess of the dye will be necessary, and the resulting high absorbance and small percentage change in absorbance will make it difficult to obtain accurate galvanometer readings.

A selective titration is also possible in the region where the zinc-dye complex absorbs most strongly. Difference curves between the metal-dye and dye solutions can be obtained by use of the absorbance curves shown in Figure 4. For zinc the difference curve has a maximum at about 470 mμ. Thus the largest slope in the segment of the titration curve where zinc is being titrated will be obtained when this wave length is used. Use of a somewhat shorter wave length may be appropriate in order to avoid interference caused by decomposition of the dye.

Unless cadmium is masked with respect to the reaction with the dye, the absorbance of this complex must also be taken into account when selecting the wave length. The ratio of the slope of the zinc segment of the titration

to that of the cadmium segment is obtained from the ratio of the values obtained at any wave length from the corresponding difference curves. This ratio becomes progressively larger as the wave length decreases and has values of 1.7 at 480 mu and 2.4 at 440 mu.

Murexide has been reported to form only a one-to-one complex with zinc (22). This was checked by applying the methods of photometric titration, continuous variation, and tristimulus colorimetry to the system zinc-murexide at pH 10. No evidence for any other than a one-to-one metal dye complex formation was found.

Some attempts were made to stabilize solutions of murexide at pH 10. De-aeration with nitrogen was partially effective as was ascorbic acid. However, it was later found that galvanometer drift was so slight that it was not a problem in titrations performed in the vicinity of 450 mu, even when no precautions were taken to inhibit decomposition of the dye.

The conditions necessary for a working self-indicating system, zinc-murexide-EGTA at pH 10, were established by titrating solutions of zinc in which the amount of ammonia buffer and the excess of dye added were varied. The 456 mu filter, the 1 cm cell, and the ultramicroburette were used in conjunction with the phototitrator. The total concentration of zinc present was about 10^{-5} M. Approximately a five-fold excess of murexide was found to be at

least necessary to get a straight-line titration curve. Thus, a total concentration of murexide not complexed with zinc of the order of 5×10^{-5} M is necessary for a working self-indicating system. Next, the amount of dye used was held constant and the concentration of ammonia present was varied. The slope of the titration curve was found to decrease as the concentration of ammonia was increased for total ammonia concentrations above 0.01 M. This concentration of ammonia is high enough to keep the pH of the solution constant during the titration of microgram quantities of cadmium and zinc but is not high enough to help prevent the precipitation of cadmium or zinc as the hydroxides. However, this is not a serious problem since the dye will prevent precipitation when it is in excess of the metal present.

The titration curve for cadmium and zinc in the presence of excess murexide was studied. Cadmium was found to react with the titrant before the zinc, as expected. When the concentration of ammonia buffer was kept low (0.01 molar or less) and a sufficiently high excess of murexide was present, the ratio of the slope of the zinc segment to that of the cadmium segment was found to be approximately the value expected from the spectral curves obtained. However, increasing the total ammonia concentration to 0.02 to 0.03 molar and keeping the excess of murexide moderate (but sufficient to maintain a working self-indicating system

for zinc) resulted in lowering the slope of the cadmium segment without appreciably affecting the slope of the zinc segment, thus increasing the precision obtainable in locating the cadmium endpoint. Typical titration curves for cadmium and zinc in the presence of excess murexide are shown in Figure 5.

If a sufficiently large excess of murexide is not present, the cadmium segment of the titration curve shows a curvature which is more pronounced than that expected from the dilution effect of the titrant. However, for precise endpoint location it is not necessary that the cadmium segment be linear throughout and thus the amount of murexide used need only reflect the amount of zinc present. For large amounts of cadmium it would be impractical to use an amount of dye which exceeds the amount of cadmium present.

When titrating very dilute solutions of metal ions, it is difficult to reduce the amount of calcium and magnesium ions present, introduced from various sources as impurities, to a negligible value. Thus the effect of the presence of small amounts of these ions was studied.

Magnesium was found not to interfere at all in the determination. This was expected from the low stability of the Mg-EGTA complex (see Table 2) and the fact that magnesium shows little tendency to form a complex with murexide.

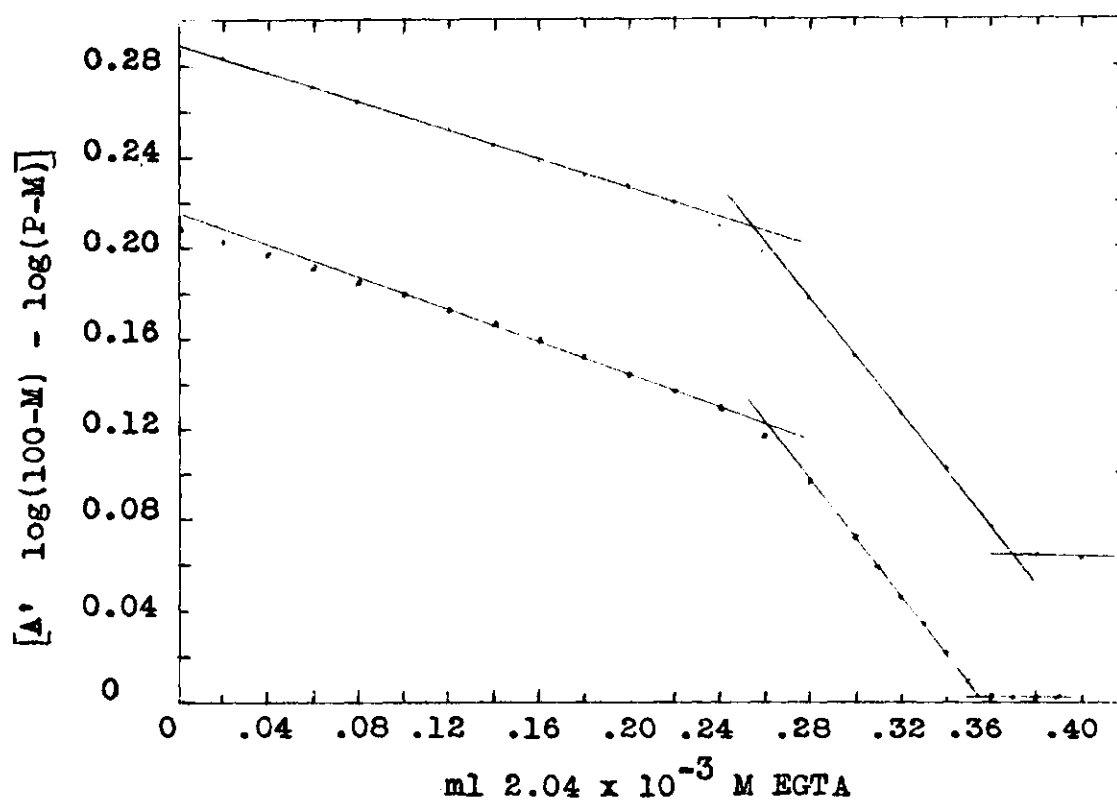


Figure 5. Titration of Cadmium and Zinc Using Murexide

Calcium is titrated after cadmium and before zinc in this system. The slope of the titration curve for calcium is comparable to that for cadmium under the conditions of the determination and thus calcium will be included in the titer for cadmium and the results for cadmium can be corrected for a blank.

One source of calcium ions is dust from the air. Dust in the solution titrated can also cause an optical interference and thus makes it nearly impossible to obtain precise galvanometer readings. In order to reduce the chemical and optical interference caused by dust particles falling into the solution, further titrations were performed in a larger cell which had a smaller top surface area to volume ratio.

Known quantities of cadmium and zinc were titrated with EGTA. The 50 ml titration cell was used. The volume of the solution titrated was adjusted to about 35 ml in each case and the solution contained 0.5 to 1.0 mg of murexide. Ammonia buffer was present to give a total ammonia concentration of about 0.02 molar. Both the 444 m μ and 456 m μ filters were used. Representative results are shown in Table 3. The results for cadmium have been corrected for a blank of 0.007 ml of a 2.04×10^{-3} molar EGTA solution. This corresponds to about three times the concentration of calcium which Flaschka and Sawyer were able to attain as a blank in the determination of submicrogram quantities of

Table 3. Titration of Cadmium and Zinc
with EGTA Using Murexide

Zinc (4.71×10^{-4} M)			Cadmium (5.06×10^{-4} M)		
Taken (ml)	Found (ml)	Diff. (ml)	Taken (ml)	Found (ml)	Diff. (ml)
0.353	0.340	-0.013	0.521	0.530	+0.009
0.429	0.427	-0.002	1.526	1.530	+0.004
0.500	0.492	-0.008	1.000	0.986	+0.003
0.500	0.495	-0.005	1.000	0.983	-0.017
0.529	0.552	+0.023	5.005	5.000	-0.005
0.555	0.564	+0.009	1.036	1.038	+0.002
0.735	0.716	-0.019	1.637	1.621	-0.016
1.915	1.910	-0.005	0.577	0.569	-0.008

calcium and magnesium.

It was not necessary to weigh the murexide used in each titration. Instead, small portions of murexide were dissolved in the solution in the titration cell which contained buffer but no metal until the per cent transmittance decreased to a predetermined value.

The precision obtained in locating the cadmium endpoint was compared with the precision obtainable in locating the zinc endpoint by the pretitration method in the following manner. A small amount of zinc (not necessarily accurately known) was first titrated. Then a known quantity of cadmium or zinc was added and the titration continued to the zinc endpoint. Thus the amount of metal ion added after the pretitration corresponded to the difference between two zinc endpoints and the results did not have to be corrected for a blank. Representative results for these titrations are shown in Table 4.

The effect of foreign ions other than calcium and magnesium was not studied since cadmium and zinc can be readily separated from most other ions by ion exchange (23).

Conclusions

The determination of microgram quantities of cadmium and zinc with very good precision and accuracy, considering the low concentrations involved, is readily achieved by the evaluation of a single titration curve.

Table 4. Titration of Zinc or Cadmium Using
the Pretitration Technique

Zinc (4.71×10^{-4} M)		
Taken (ml)	Found (ml)	Diff. (ml)
0.474	0.477	+0.003
0.480	0.484	+0.004
0.514	0.511	-0.003
0.578	0.576	-0.002
0.627	0.620	-0.007
0.742	0.756	+0.014
0.881	0.871	-0.010
0.910	0.910	0.000
1.121	1.100	-0.021
Cadmium (5.06×10^{-4} M)		
1.063	1.068	+0.005
0.916	0.914	-0.002
1.313	1.306	-0.007

The lower limit in the concentrations of metal ions titratable is certainly much lower than the concentrations involved in this work. However, a considerable increase in the difficulties caused by impurities will be encountered as the concentrations are lowered. In addition, obtaining a sufficiently large galvanometer deflection during the titration for accurate endpoint location will become inconvenient, at least. For the 456 mμ filter and a light path of 2 cm, a 20 S.D. change (160 S.D. to 180 S.D.) during the titration of zinc will be obtained when its concentration is about 3×10^{-6} molar. The magnitude of the scale deflection which occurs when zinc is titrated is practically independent of the amount of excess of dye present since initial adjustment of the light intensity compensates for the excess dye.

For an apparatus of fixed light patch and light detecting sensitivity, the upper limit of the concentration of zinc titratable is fixed primarily by the intensity of light which the instrument is capable of producing, since the initial light intensity must be adjusted so that the cadmium endpoint does not occur at a scale reading close to that for zero light intensity. The upper limit for the instrument used in this work is considerably higher than the maximum concentrations titrated.

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*Abbreviations used are found in Chemical Abstracts, "Index of Periodicals," 1956.