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The study of kojic acid as a chelating agent for cadmium analysis

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THE STUDY OF KOJIC ACID AS A CHELATING AGENT
FOR CADMIUM ANALYSIS

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Norman Elliott Conger

A thesis presented to the Department of Chemistry
of Union College in partial fulfillment of the require-
ments for the degree of Bachelor of Science with a
Major in Chemistry.

By Norman Elliott Conger

Approved by Ruef Schaefer

May 1956

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Gift of Author January 8, 1957

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ABSTRACT

The absorption spectra of kojic acid and of cadmium kojate in various solvents have been obtained. From this data, the suitability of kojic acid as a possible analytical reagent for the determination of very small amounts of cadmium in water using ultraviolet absorption methods is discussed. Kojic acid is found to be not suitable for analysis of cadmium using ultraviolet absorption methods.

INTRODUCTION

The qualitative and the quantitative aspect of man's surroundings will always be of primary interest to him. A knowledge of the nature and the composition of substances, besides arousing our curiosity, is very essential in our daily existence. For this reason, the field of analytical chemistry has received much attention.

Analytical chemistry is based upon the qualitative and quantitative determination of particular properties of an unknown substance. From the data obtained for a particular property of a substance, the nature and the composition of the substance is that much more known.

In trying to find out all that can be known about a substance, it is quite natural to wish to investigate as many different properties of the substance as possible. Thus the nature of color, one of the most striking properties of many substances, was early investigated. It was found that color in substances is due to the selective absorption of visible light.(19)

Through much experimental and theoretical research, it is known that visible light is part of a vast system of electromagnetic radiation or radiant energy. The radiant energy, which is more popularly termed light, is quantized,

INTRODUCTION (Cont.)

and has certain frequencies. The frequency times the wavelength is a constant, the speed of light. The frequency times a constant, known as Planck's constant, gives the amount of energy per unit measurement. The value of the frequency determines the type of radiant energy that is present. Radiant energy with very large amounts of energy or very short wavelengths are termed cosmic rays. (4) As the wavelength of the radiant energy is increased, there are obtained respectively: gamma rays, x-rays, ultraviolet light, visible light, infra red light, Hertzian waves, and lastly wireless waves. (18) The latter have very long wavelengths and very small amounts of energy.

Not only visible light, but radiant energy of all other wavelengths may also be absorbed. The wavelengths of radiant energy absorbed depend upon the atomic and molecular structure of the absorbing substance (9), and the amount of radiant energy absorbed depends upon the concentration and the quantity of substance present. (28)

In this research, we are interested in absorption analysis in the ultraviolet and visible region. Spectrophotometric methods of analysis are useful in the determination of very small amounts of substances, amounts of the order of a few parts per million, provided the molar absorptivity of the measured substance is high enough.

The analysis of cadmium in water is quite useful, especially for determining traces of cadmium in industrial

INTRODUCTION (Cont.)

wastes (1). A number of spectrophotometric methods are in use today for cadmium, but none of these is completely satisfactory for one reason or another (1) (33). In the case of the colorimetric determination using dithizone, which is probably one of the better known methods for cadmium, the main problem is the interference from other ions, especially zinc and lead. Devising the analytical procedure in order to eliminate this interference makes the entire analysis too long and complex to be satisfactory for making many rapid determinations.

A simpler and quicker method of determining traces of cadmium would be very welcome. The purpose of this research was to determine the usefulness of the chelate, cadmium kojate, for the quantitative determination of traces of cadmium in water, using absorption spectroscopy.

HISTORICAL

In 1868, Graebe and Liebermann (19) realized that in order for a compound to possess color, visible light had to be absorbed. This was one of the early reports of the existence of a relationship between light absorption and molecular structure.

In 1876, Witt (38) produced a theory which attempted to correlate light absorption with the molecular structure. His theory held that a substance, in order to selectively absorb light, had to contain certain unsaturated groups which he termed chromophores. He also said there were other groups capable of increasing the intensity of absorption without themselves absorbing. These groups he termed auxochromes. Witt's theories are still valid today. Henri (25) extended Witt's theories to include other regions of the spectrum besides just the visible.

The currently used theory on absorption phenomena was put forth by Bury (5) in 1935. His theory stressed the importance of resonance in the molecule upon the selective absorption, and correlated the resonance theory with the ideas about auxochromes.

The theoretical quantitative aspect of selective absorption can be achieved through the approximate solution

HISTORICAL (Cont.)

of the wave equations which describe a particular molecule (9). It is presently thought that the absorption of ultraviolet and visible light is due to the vibration of electrons within the molecule.

One of the early records of work in quantitative spectrophotometric analysis is given by Hartley in 1883 (22), when he published some observations on his experiments with absorptiometric quantitative analysis. In these experiments, Hartley noted the thickness of the cell, containing the solution, at which the transmitted light was reduced to zero. By varying the cell thickness with the wavelength, he was able to record quantitatively the absorption band shape. Other work consisted in keeping the cell thickness constant and varying the concentration of the solution till the transmitted light was reduced to zero. An absorption curve is then obtained by plotting the wavelength against the concentration.

Kruss (4)(24) in 1890 recognized the possibility of the application of absorptiometric methods to quantitative analysis. He wrote a book at the time, in which quantitative absorptiometric methods were treated. This was later revised in 1909 (24). Since then there has been numerous data and literature on quantitative absorptiometric methods (4).

HISTORICAL (Cont.)

The dithizone complex with cadmium is the most commonly used method today for the spectrophotometric analysis of very small amounts of cadmium. The use of dithizone as an analytical reagent for heavy metals was first realized in 1925 by Fischer (12). He and coworkers have developed methods for the determination of traces of many of the heavy metals with this reagent (13).

A more recent method for traces of cadmium, described by Serfass (1) in 1952, was based on a method developed for traces of cadmium in electroplating baths by the American Electroplaters Society Research Committee from 1947-1951. Sandell (33) describes three extraction methods using a complexing agent with cadmium and using spectrophotometric analysis. Two of these use dithizone as the complexing agent. One was developed by Church (7) and the other by Fischer and Leopoldi (14). The third method given was developed by Cholak and Hubbard (6) and it uses Di-2-Naphthylthiocarbazonone as the complexing agent. A method using 2-mercaptobenzothiazole is given by Serfass (34). Methods for cadmium using heptoxime, diphenylcarbazide, mercaptobenzothiazole, dimethylglyoxime and 1, 10 phenanthrene as complexing agents are also known(1).

Most of these methods for cadmium work quite satisfactorily only after the interference from other cations

HISTORICAL (Contd.)

is removed. The procedure in removing these cations usually consists of long and involved extractions with different solvents at various pH's. Even though the procedure may be fairly foolproof, it is too long and not suitable for a technician to run. This is undesirable if it is to be applied to routine analysis.

For further reading on the historical aspect of radiant energy, the reader is referred to (10,11,20,23). For further reading on the historical aspect of quantitative spectrophotometric analysis, the reader is referred to (1,4,22,24,33).

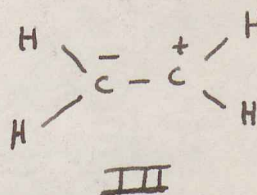
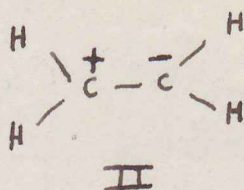
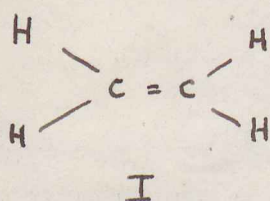
THEORY, Part One: Absorption and Molecular Structure

Radiant energy, of which visible light and ultraviolet light are parts, has a certain amount of energy depending upon the frequency of the radiation. The relationship between the frequency of light ν , the wavelength of light λ , and the speed of light c is given by the formula $c = \nu \lambda$. The energy of the radiation is directly proportional to the frequency. It is given by the formula $E = h\nu$, where the proportionality constant is Planck's constant h . When an atom or a molecule absorbs radiant energy, it is believed that the atom or the molecule undergoes certain energy changes (28). There are several different ways in which an atom or a molecule may absorb energy. There may be electron transitions in the atom, vibrations of the atom or rotations of the molecule. In molecules, the different atoms produce enough possibilities of energy changes so that some light is absorbed at every wavelength. This produces a continuous spectrum which is known as a band spectrum.

The manner in which the radiant energy is absorbed and the amount of energy which is absorbed depends upon the structure of the molecule and of the constituent atoms. After absorbing a certain amount of radiant energy, the molecule is in a state of higher energy or what is often termed, an excited state. According to the resonance theory, this excited state would be one or a combination of the

THEORY, Part One (Cont.)

higher energy resonance states. Using ethylene as an example: Below are shown the three resonance forms possible (10). (I) is the stable or the lower energy state and the other two are the higher energy states or excited states. The ethylene molecule will be transformed from the structure represented in (I) to that represented by the two excited states upon the absorption of light with the corresponding amount of energy.

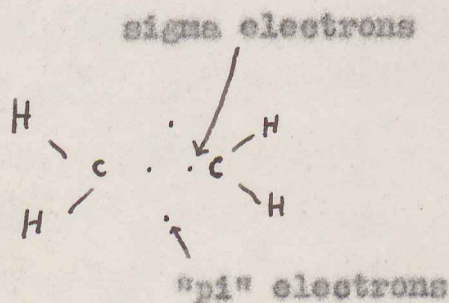


According to the molecular orbital theory, the arrangement of the carbon-carbon bonding is the deciding factor. In a compound with a single carbon bond, the bond between the carbon atoms is very stable and is termed a sigma type bond. It takes a large amount of energy to put a compound of this type into an excited state. That is why a compound such as ethane absorbs at such a low wavelength which corresponds to a high frequency and a high amount of energy.

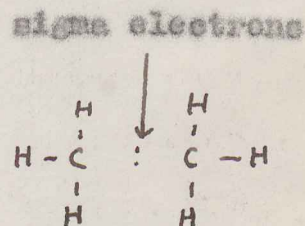
In the carbon double bond, two of the four electrons between the two carbon atoms form the sigma type bonding. The other two electrons are more mobile and not

THEORY, Part One (Cont.)

as closely attached. They are termed "pi" electrons. This is shown by the structural representations of the ethylene and ethane molecules in IV and V respectively.



IV Ethylene



V Ethane

To excite these electrons to another molecular orbit of a higher energy state is much easier than it is to excite the electrons of the sigma type. Thus the compounds with carbon double bonding absorb radiant energy of longer wavelength or less energy. This moves the absorption spectra into the ultraviolet region for many compounds that have carbon-carbon bonding other than single bonding. Compounds which have yet more complex bonding and certain chemical groups known as chromophores have absorption spectra in the visible region, thus making the compound colored.

For further information on absorption and molecular structure, the reader is referred to (3,4,8,9,10,11,17,18, 20,23,28,35,36,37).

THEORY, Part Two: The Beer-Bouguer Law of Light Absorption

The Beer-Bouguer law (28), which relates the amount of incident light absorbed with the number of absorbing molecules present in the path of the light beam, is the basic law of the absorption of radiant energy. This law is often referred to as the Beer-Lambert law but the Lambert part of the law was actually formulated by Bouguer (2)(28).

stated mathematically:

$$dI/I = -Kdn$$

where I is the intensity of the monochromatic light, K is the proportionality constant and n is the number of molecules in the path of the light beam. This equation is integrated between the limits I_0 and I and between the limits of 0 and n . Thus:

$$\ln I/I_0 = -Kn \quad \text{or} \quad \log I_0/I = K_1n$$

At a particular temperature, the number of the molecules present in the path of light is determined by the concentration and the amount of solution (that is, the length of path through the absorbing solution). Now the law may be stated in its usual form:

$$\log I_0/I = K_1cl = A$$

THEORY, Part Two (Cont.)

where c is the concentration, l is the length of path and A is the absorption or absorbancy.

Bouguer's part of the law relates the amount of absorption with the length of path while keeping the concentration constant. It was worked out separately from Beer's law which relates the amount of absorption with the concentration while keeping the length of path constant. The Bouguer part of the law has no exceptions. However, the Beer part of the law will deviate from linearity if there is any change in the structure of the solute in solution caused by dissociation, association or a tautomeric shift or if the blank cell does not compensate for losses due to reflection (28).

The units of path length, which corresponds to the inside dimensions of the cell used to hold the solution, is almost always the centimeter. The units of concentration vary, however. Grams per liter and gram moles per liter are the most commonly used.

The units of the proportionality constant depend upon the units chosen for the concentration and the path length. The proportionality constant is numerically equal to the absorbancy of a solution of unit concentration in a cell of unit length. When centimeters and grams per liter are chosen for the units of cell length and concentration

THEORY, Part two (Cont.)

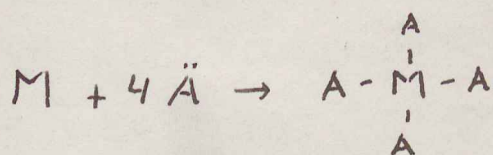
respectively, then k is the symbol of the proportionality constant and it is known as the specific extinction coefficient or the absorbancy index. When centimeters and gram moles per liter are chosen as the units, then A_m or ϵ is the symbol given to the proportionality constant and it is known as the molar extinction coefficient or the molar absorbancy index.

For further information about the Beer-Bouguer Law, the reader is referred to (4,6,10,11,20,28).

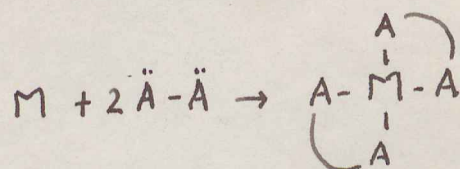
THEORY, Part Three: The Chelate Cadmium Kojate

A chelate compound is formed by the chemical combination of a metal ion and a compound which has two or more donor groups. Thus a compound with one or more rings, respectively, is formed. By a donor group is meant a group which donates one or more electrons. The metal ion is anxious to acquire one or more electrons to make its electronic structure more complete and stable. The number of electrons a metal wishes to acquire depends upon its valence and its coordination number (35). In the chelate, the bonds are all electron pair bonds, which may be either essentially ionic or essentially covalent in character, depending upon the chelating agent and the metal ion.

If the metal ion combines with a compound with only one donor group, the resulting compound has no rings and is known as a simple metal complex. Following is a schematic diagram of the distinction between the simple metal complex and the chelate, the complex metal complex:



simple metal complex



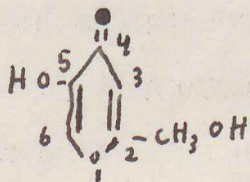
metal chelate

where M represents a metal ion, \ddot{A} represents a complexing

THEORY, Part Three (Cont.)

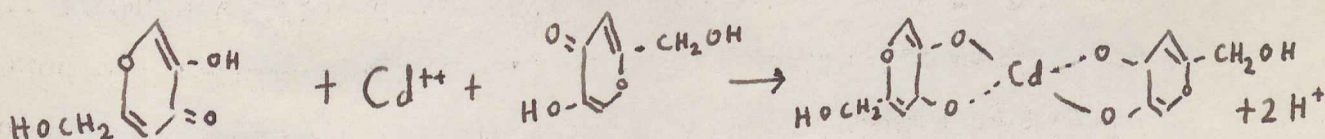
agent with one electron donor group, and $\ddot{A}-\ddot{A}$ represents a chelating agent with two electron donor groups (26).

Kojic acid, whose structural formula (27,29,31) is given in I, is a chelating agent with the nuclear hydroxyl group and the double bonded oxygen most likely being the two donor groups.



I 2-hydroxymethyl-5-hydroxy- γ -pyrone
(Kojic acid)

Following is the reaction of cadmium with kojic acid:



kojic acid

cadmium kojate

W.C.O'Kane and G.H.Morey (30), on the basis of magnetic susceptibility measurements, consider this to be the most probable structure of cadmium kojate.

For further reading on chelate compounds and on kojic acid and its chelates, the reader is referred to (26,27); (27,29,30,31) respectively.

THEORY, Part Four: Quantitative Spectrophotometric Analysis

In quantitative analysis using ultraviolet spectrophotometric methods, the sample under examination is extracted with a suitable solvent, one which does not absorb appreciably. To operate the spectrophotometer, the wavelength is fixed and the corresponding light is sent, first through the solvent alone and then through the compound under examination dissolved in the solvent. The length of path corresponds to the dimensions of the cell containing the solution and is fixed. The absorption of the solvent is set at zero. Then by means of a photoelectric cell system and a galvanometer, the absorption of the compound can be read directly from a potentiometer scale.

If a particular compound absorbs, then a characteristic graph can usually be obtained by plotting the absorption against the wavelength. To be suitable for analytical work, this curve should contain a maximum. In an analytical procedure, the wavelength at which the maximum occurs is taken as the fixed wavelength, since it is usually the most accurate portion of the curve, the most distinguishable portion of the curve and the most easily attainable. By keeping the wavelength constant, a straight line graph can be obtained by plotting concentration against absorption, if

THEORY, Part Four (Cont.)

there is no deviation from Beer's law. As soon as a Beer's law curve is established as a standard, the absorption of a sample of unknown concentration is determined and the corresponding concentration of the unknown is read directly from the standard graph.

For further information on quantitative spectrophotometric analysis, the reader is referred to (1,4,8,16, 28,33).

THEORY, Part Five: Requirements for Analytical Reagents in Spectrophotometric Analysis

This research involved the investigation of kojic acid to determine its usefulness as a reagent for the quantitative analysis of very small amounts of cadmium in water, amounts less than several parts of cadmium per million parts of water.

In order for cadmium kojate to be suitable for spectrophotometric analysis, there are a number of requirements that must be fulfilled. First of all, a suitable solvent for the cadmium kojate would have to be found. The solubility of cadmium kojate in this solvent would have to be large enough to give absorbancies from .2 to .8 on the spectrophotometer.

The next requirement is that the absorption spectrum of the cadmium kojate in the solvent be significantly different from the absorption spectrum of the kojic acid in the solvent, especially if the kojic acid dissolves to any degree in the same solvent as the cadmium kojate does. If only the cadmium kojate readily dissolves in the solvent, then the absorption at the maximum will be mainly due to the cadmium kojate. This would be the desired situation, for then the concentration of the cadmium kojate would be direct-

THEORY, Part Five (Cont.)

ly proportional to the amount of absorption, at a particular wavelength.

However, if the kojic acid is also soluble in the solvent, then both the kojic acid and the cadmium kojate will be extracted with the solvent. If the absorption maxima for the kojic acid and the cadmium kojate in the same solvent occur at different wavelengths, then it is possible to run a quantitative determination on the cadmium kojate by observing the absorption maximum for the cadmium kojate and subtracting the small amount of absorption due to the kojic acid. However, if the maxima of the absorption spectra for kojic acid and for cadmium kojate occur at the same wavelength, then the absorption of the two compounds will reinforce each other and it will be difficult to determine what fraction of the total absorption is contributed by each of the components.

If the absorption spectrum of the chelate in some solvent is found to be suitable for the analysis of cadmium alone, then it is necessary to determine if other ions (mainly cations) would interfere. If there is interference from other ions, then the nature of the interference and a means of getting rid of it must be determined. Interference that is not easily eliminated would render the kojic acid useless as an analytical reagent for this type of analysis.

EXPERIMENTAL, Part One: Apparatus

A Model DU Beckman Spectrophotometer, Serial No. 3210, was used to obtain all of the ultraviolet absorption spectra. The sensitivity control was set as far counterclockwise as possible in order to give a minimum sensitivity and enable the readings to be taken at as low wavelengths as possible. If the solvent is water, this enables the readings to be taken down to 210 m μ . The slit width for each reading was somewhere in the range of .2mm to 1.8mm.

Most of the time, the readings were taken at 10m μ intervals and, as the maxima or minima in the absorption were approached, the interval between the readings was reduced to 5 m μ and then to 2 m μ . Sometimes, an interval of 5 m μ was maintained throughout an entire run.

Hatched, fused-silica cells of square cross section were used. They were 10 mm \pm 0.01 mm on the inside.

The Roller-Smith torsion type balance with a full scale of 50 mg. was used in all of weighings where the sample weighed less than 400mg.

EXPERIMENTAL, Part Two: Compounds used

1. The kojic acid used in the research work was obtained as a reagent chemical sample from the Chas. Pfizer and Co., Inc., New York.

2. The cadmium metal used to make up one of the stock solutions of cadmium was Baker chemically pure metal.

3. The HCl used in the dissolution of the cadmium was chemically pure, concentrated HCl.

4. Solvents: (a). The water used was distilled water that had been redistilled from an alkaline permanganate solution. This procedure removed minute traces of metals, if there were any. About 2 grams of KMnO_4 and 3 grams of NaOH were mixed with about 700 mls. of distilled water in a one liter distilling flask. The KMnO_4 and the NaOH were replenished periodically.

(b). The 95% ethyl alcohol used was of reagent quality.

(c). The solvents dioxane, isooctane, and chloroform were all chemically pure.

EXPERIMENTAL, Part Three: Solutions

The cadmium stock solution was prepared by dissolving 50 mg. of cadmium in 10 mls. of concentrated HCl and then diluting to 2 liters with the doubly distilled water. This produces a 0.0002224 Molar solution of cadmium in water that is very slightly acidic. Also used as a source for cadmium ion was a 1.16 N $\text{Cd}(\text{NO}_3)_2$ solution. This had been previously made by dissolving 275 grams of $\text{Cd}(\text{NO}_3)_2$ in distilled water and diluting up to a liter. The latter solution was used more than the former due to the greater concentration of cadmium ions.

The 0.1000 N NaOH solution, used as a solvent, previously had been made up with reagent NaOH and distilled water.

It was attempted to make solutions of kojic acid in each of the solvents selected. Kojic acid solutions were successfully made with water, 95% ethyl alcohol, and 0.1000 N NaOH, all of which are quite polar, and with dioxane which is less polar. The kojic acid solution in water was 0.0002224 M, in 95% ethyl alcohol 0.000353 M, and in 0.1000 N NaOH 0.0002224 M. The solution of kojic acid in dioxane was made as concentrated as possible. The dioxane with excess kojic acid was stirred thoroughly and allowed to sit long enough to assume that a nearly saturated solution had been obtained.

EXPERIMENTAL, Part Three (Cont.)

It was found that kojic acid does not dissolve very readily in isooctane and other nonpolar solvents. An absorption spectrum on isooctane with excess kojic acid in it showed no absorption, indicating that there was at the most very little kojic acid dissolved in the isooctane. No attempt was made to make a solution of kojic acid in chloroform, the other solvent selected, because it had already been found out that chloroform was not a suitable solvent for cadmium kojate.

Cadmium kojate solutions were successfully made in water, 0.1000 N NaOH, 95% ethyl alcohol and dioxane. Each of these solutions was made as concentrated as possible.

It was found that cadmium kojate would not dissolve appreciably in either isooctane or chloroform. Absorption spectra of isooctane and chloroform with excess kojic acid put in showed practically no absorption, indicating that very little cadmium kojate had dissolved in these solvents.

EXPERIMENTAL RESULTS, Part One: Preparation of the Cadmium Kojate

The cadmium kojate was successfully prepared by following fairly closely the procedure described in an article by Carlo Musante (29) for the formation of metal kojates. According to the method described, the solution of an easily soluble salt of the metal is added to a solution of the kojic acid in stoichiometric quantities, keeping in mind that the kojic acid is monobasic. The resulting solution is then buffered with a necessary quantity of sodium acetate and heated to the boiling point, till when, through cooling and standing undisturbed, the expected compound crystallizes out. This is filtered, washed with water and dried at 130°C.

In the laboratory, 25.0 cc of a 0.0116 M $\text{Cd}(\text{NO}_3)_2$ solution and 25.0 cc of a 0.02224 M kojic acid solution were mixed together. 10 mls. of a 0.38 N sodium acetate solution and 20 mls. of a 2.0 N sodium acetate solution were added to the cadmium nitrate-kojic acid solution. The resulting solution was heated to boiling for a short time and then allowed to cool slowly and undisturbed. Upon cooling, no precipitate formed in the yellowish green-brown liquid as should have according to the method described.

Assuming that the concentration of the cadmium kojate formed was small enough to remain in solution, about

EXPERIMENTAL RESULTS, Part One (Cont.)

20 mls. of the yellowish green-brown solution was evaporated to dryness at room temperature. A precipitate of the same color remained.

It was pretty conclusive that this precipitate contained the cadmium kojate desired. In the literature (29), the color of hazel is given as the color of cadmium kojate. Hazel could probably be considered to be fairly close to a yellowish green-brown color. The point of decomposition of the cadmium kojate is reported (29) to be around 290°C . Upon heating the prepared sample up to 300°C ., it turned to a grey color and powdered easily, showing that a change of some sort, quite probably decomposition, had taken place. The similarities of the properties of the precipitate with the properties of cadmium kojate cited in the literature and the fairly accurately following of the procedure described, leads to the assumption that this precipitate contains cadmium kojate.

Other compounds must have also been present in the precipitate since they were present in the solution that was evaporated to dryness. However, considering the effects these other components of the precipitate would have upon the qualitative experimental work to be run first, it

EXPERIMENTAL RESULTS, Part One (Cont.)

was decided that purification of the cadmium kojate was not necessary.

When equal amounts of a 0.0232 N $\text{Cd}(\text{NO}_3)_2$ solution and a 0.02224 N kojic acid solution are mixed together, theoretically all of the kojic acid would react to form cadmium kojate. The number of moles of cadmium kojate formed from the evaporation of 20 mls. of the solution would be 0.000070. After the formation of the cadmium kojate, there would be 6.2×10^{-6} gram equivalents of cadmium ion, less than 0.00015 gram equivalents of NO_3^- , less than 0.012 gram equivalents of $\text{C}_2\text{H}_3\text{O}_2^-$, and 0.012 gram equivalents of Na^+ . There would be less NO_3^- and $\text{C}_2\text{H}_3\text{O}_2^-$ than the total original concentration of these ions since some of each of these ions distill off as nitric and acetic acids respectively, as the evaporation is proceeding. Hence, the precipitate is likely to contain very small amounts of $\text{Cd}(\text{C}_2\text{H}_3\text{O}_2)_2$ and $\text{Cd}(\text{NO}_3)_2$ and relatively larger amounts of NaNO_3 and $\text{NaC}_2\text{H}_3\text{O}_2$.

Since all of these compounds are either colorless or white (21), they would have no effect upon the color of the cadmium kojate in the precipitate. Likewise, since all of these components have distinct melting points, most of which are above $300^\circ\text{C}.$, the decomposition of the cadmium kojate in the precipitate would not be affected. Hence,

EXPERIMENTAL RESULTS, Part One (Cont.)

these additional compounds in the precipitate had no effect upon the properties of the precipitate which led to the assumption that it contained cadmium kojate.

By running water through the precipitate, these salts could have been extracted from the cadmium kojate. This would have been necessary if quantitative experimental work had been done.

Only two harmful effects that these compounds might have upon future experimental work present themselves to the author. First, the amount of absorption that they would produce in solution relative to that of the cadmium kojate might be large enough to reduce greatly the sensitivity of the cadmium analysis. By running absorption spectra on $\text{Cd}(\text{NO}_3)_2$ in water and $\text{NaC}_2\text{H}_3\text{O}_2$ in water, shown in graph V, it was found that the ions in these concentrations have a negligible absorption. It would also be supposed that these ions in other solvents would not absorb appreciably.

Secondly, these salts might hinder the total solubility of the cadmium kojate. However, the only salts that would have any effect upon the solubility limit of the cadmium kojate would be those with a common ion; in other words, the cadmium salts. However, the relatively low concentration

EXPERIMENTAL RESULTS, Part One (Cont.)

of the cadmium salts in comparison with the concentration of the cadmium kojate would make the common ion effect negligible.

Having sodium acetate present has one disadvantage in that, if it was desired to make a solution of the cadmium kojate in either acid or alkali, the sodium acetate would act as a buffer and keep the solution neutral.

EXPERIMENTAL RESULTS, Part Two: Absorption Spectra of Kojic Acid in Various Solvents

Absorption spectra were taken on the various solutions of kojic acid. They were determined using the pure solvent as the reference liquid. Graphs I,II,III show respectively the absorption spectrum of 0.0002224 M kojic acid in 0.1000 N NaOH, of 0.0002224 M kojic acid in water, and of 0.000353 M kojic acid in 95% ethyl alcohol. In determining the absorption spectrum of kojic acid in 0.1000 N NaOH, the reference liquid was pure water. An absorption spectrum was run on 0.1000 N NaOH against water to determine if 0.1000 N NaOH had any significant absorption. It is evident from the absorption spectrum, shown in graph V, that 0.1000 N NaOH has a negligible absorption. It was also found that the absorption spectrum of kojic acid in acidic solution is very similar to that of kojic acid in water.

Since the kojic acid dissolved so well in the dioxane, it was necessary to dilute the nearly saturated solution in order for its absorption to be compatible with the capacity of the spectrophotometer. Upon dilution of the solution 625 times, the absorption of the diluted solution could be taken. This absorption spectrum is shown in graph IV.

As has already been noted in the section on solutions, there was no absorption in the isooctane containing excess

EXPERIMENTAL RESULTS, Part Two (Cont.)

kojic acid, indicating that, at most, a negligible amount of kojic acid had dissolved in the isooctane.

EXPERIMENTAL RESULTS, Part Three: Absorption Spectra of
Cadmium Kojate in various solvents

Absorption spectra were taken on the various solutions of Cadmium kojate. The saturated solution of cadmium kojate in water was diluted 25 times in order to get a suitable absorption spectrum. This is shown in graph II. It was found that the absorption spectrum of cadmium kojate in 0.1000 N NaOH is very similar to that of cadmium kojate in water. The reason for this is probably due to the buffering action of the sodium acetate. The absorption spectra of the saturated solutions of cadmium kojate in 95% ethyl alcohol and dioxane are shown in graphs III and IV respectively.

The absorption of saturated solutions of cadmium kojate in chloroform and isooctane was negligible, indicating that cadmium kojate does not dissolve readily in either of these solvents.

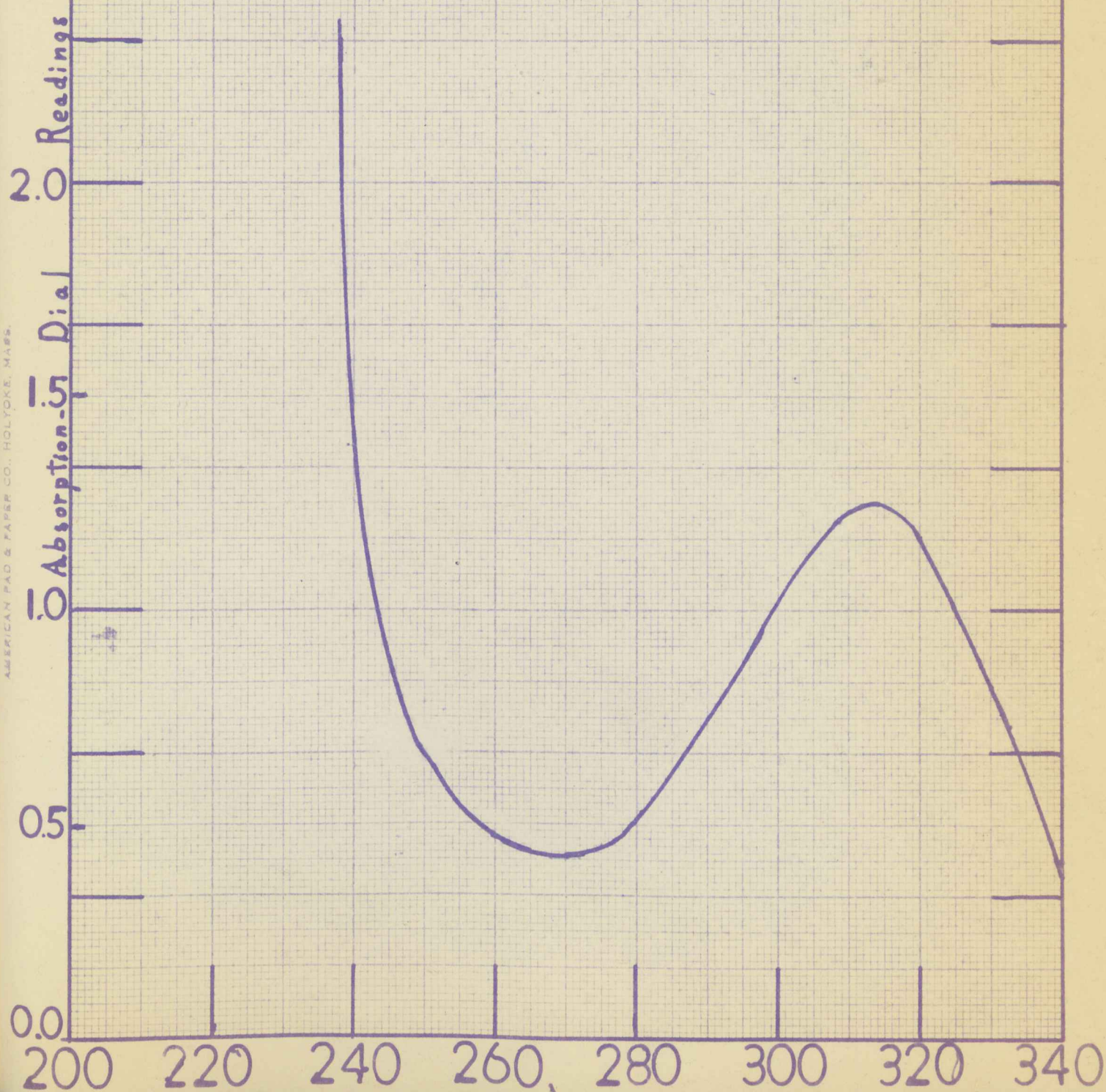
In showing the absorption spectra in graphical form, the value of the optical density or absorption read off the spectrophotometer is plotted against the wavelength. The value of the optical density on the spectrophotometer dial is linearly calibrated with respect to concentration so that a reading of 1.0 means that the absorption is 10 times greater than that at a reading of .10 and, hence, the concentration is also 10 times greater. The absorption is usually scaled

EXPERIMENTAL RESULTS, Part Three (Cont.)

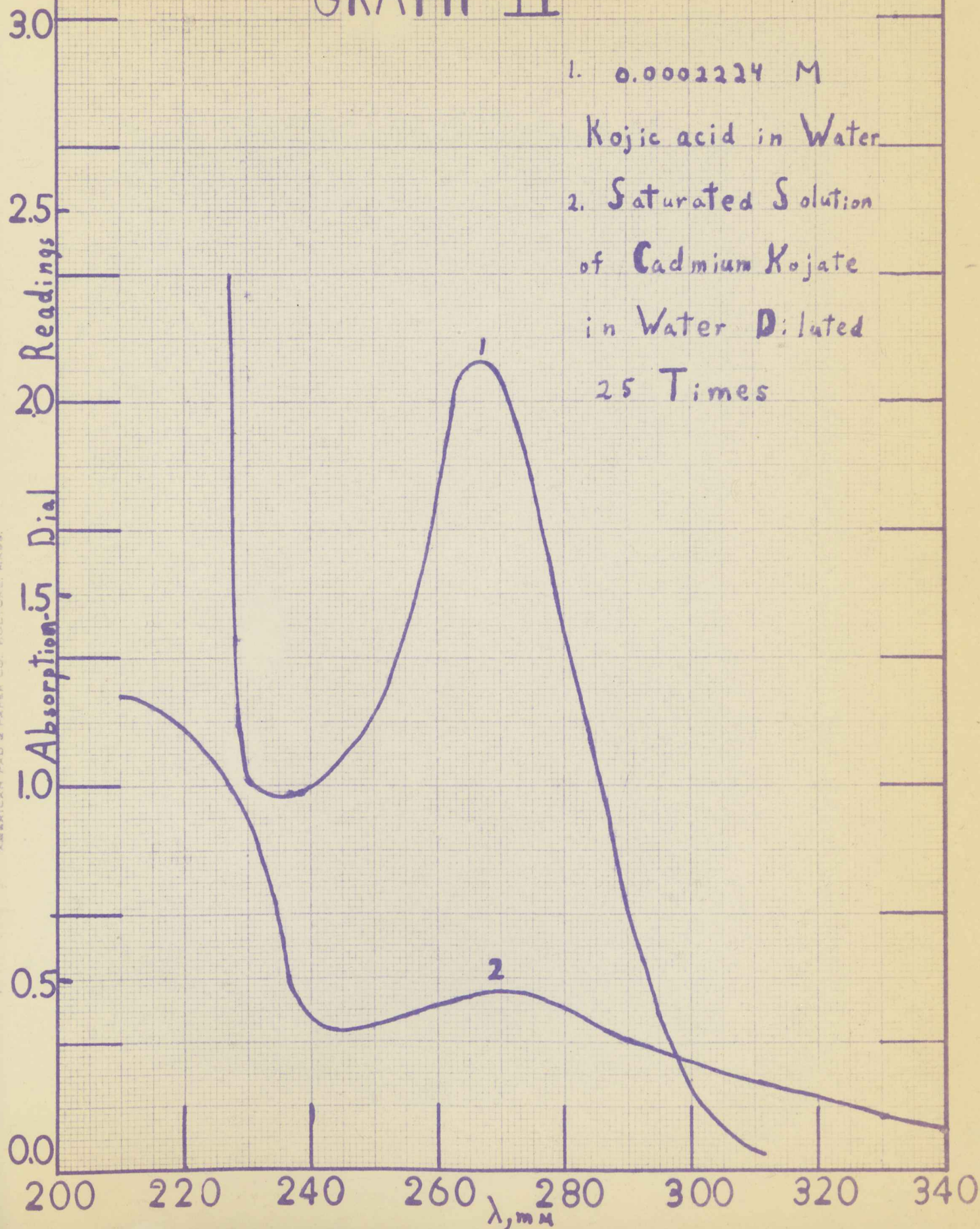
in molar absorbancy units. However, because the data was to be used in only a qualitative manner at first, conversion to the molar scale was deemed unnecessary.

GRAPH I

0.0002224 M Kojic Acid
in 0.1000 N NaOH

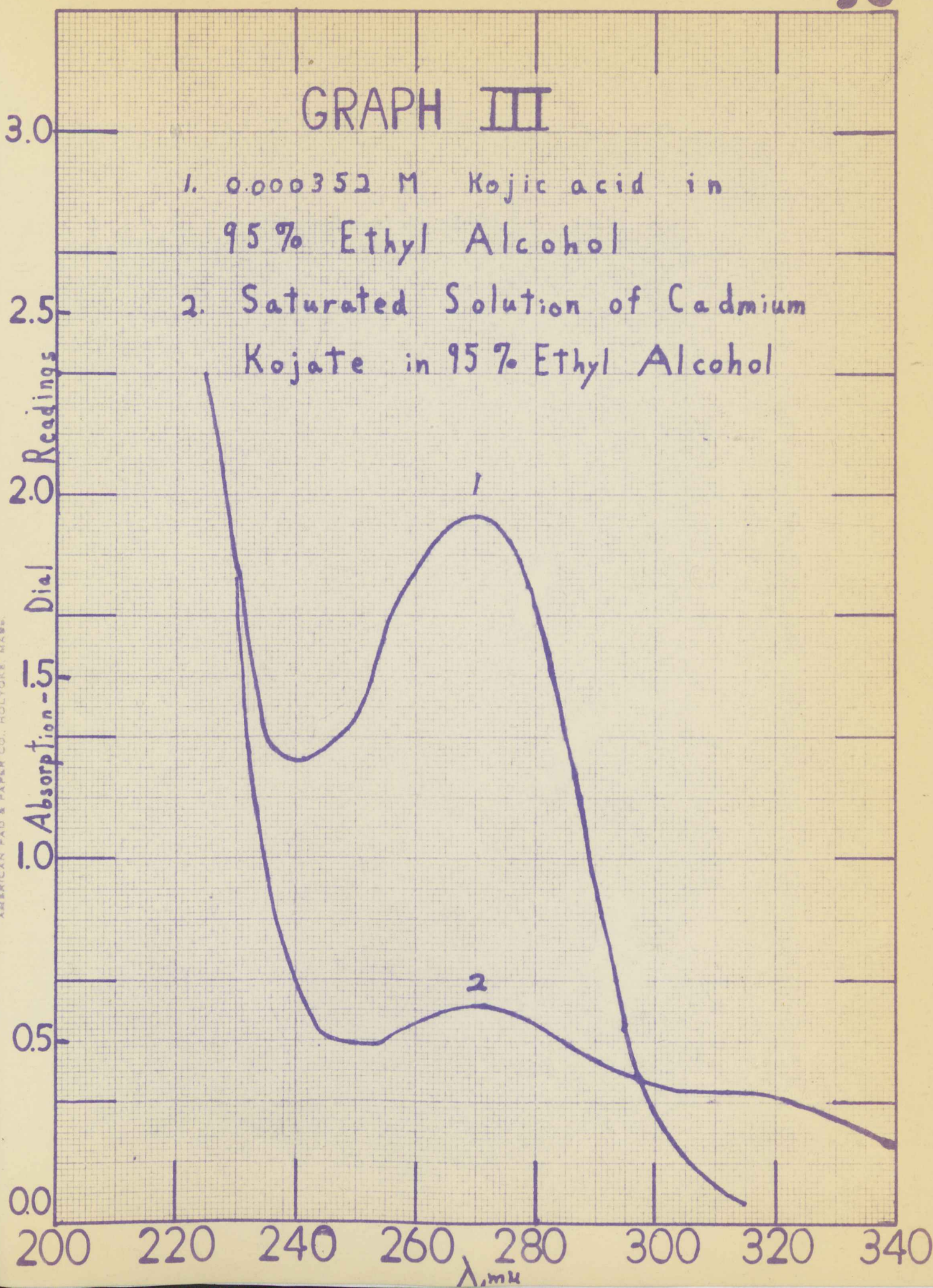


GRAPH II



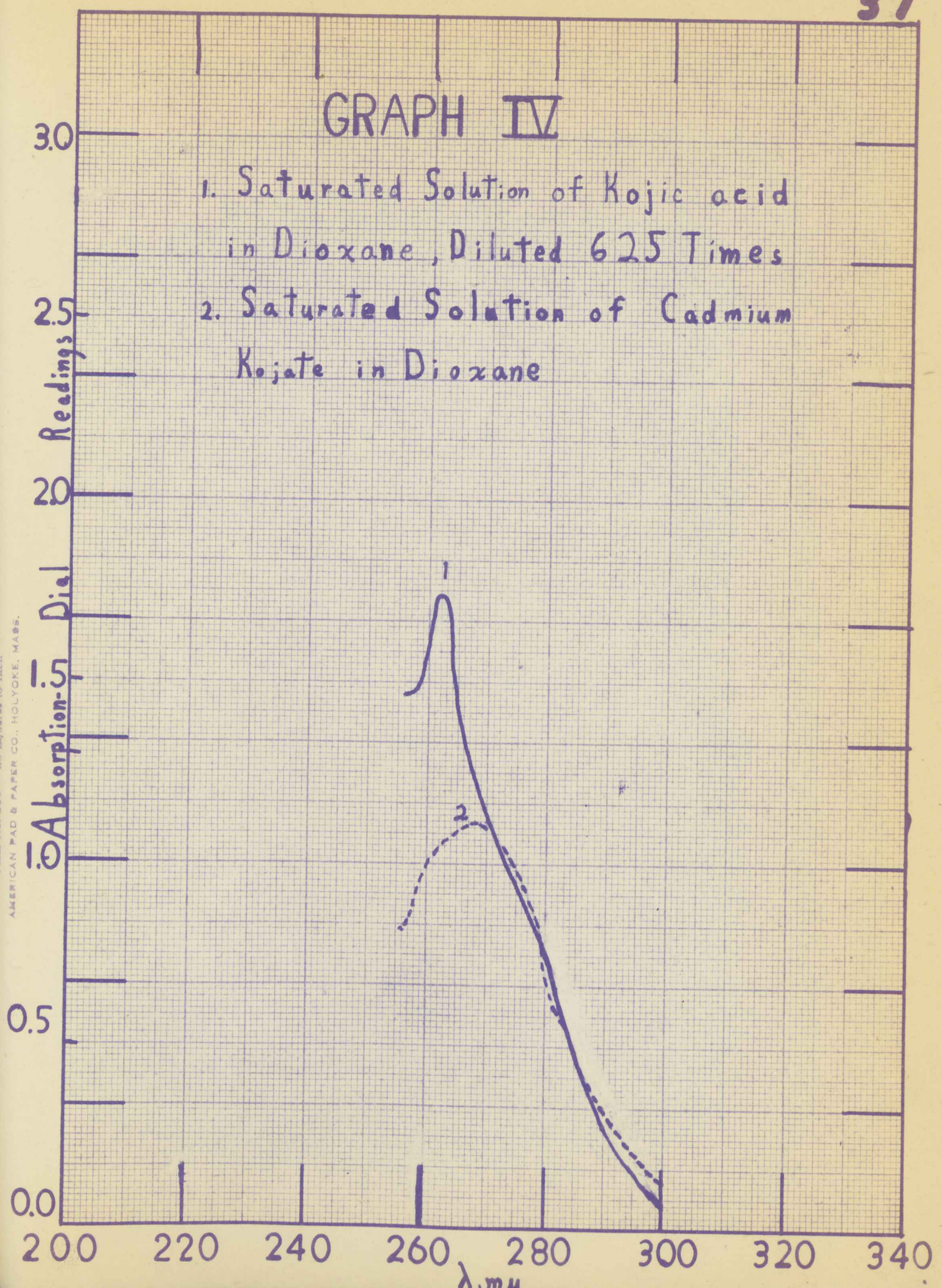
GRAPH III

1. 0.000352 M Kojic acid in 95% Ethyl Alcohol
2. Saturated Solution of Cadmium Kojate in 95% Ethyl Alcohol

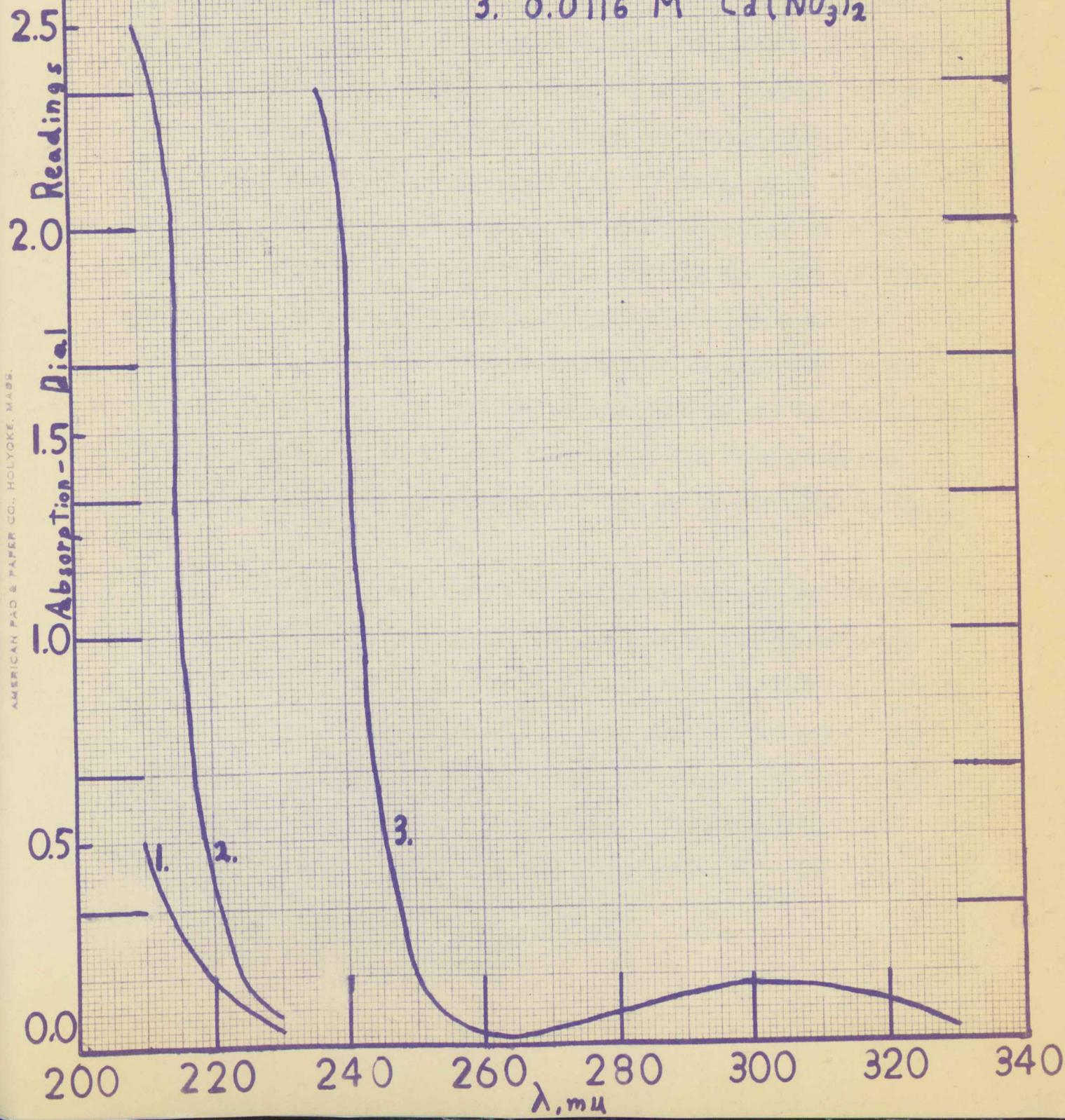


GRAPH IV

1. Saturated Solution of Kojic acid in Dioxane, Diluted 625 Times
2. Saturated Solution of Cadmium Kojate in Dioxane



GRAPH V

1. 0.0153 M $\text{NaC}_2\text{H}_3\text{O}_2$ 2. 0.1000 N NaOH 3. 0.0116 M $\text{Cd}(\text{NO}_3)_2$ 

DISCUSSION

For cadmium kojate to be suitable in spectrophotometric analysis, it is first necessary to find a good solvent for it, one in which the cadmium kojate is soluble enough to give an absorption of from .2 to .8 on the spectrophotometer. It was attempted to make solutions of cadmium kojate in water, in 0.1000 N NaOH, 95% ethyl alcohol, dioxane, isooctane and chloroform. These solvents represent a wide range in polarity and type. As is shown by graphs II, III, and IV, the cadmium kojate is soluble enough in water, 95% ethyl alcohol, and dioxane respectively to give suitable absorption spectra. The cadmium kojate did not dissolve enough in either chloroform or isooctane to make them useful solvents. The solution of cadmium kojate in 0.1000 N NaOH was buffered by the sodium acetate and this produced an absorption spectrum similar to that of cadmium kojate in water.

Having found suitable solvents for cadmium kojate, it was necessary to determine if the absorption spectrum of kojic acid in the solvent would interfere with that of cadmium kojate. Interference from kojic acid will be caused if the wavelengths, at which the maxima of kojic acid and the maxima of cadmium kojate occur, are the same. The absorption of each component would then greatly reinforce the other and it

DISCUSSION (Cont.)

would be difficult to know what fraction of the absorption was due to a specific component.

A comparison of the absorption spectra, run on the solutions of kojic acid and cadmium kojate, show that the absorption maxima of cadmium kojate are nearly identical in each case to the absorption maxima of kojic acid. In graph II, the wavelength at which the absorption maximum of the kojic acid in water occurs is around 265 mμ and that of the cadmium kojate in water is around 270 mμ. Even though there is a slight difference in the wavelengths, the absorption of the two compounds at the maxima would principally reinforce each other, and make quantitative determination of the cadmium kojate difficult. In spectrophotometric analysis, these two compounds would very likely be in solution together, because of their similar solubility properties. Hence, water would not be a suitable solvent.

In graph III, the wavelength at which the absorption maximum of kojic acid occurs is around 270 mμ and that of cadmium kojate is also around 270 mμ. Thus when both of these compounds are in solution together, the absorption at the maxima is reinforced by each other and the quantitative determination of the cadmium kojate is difficult. Hence, 95% ethyl alcohol is not a suitable solvent either.

DISCUSSION (Cont.)

In graph IV, the wavelength at which the absorption maximum of kojic acid in dioxane occurs is round 262 mμ and that of cadmium kojate in dioxane is around 268 mμ. The slight difference in the wavelength at the maxima is not enough to keep the absorption of each component from interfering with that of the other. Hence, dioxane is not a suitable solvent either.

It appears that the cadmium kojate must be somewhat ionic since it dissolves in polar solvents and hardly at all in nonpolar solvents. The two free hydroxymethyl groups probably also contribute to its being soluble in polar solvents.

Since a fairly representative group of solvents in respect to polarity were tried and none of these was found suitable, it was concluded that most other solvents would also be unsuitable. On the basis of the experimental work reported here, the kojic acid is not useful as an analytical reagent for the spectrophotometric determination of very small amounts of cadmium.

It is interesting to note that the absorption of the saturated solution of cadmium kojate in dioxane was compatible to the absorption capacity of the spectrophotometer, whereas the saturated solution of kojic acid in dioxane had to be diluted about 400 times in order to be within the same general

DISCUSSION (Cont.)

magnitude of absorption. This means either the cadmium kojate produces the same amount of absorption as the kojic acid but is only about $\frac{1}{400}$ as soluble in dioxane, or the solubility of the cadmium kojate in dioxane is the same as that of kojic acid while the absorption of the cadmium kojate is 400 times less. Maybe a combination of different solubility and different absorption is actually the case. Since the absorption spectrum of the cadmium kojate is so similar to that of kojic acid, it is thought by the author that the former is the case. If it is, the absorption spectrum in each case is due to the kojic acid ion in solution. The much lesser solubility of cadmium kojate is probably due to a lesser degree of ionization of the chelate and to fewer free hydrophillic functional groups in the chelate.

For future work with cadmium analysis, kojic acid could be investigated further. If the kojic acid could be extracted in some solvent much more readily than the cadmium kojate, then a suitable analysis might be possible on the cadmium kojate remaining behind.

SUMMARY

The absorption spectra of kojic acid in water, 95% ethyl alcohol, and dioxane have been determined. The cadmium kojate was prepared by a method described by Carlo Musante (29) and the absorption spectra of cadmium kojate in water, 95% ethyl alcohol, and dioxane have been determined.

The negligible absorption of isooctane and chloroform with excess cadmium kojate and of isooctane with excess kojic acid indicate that cadmium kojate is not appreciably soluble in either isooctane or chloroform and that kojic acid is not appreciably soluble in isooctane.

Since the absorption spectra of the cadmium kojate in the various solvents is similar to that of the absorption spectra of kojic acid, it is readily seen that these particular solvents are not suitable for the ultraviolet spectrophotometric determination of cadmium with kojic acid.

As these solvents represent quite a wide range of polarity, it can be inferred that work with other solvents would probably not be fruitful. However, if a method was found of extracting the kojic acid in some solvent much more readily than the cadmium kojate, then it would be possible to run a quantitative analysis on the cadmium kojate remaining behind.

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