

COLORIMETRIC DETERMINATION
OF ZIRCONIUM

by

DOUGLAS EUGENE MARCY

B. S., Kansas State Teachers
College of Emporia, 1954

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1963

Approved by:

Jack L. Lambert

Major Professor

LD
2668
T4
1403
M38
C.2

TABLE OF CONTENTS

Document

	Page
INTRODUCTION	1
EXPERIMENTAL	2
Apparatus and Chemicals	2
Investigation of Dyes	3
Visible Spectrum of Sodium Indigo Disulfonate	6
Stability	12
Interferences	13
Beer's Law Investigation	18
Analytical	23
Structure	23
DISCUSSION	28
LITERATURE CITED	33
ACKNOWLEDGMENTS	34

INTRODUCTION

The quantitative determination of zirconium has been largely dependent upon gravimetric methods of analysis. Cupferron, pyridine, and phosphate are probably the best known of the historical methods, but the use of mandelic acid, reported by Kumins (6) in 1947, has largely dominated the field. Mandelic acid is a highly selective reagent for zirconium.

Organic dyes have played an important role in analytical chemistry as pH and oxidation-reduction indicators, and as qualitative or quantitative reagents for inorganic analysis. One of the first organic dyes used for the determination of zirconium was para-dimethylaminoazobenzeneearsonic acid (Feigl, et al., 3) which was used as a spot test reagent and quantitative precipitant in acid solution. A more rapid procedure, such as colorimetric, would be desirable for multiple analysis.

As early as 1925, de Boer (2) noticed a sensitive color reaction of zirconyl ion with hydroxyanthraquinones. Most metal ions produce red to violet colors when reacted with Alizarin Red S, (1,2-dihydroxyanthraquinone-3-sulfonic acid), but with the exception of the red-violet color formed with zirconium the color disappeared on the addition of hydrochloric acid. The zirconium-Alizarin Red S method has been modified by Taylor and Frasier (10), Yasuda and Lambert (11), and others.

Grotheer and Lambert (4) reported a method for the determination of bismuth colorimetrically. A bismuth amalgam was dissolved in a boric acid-nitric acid mixture, diluted with

boric acid solution, and bismuth precipitated from aliquots of the diluted sample solution by the addition of Amaranth dye solution. The mixture is filtered and the Amaranth released in a definite volume of disodium hydrogen phosphate solution. The absorbance of the released dye solution at 521 m μ . is proportional to the bismuth concentration. Thorium, zirconium, bismuth, ferric and cerous ions form nearly insoluble compounds with Amaranth in the pH range of 2.3 to 3.0.

The purpose of the investigation here undertaken has been to develop a direct colorimetric method for determining zirconium in moderate concentrations. The proposed method consists in reacting zirconyl chloride with a dye, separating the precipitate, and colorimetrically determining the remaining unreacted dye. Comparison with a standard curve gives the original concentration of zirconium.

The dye must react stoichiometrically and follow Beer's Law over a range of values.

EXPERIMENTAL

Apparatus and Chemicals

Zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$, was used to prepare a stock solution with 0.12 F hydrochloric acid. This solution was standardized by the method of Kumins (6), and found to contain 0.384 mg. of zirconium per ml.. The various zirconium samples used in the investigations were all prepared by taking aliquots of this stock solution and diluting to volume with 0.12 F hydrochloric acid.

All of the dyes used were obtained from National Aniline Division of Allied Chemical and Dye Corporation. The dye selected for further study, Sodium Indigo Disulfonate (Indigo Carmine), was certified 93% pure. The method of analysis did not depend upon the Indigo Carmine being 100% pure so there was no need for purifying and the dye was used as commercially obtained. The dye is readily soluble in water but was dissolved in 0.12 F hydrochloric acid so all future solutions would be of the same acidity. Because of the instability of the dye solution it was necessary to mix fresh solutions of dye each time it was needed. The dye was later found to follow Beer's Law so it was very easily compared to the different batches.

The precipitate of zirconium-Indigo Carmine was separated by either filtering through Whatman #42 filter paper in a Buchner funnel with an aspirator, or by centrifuging.

The spectrophotometer used was a Beckman model DU. When determining the spectrum of the dye solutions a Minneapolis-Honeywell recording attachment was used to facilitate the graphing. The paper used was calibrated as per cent transmission.

For the infra-red studies the instrument used was a Perkin-Elmer model 137 (Infracord). The Infracord has the advantages of being very simple to operate, giving a fast spectrum on calibrated paper, and still has a resolution of 0.04μ at 10μ .

Investigation of Dyes

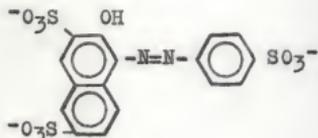
It was desired to find a dye that would form a precipitate

with zirconyl chloride. The precipitate should be formed rapidly, be fairly voluminous and quite insoluble. Dyes were tested by dissolving a small quantity of dye in two milliliters of water and then adding one milliliter of zirconyl chloride solution, $ZrOCl_2$. If a precipitate formed it was filtered through Whatman #42 filter paper, washed once with water, and then washed with 0.12 F hydrochloric acid. If there was a bleeding of the color from the precipitate on the addition of the hydrochloric acid, the precipitate was considered to be too soluble.

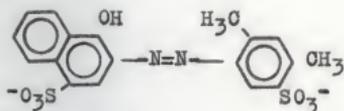
Yellow O.B. and Yellow A.B. were found to be insoluble in water and were therefore not tested. Fast Green F.O.F., Light Green S.F., and Naphthol Yellow gave very fine precipitates, or no precipitate. Guinia Green B. gave a rather fine precipitate which was not easily filtered.

Amaranth, Ponceau S.X., Ponceau S.R., and Erythrosine all gave voluminous red precipitates which were insoluble in 0.12 F hydrochloric acid. Erythrosine gave a precipitate which with stirring settled out, leaving a clear colorless solution. Sunset Yellow, F.D. & C. Yellow #6 and F.D. & C. Orange #1 gave bright orange, easily filtered precipitates which were insoluble in 0.12 F hydrochloric acid. A more rigorous study of any of these last six dyes and zirconium-dye complexes could result in new and better methods of colorimetric, volumetric, or even gravimetric quantitative determinations of zirconium or other similar metals. It should be noted that the Orange #1 is the only dye that could be workable that contains only one sulfonate group.

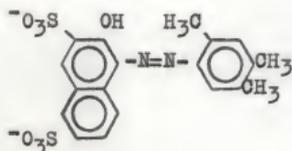
Amaranth



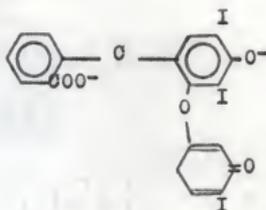
Ponceau S.X.



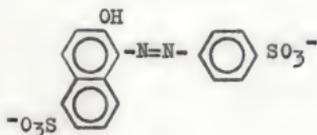
Ponceau S.R.



Erythrosine



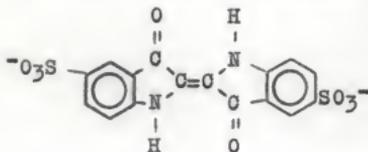
Sunset Yellow



Orange #1



Sodium Indigo Disulfonate



Sodium Indigo Disulfonate (Indigo Carmine) gave a very voluminous dark blue precipitate. The precipitate was insoluble in a strongly acidio solution and was easily filtered. The precipitate formed rapidly and tended to settle out in a short time. The remaining studies were concentrated on Sodium Indigo Disulfonate.

Visible Spectrum of Sodium Indigo Disulfonate

A solution was prepared by weighing the Indigo Carmine and diluting to volume in a volumetric flask. The concentration of this original solution was 0.003 F. Three other solutions were prepared by taking aliquots of this original solution and diluting to volume. Solutions were prepared with concentrations down to 0.00003 F. An absorption spectrum was run in the visible range on the Beckman spectrophotometer.

Because of the very large variance in concentration of the solutions and the resulting wide range of absorbance it was necessary to use a wide range of slit widths. The absorbance at various wave lengths was so different that it was even necessary to use different slit widths on the same concentration. A means was needed to correlate the per cent absorbance with the varying slit widths. Ayres (1) reported a method of plotting data in which the per cent absorptance is plotted against concentration. The absorptance is defined as being 1-transmittance from which it follows that per cent absorptance equals 100-per cent transmittance. The square of

the slit width is proportional to the energy transmitted through the sample and therefore the constant, k , is proportional to the logarithm of the ratio of transmitted energy divided by the incident energy. Using this information in equation form it was possible to determine curves over a much greater range of wave lengths than was possible with any other method. The equation for this correlation is,

$$k = (\text{slit width})^2 (100\text{-per cent transmittance}), (\text{Equation 1}).$$

This constant was plotted on four cycle semi-logarithmic graph paper versus the wave length from 550 μ to 675 μ . The absorbance of the 0.003 F solution was too great to allow measurement even with maximum slit width. The absorbance of the very dilute 0.00003 F dye was too slight to give a meaningful curve in this range of wave lengths. With the 0.0003 F solution (Plate I) a very distinct peak was formed at 610 μ , but at lower concentrations there was a slight shifting of the maximum to higher wave lengths. The curve also flattened considerably giving only a slight ripple at 660 μ with the 0.00003 F solution. Holmes (5) reported a peak at 610 μ and Lambert and Grotheer (7) reported a peak at 609 μ , but neither mentioned a shifting of the peak at lower concentrations.

At higher wave lengths of 650 μ to 775 μ (Plate II) the curves were plotted on two cycle semi-logarithmic paper. The 0.00003 F absorbance was too weak to indicate any breaks in the curve. At a concentration of 0.00012 F the curve produced a very sharp minimum at 680 μ while the higher concen-

EXPLANATION OF PLATE I

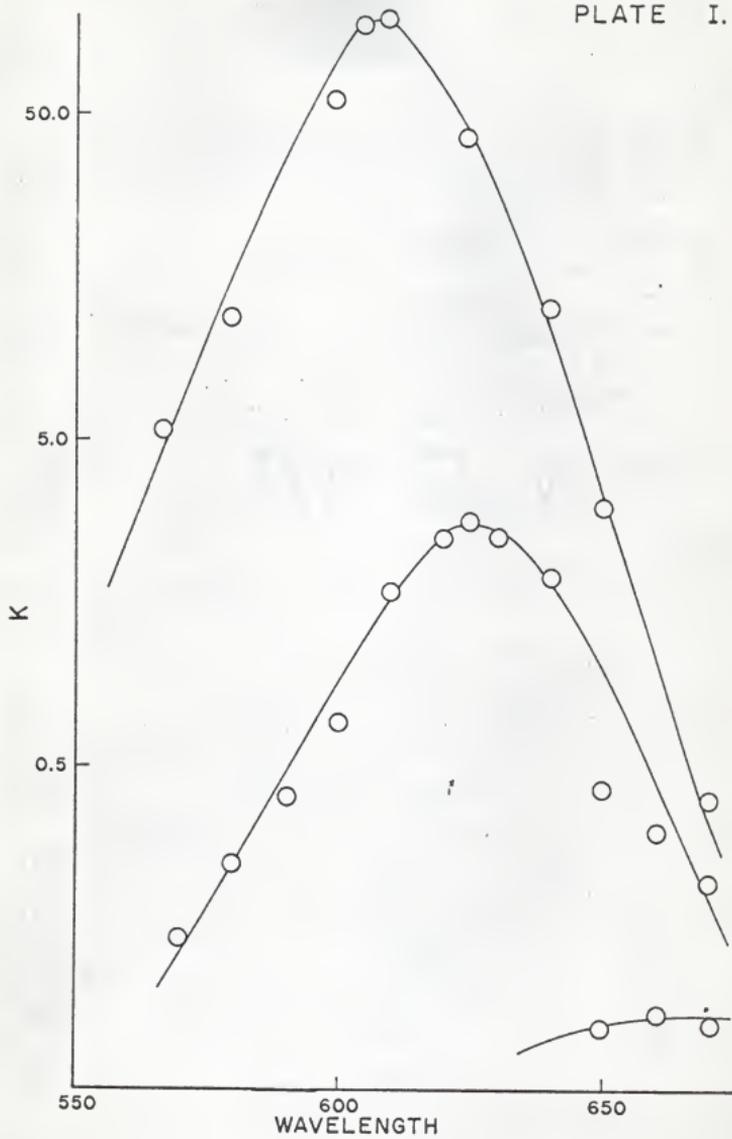
Spectrum of Sodium Indigo Disulfonate

Curve 1. 0.0003 F dye.

Curve 2. 0.00012 F dye.

Curve 3. 0.00003 F dye.

PLATE I.



EXPLANATION OF PLATE II

Spectrum of Sodium Indigo Disulfonate

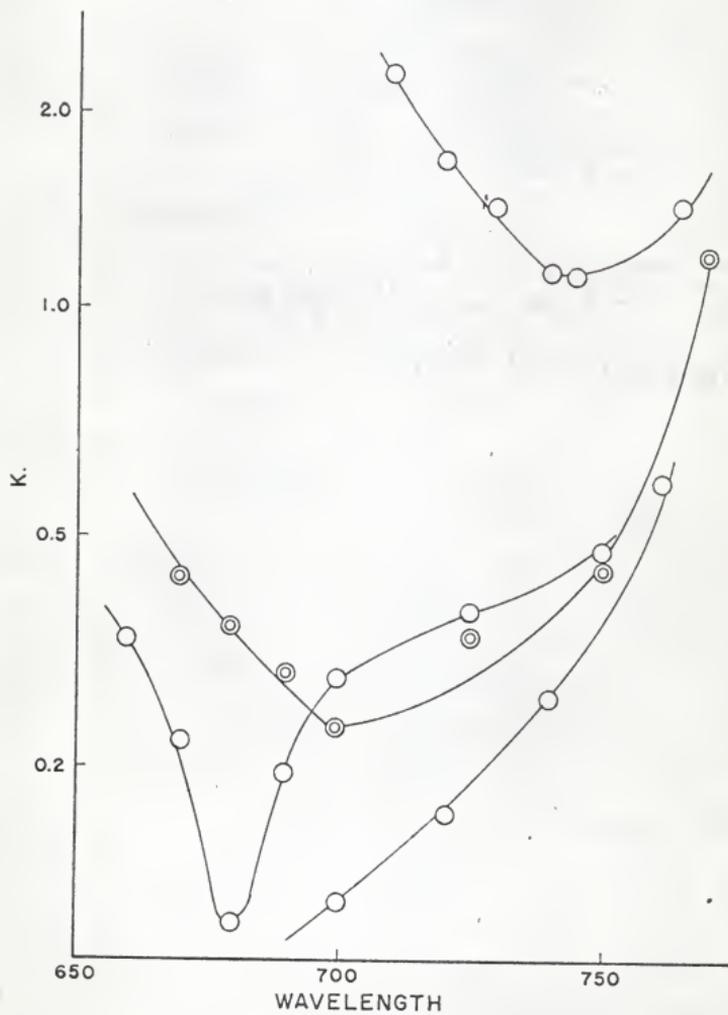
Curve 1. 0.003 F dye

Curve 2. 0.0003 F dye

Curve 3. 0.00012 F dye

Curve 4. 0.00003 F dye

PLATE II.



trations produced somewhat less pronounced minimums at slightly higher wave lengths.

The best resolution was obtained at the maximum of 610 μ so all future studies were limited to readings taken at the wave length of 610 μ .

Stability

The dye is relatively unstable, oxidizing to the golden yellow isatin on standing. The concentration of the dye can be determined by titration with a strong oxidizing agent. This method has had extensive investigation and could be used to determine the excess dye after precipitation of the metal-dye complex. The dye has also been used as an indicator in various oxidation-reduction titrations in which the end point is detected by the disappearance of the blue color and the production of the yellow.

The instability of the dye was not desirable for this investigation so methods were tried to decrease the decomposition. It was felt that the reaction might be catalysed by light or by heat so two methods were tried to lower the decomposition. One solution was put into an Erlenmeyer flask which had been previously prepared by painting with numerous coats of black paint. The other solution was put in a regular Erlenmeyer and placed in the refrigerator. The results in Table 1 indicated the solution in the refrigerator was much more stable, but even in the refrigerator there was a noticeable decomposition.

Table 1. Stability comparison

Elapsed time (hours)	Black Erlenmeyer	Refrigerator
0	.590	.580
48	.560	.568
75	.559	
110	.554	.555
150	.533	.555
200	.520	
700	.420	.520

Another stability test was run by mixing a solution of 0.00012 F Indigo Carmine and titrating this with 0.008 F zirconyl chloride. The mixture was centrifuged and a sample of the clear solution was measured in the Beckman Spectrophotometer. The blank was prepared by diluting a five milliliter sample of the original dye solution with ten milliliters of water to produce the blank. The original solution was allowed to stand for 145 hours and the process of titrating, and preparing the blank was repeated. There was a general decrease in the absorption of the solution as is shown by Plate III. The decrease seemed to be fairly constant as shown by the approximately parallel lines.

Interferences

Interference studies were made on a number of ions. It was discovered that cobalt (II), calcium, copper (II), ammonium,

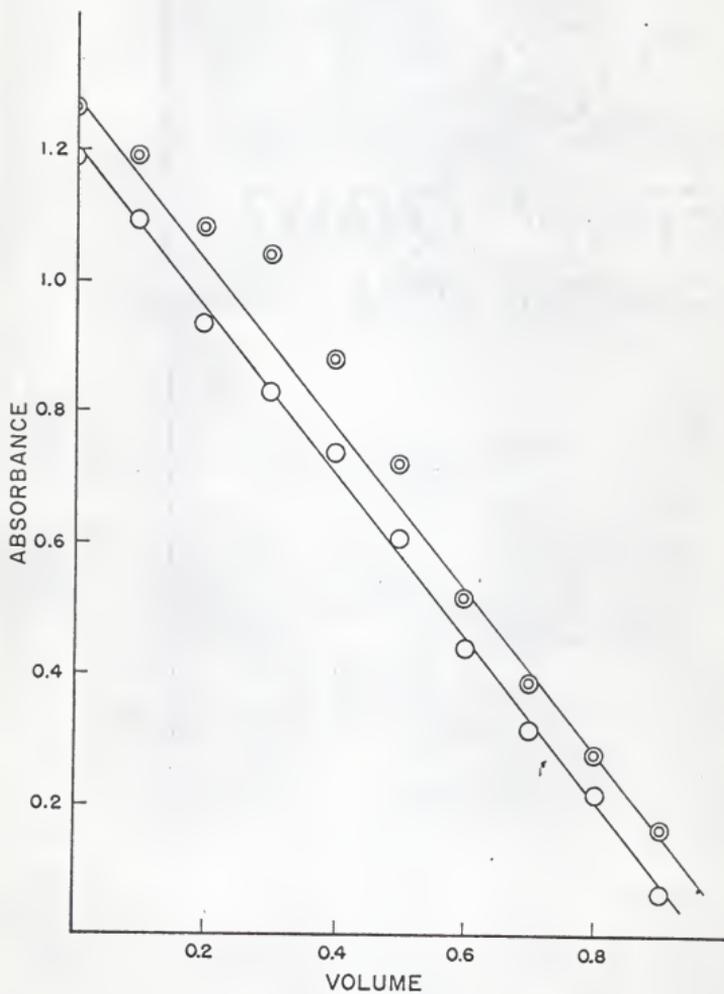
EXPLANATION OF PLATE III

Stability Studies

Curve 1. fresh dye

Curve 2. 145 hour old dye

PLATE III.



sodium, and potassium ions gave no interference even when their concentration exceeded that of the zirconyl by a factor of one hundred. Ten times the zirconyl concentration gave no interference with bismuth (III), mercury (I), mercury (II), manganese (II), strontium, cadmium, zinc, or aluminum. Lead (II), iron (II), barium, and sulfate gave no interference at a 1:1 ratio while nickel (II), uranyl, lanthanum, cerium (II), thorium, and iron (III) gave no interference when their concentration was 0.1 the zirconyl concentration.

A method of removal of the ions was used if the concentration of the interfering ions exceeded the preceding values. Moore (9) reported the use of 2-thionyltrifluoroacetone (TTA, 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione) to separate zirconyl from other cations. The zirconium was dissolved in 6 F hydrochloric acid and stirred, by vacuum mixing, with 0.5 F TTA solution in xylene. Care must be taken to not mix too strongly as a colloidal dispersion can form. A ten minute period was used to extract the zirconium to the organic phase, giving 98% extraction. The organic phase was diluted to 100 times its volume and two 10-minute extractions were made with 100 milliliters of 6 F hydrochloric acid. A modification was necessary to adjust the pH and the zirconyl concentration. The solution was evaporated to ten milliliters and sodium hydroxide pellets were added to adjust the pH to 1.0. This extraction was not necessary in most cases and was not normally used.

The following ions do not extract into the organic phase;

the alkaline earth elements, the trivalent rare earth elements, tin (II), nickel (II), cobalt (II), chromium (III), uranyl, thorium (IV), iron (II), aluminum (III), bismuth (III), and niobium (V). With lower concentrations of hydrochloric acid the iron (II) is not separated, but at 6 F it was found that in a typical 10-minute extraction the extraction of iron (III) is approximately 0.1% while the zirconium is extracted quantitatively. The decrease in the extraction efficiency of iron (III) is probably due to the formation of the chloro-ferric acid complex, HFeCl_4 , in the aqueous hydrochloric acid solution.

Study of the organic phase might produce a direct method of determining the zirconium without the problem of re-extraction.

Nitrate and the halides do not interfere. Whenever possible the original solution is prepared free of sulfate, oxalate, or phosphate. If any of these interfering anions are present they must be removed by an extraction process. It was found that the use of a strong base type of resin such as Amberlite IRA-400 did an acceptable job of absorbing the interfering anions. This method was first reported by Maddock and Pugh (8).

The preceding methods can be used to remove every ion that was found to be undesirable, but they should not be used unless necessary.

Beer's Law Investigation

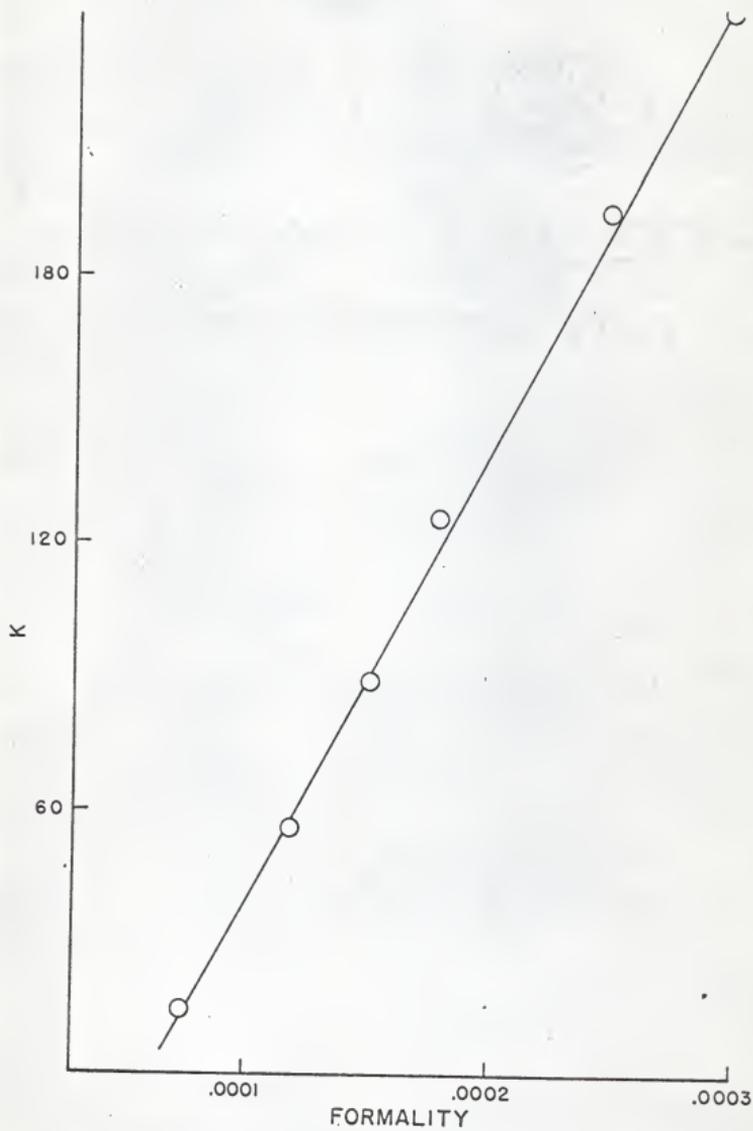
It was hoped that the solution would follow Beer's Law. To test for Beer's Law a solution of Indigo Carmine was prepared with a concentration of 0.0003 F. By dilution of aliquot portions of this solution, solutions were prepared with concentrations ranging down to 0.00003 F. The per cent transmittance was measured for each solution at a number of different slit widths. For each solution it was possible to use four to seven different slit widths but the smallest width for the most concentrated was 1.6 while the largest width for the most dilute was 0.3. Because of this it was again necessary to use Equation 1 to correlate the absorbance at different slit widths. It was found that for each solution the large and the small slit widths produced a large variance in the value of k so that only the middle three values were averaged for purposes of graphing. This value for k was plotted against the concentrations on regular graph paper giving a straight line (Plate IV) between 0.000075 F and 0.0003 F.

As a double check on Beer's Law another graph (Plate V) was constructed. There was a small amount of duplication in the slit widths at the various concentrations. It was possible to plot $\log I_0/I$ versus concentration at slit widths of 1.6 to 1.4. These gave straight lines proving the Indigo Carmine obeys Beer's Law in the range of concentrations from 0.000075 F to 0.0003 F. This also proved that k the constant from Equation 1 was proportional to $\log I_0/I$.

EXPLANATION OF PLATE IV

Beer's Law curve with
various slit widths

PLATE IV.



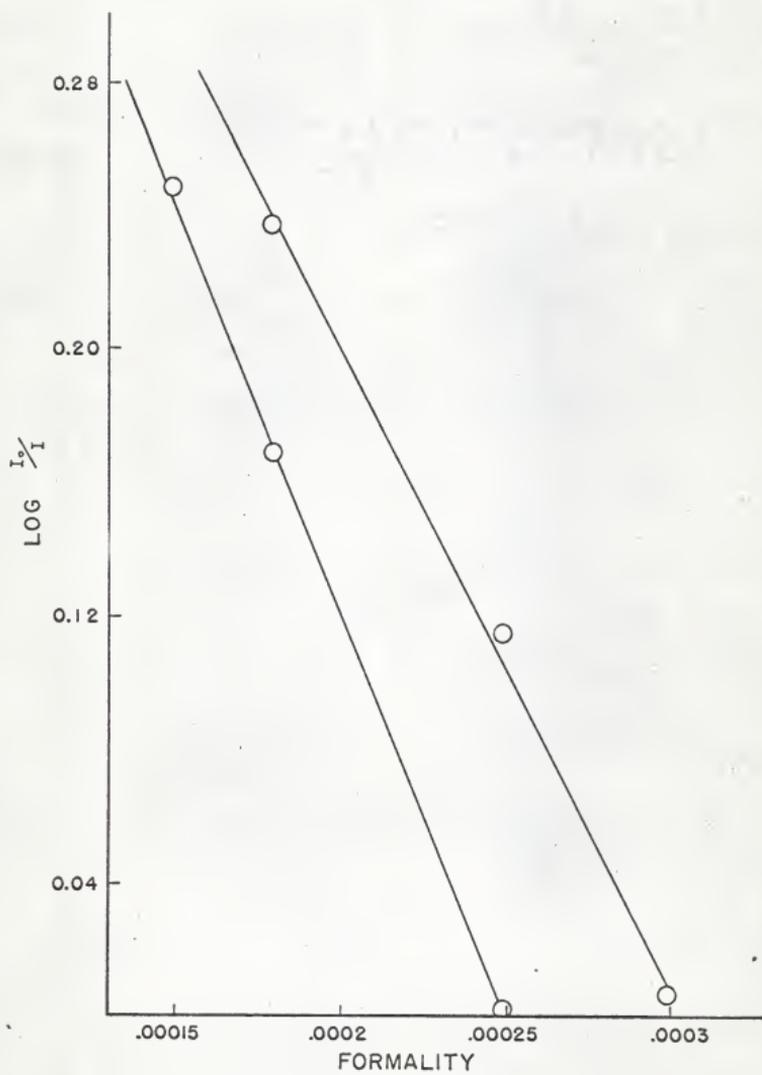
EXPLANATION OF PLATE V

Beer's Law

Curve 1. slit width 1.6

Curve 2. slit width 1.4

PLATE V.



Analytical

Ten milliliter aliquots of 0.003 F Indigo Carmine were reacted with five milliliters of a standardized $ZrOCl_2$ solution to produce a standard curve. The $ZrOCl_2$ solutions were in the range of 0.3% to 0.8%. The mixture was filtered and the absorbance of the filtrate was measured with the Beckman Spectrophotometer. Equation 1 was used to correlate the different slit widths and the constant k was plotted on semi-logarithmic paper against concentration of $ZrOCl_2$ (Plate VI).

Structure

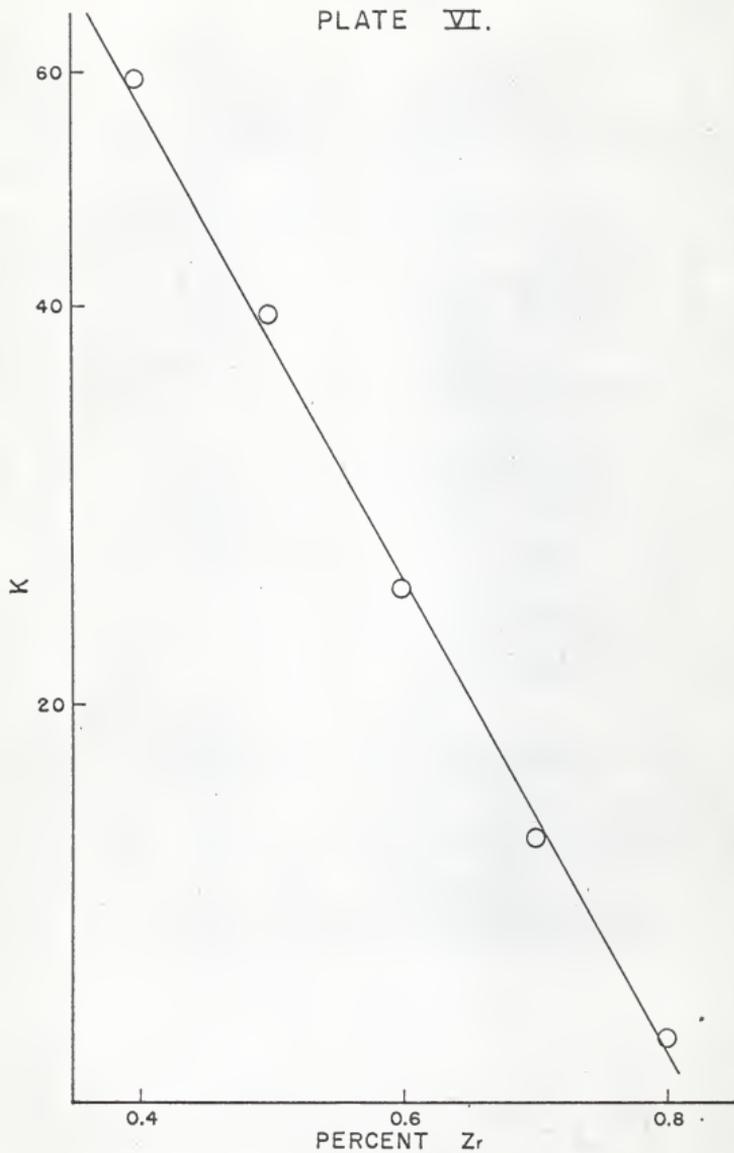
Two methods were used to study the possible structure of the zirconium-Indigo Carmine precipitate. Based on the method of continuous variations, the combining ratios of 0.003 F zirconyl chloride and Sodium Indigo Disulfonate dye solutions were studied. One to 10 milliliters of zirconyl chloride solution was pipetted into 25 ml. Erlenmeyer flasks and sufficient Indigo Carmine was added to bring the total volume to 10 ml.

The prepared mixture of the dye and zirconium solutions was then filtered with suction. The filtrate was collected and its absorbance was measured at 610 $m\mu$. As the zirconyl ion concentration increased the absorbance value decreased at a very rapid rate until the 1:1 zirconium-to-dye ratio was formed. The absorbance of the filtrate was measured and correlated by means of Equation 1 to give k which was plotted against milliliters of dye to give the curve which is reproduced on Plate VII.

EXPLANATION OF PLATE VI

Standardization curve for
zirconium from 0.3% to 0.8%.

PLATE VI.

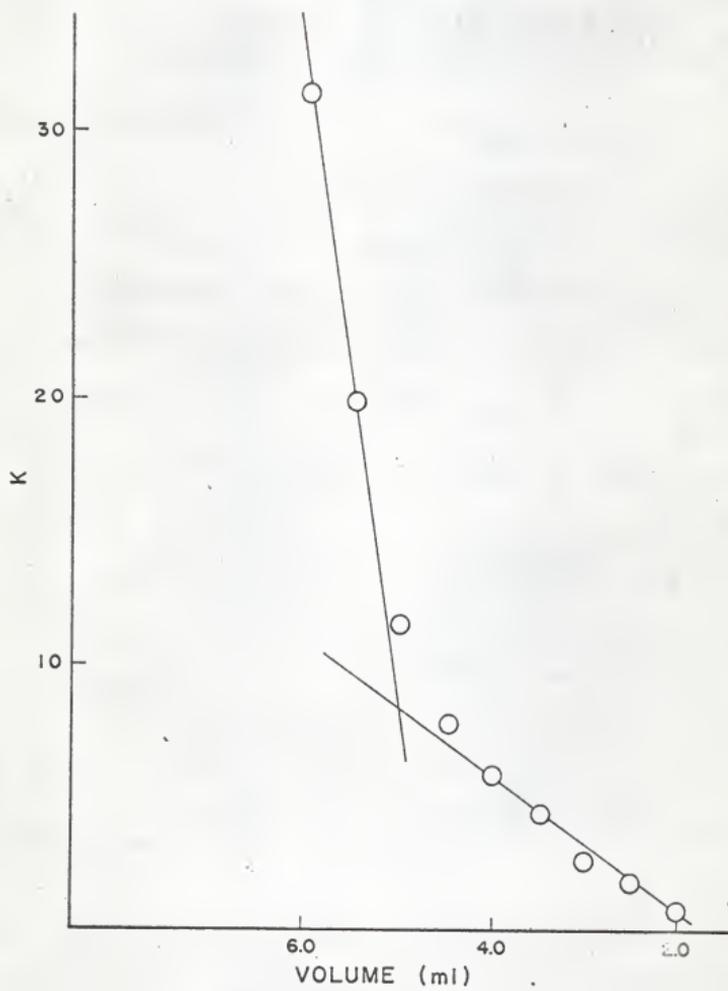


EXPLANATION OF PLATE VII

Absorbance of filtrate

Varying mixture of 0.003 F zirconyl
chloride and sodium indigo disulfonate.

PLATE VII.



Infrared spectra of the Sodium Indigo Disulfonate and its zirconium compound were studied to determine the functional groups of the dye anions involved in the compound formation. Approximately equal amounts of the dye and the compound samples each were ground and thoroughly mixed with nujol in a mortar and pestle. The mulls were placed between sodium chloride plates and the spectrum range from 0 to 14 μ was obtained (Plate VIII).

DISCUSSION

The Sodium Indigo Disulfonate was found to give maximum absorption at a wave length of 610 m μ . The dye was found to follow Beer's Law in the range of 0.000075 F to 0.0003 F. The concentration of the filtrate must necessarily be in this range to assure accurate determination of the concentration of zirconium. The use of Equation 1 to correlate absorbance measured at different slit widths was found to work very well with the Indigo Carmine. For highly absorbant solutions such as are formed by this dye it can be extremely useful to be able to use any slit width and then compare it to a reading made at a different slit width.

The dye is quite unstable, oxidizing to yellow isatin on standing. Stability tests indicated that although light catalysed the reaction, the decomposition is more dependent on the temperature. Even at a lower temperature the oxidation is so great that it was necessary to mix a fresh solution of dye each time it was needed.

EXPLANATION OF PLATE VIII

Infrared spectra

Spectrum 1. Sodium Indigo Disulfonate

Spectrum 2. Zirconium-Indigo Carmine compound

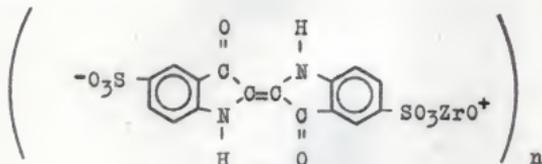
Interference studies revealed a number of ions that would cause interference at various concentrations. All interfering anions can be removed by a strong base anion exchanger. All of the interfering cations can be removed by extraction with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione. It is usually possible to eliminate these procedures.

The analytical studies showed that the method could be used for the indicated range of concentrations. There are apparently two limiting factors to the range. The original concentration of the $ZrOCl_2$ must be less than that of the original Sodium Indigo Disulfonate. This of course can be varied by using less than five milliliters of the $ZrOCl_2$ solution and adding sufficient 0.12 F hydrochloric acid to bring the total volume to five milliliters. It is also essential that the final concentration of the dye be in the range of 0.000075 F to 0.0003 F to be certain that it will follow Beer's Law.

The 1:1 ratio of zirconium to dye seems to indicate a strictly ionic bonding of the zirconyl ion to the two sulfonate groups of the dye. Molecular models indicate too great a strain for the formation of the chelate between the amine and carbonyl groups. The models also tend to support the belief that the entire dye anion could not bend sufficiently to attach the two sulfonate groups of the same anion to a single zirconyl ion. The relatively low solubility of the zirconium-dye compound would also seem to point to an extensive polymer rather than a finite molecule.

A comparison of the zirconium-Indigo Carmine compound spectrum with that of the Sodium Indigo Disulfonate indicated that bands due to the sulfonate group were symmetrical and at a slightly higher wave length with relatively small changes in the intensity of the overall spectrum. These changes are probably due to the small differences in the electrostatic bonding of zirconium as compared to the lower molecular weight of sodium.

The following is the proposed structure of the metal dye complex:



LITERATURE CITED

- (1) Ayres, G. H.
Evaluation of accuracy in photometric analysis. *Anal. Chem.* 21:652-657. 1949.
- (2) de Boer, J. H.
Sensitive color reaction of zirconium, hafnium and fluorine with hydroxyanthraquinones. *Rec. Trav. Chim.* 44:1071-1076. 1925. Original not seen. Abstract in *Chem. Abs.* 20:1042. 1926.
- (3) Feigl, F., P. Krumholz and E. Rajmann.
A specific test for zirconium. *Mikrochemie.* 3:395-400. 1931. Original not seen. Abstract in *Chem. Abs.* 25:4197. 1931.
- (4) Grotheer, M. P., and J. L. Lambert.
Colorimetric determination of bismuth in alloys. *Anal. Chem.* 30:1997-1999. 1958.
- (5) Holmes, W. C.
The spectroscopy of the sulfonated indigotins. *J. Am. Chem. Soc.* 46:208-214. 1924.
- (6) Kumins, C. A.
Zirconium determination in presence of interfering ions. *Anal. Chem.* 19:376-377. 1947.
- (7) Lambert, J. L., and M. P. Grotheer.
Structures of some thorium-dye compounds exhibiting selective ion-exchange properties. *Anal. Chem.* 30:1485-1489. 1958.
- (8) Maddock, A. G., and W. Pugh.
The separation of protactinium and zirconium by an anion exchange column. *J. Inor. Nuclear Chem.* 2:114-117. 1956.
- (9) Moore, F. L.
Separation of zirconium from other elements by liquid-liquid extraction. *Anal. Chem.* 28:997-1001. 1956.
- (10) Taylor, D. M., and R. E. Frasier.
Influence of phosphates on zirconium-alizarin method of fluoride determination. *J. Am. Water Works Assoc.* 39:52-56. 1947.
- (11) Yasuda, S. K., and J. L. Lambert.
Cellulose supported thorium-alizarin red S reagent for fluoride ion determination. *Anal. Chem.* 30:1485-1489. 1958.

ACKNOWLEDGMENTS

Appreciation is expressed to Dr. G. W. Leonard, original major professor, for his suggestion of the problem.

Appreciation is also expressed to Dr. J. L. Lambert, major professor, for accepting the author as a student in the middle of the problem. His guidance and encouragement have been invaluable.

Special appreciation to Teresa for spiritual guidance.

COLORIMETRIC DETERMINATION
OF ZIRCONIUM

by

DOUGLAS EUGENE MARCY

B. S., Kansas State Teachers
College of Emporia, 1954

AN ABSTRACT OF
A MASTER'S THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1963

Approved by:

Major Professor

A method for the direct colorimetric determination of zirconium was studied. Sodium Indigo Disulfonate, Indigo Carmine, was used to precipitate the zirconium and the unreacted dye was then determined.

The determination was accomplished by measuring the absorbance of the dye in a Beckman model DU Spectrophotometer and compared to a standard curve. The measurements were made at 610 m μ and correlated by means of an equation, $k = (\text{slit width})^2 (100\text{-per cent transmittance})$. The equation was used to allow comparisons to be made on different concentrations that required varying slit widths for meaningful absorbance values.

The dye was found to obey Beer's Law over a range of 0.000075 F to 0.0003 F. It was found by the method of continuous variation, by infra-red studies and by the Fischer molecular models that the most likely structure for the metal-dye complex was a 1:1 ratio. The metal-dye complex was quite easily formed and separated from the solution. The very low degree of solubility implies a high molecular weight complex.

The dye was quite unstable when in solution and rapidly oxidized to isatin. The rate of oxidation is decreased by lowering the temperature, however it is still so great that the dye can not be stored more than a day.

The original concentration of the dye must be adjusted to allow the final concentration of the dye to fall in the range of adherence to Beer's Law.

It was found that a few ions could cause noticeable interference with this method of determination. All interfering cations could be removed by extraction with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione. All interfering anions could be removed by a strong base anion exchanger. If possible these procedures should not be used as they tend to decrease much of the advantage of speed and ease of determination.