A STUDY OF NICKEL AMMONIA COMPLEXES IN SOLUTION
AND
THE DETERMINATION OF ZIRCONIUM WITH PHTHALIC ACID

by

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INTRODUCTION

This work includes an investigation of nickel ammonia complexes and an analytical method for the determination of zirconium.

The first part is concerned with an investigation of nickel ammonia complexes in solution. When ammonia is added to a nickel salt in solution a blue color is formed. As the ammonia concentration is increased this color changes to violet. This indicates the presence of different complexes. Much work has been done with these complexes both in and out of solution. There seems to be disagreement as to just what complexes are present. This work was undertaken to try to add to the knowledge of the complexes in solution mainly by an extension of the method of continuous variations.

The second part of this work is concerned with an analytical method for the determination of low concentrations of zirconium. Several methods are available, but a better one was sought. It was known that phthalic acid with zirconium ions causes a fine precipitate. Therefore it was attempted to use this for a turbidimetric method of analysis and also to investigate a method based on the spectrophotometric absorption of the phthalic acid remaining in solution after precipitation of the zirconium.

NICKEL AMMONIA COMPLEXES

History

Nickel ammonia complexes are important because they can be used for the colorimetric analysis of nickel (1), (17). Most of the complexes have been prepared in the solid form. King et al (15) prepared the pentammine nickel sulfate monohydrate (bright blue) and the hexammine nickel nitrate (blue violet). He also noted the preparation of the tetrammine dihydrate of nickel sulfate. King stated that he believed that his work supported the work of others in showing the non-existence of the tetrammine nitrate although the tetrammine had been reported.

Ephraim (9) investigated the influence of anions on stability and decided that nickel salts of strong acids made stronger nickel ammonia complexes than weak acids. He gave a list of a few complexes and he included among them the hexammine and pentammine nickel nitrate. The pentammine was the less stable.

Biltz and Fetkenheuer (3) investigated ammonia compounds of nickel halides. They made curves comparing changes of composition with pressure, effects of temperature upon composition, and changes of pressure with temperature. His procedure was to pass ammonia over the ammine at different temperatures and pressures. In this way he determined also the stability of the ammines. He found the hexammine (blue violet), the diammine (green), and the monoammine (green) present. The stability of the compounds

increased with decreasing ammonia.

Biltz also calculated the heats of solution and heats of formation of different ammine complexes. Ephraim (8) had previously calculated some heats of formation using the assumption that starting with the hexammine one ammonia was lost at a time thus giving a series of compounds with one to six ammonias in them. However Biltz (2) decided that the assumption of changes by one ammonia at a time was unwarrented. Biltz stated that hexammine nickel bromide passes over into the diammine complex by increasing the temperature. This change takes place within a temperature interval of five degrees and therefore the existence of a series of compounds with from one to six ammonias was improbable.

Clark (5) summarized the work done on the solid complexes up to 1924. He listed many ammonia complexes, their mode of preparation and properties. The only triammine in his list of the ammines of the nickel halides was the fluoride. The others were of six, two, and one ammonias. A coordination number of six is usually associated with bivalent ions of metals with an atomic volume of less than fourteen.

Solutions of the ammonia complexes have also been investigated by others. Kato (13) investigated the ammine complex ions of nickel salts and the application to chemical analysis. He believed that nickel existed mostly as the tetrammine complex in moderately concentrated ammonia. Russel et al (20) showed that the magnetic moment of nickel sulfate decreased by adding up to

six equivalents of ammonia.

Konowaloff (16) found the relation between the strength of aqueous solutions of ammonia and the pressure exerted at sixty degrees. He showed that dissolved salts decreased this pressure and used Henry's law to show that four ammonias were present in the complex. The change in conductivity of nickel sulfate when ammonia is added is also explained by the formations of such compounds. The change in freezing point elevation due to the addition of salt can also be used to determine complexes.

Dawson and McCrae (6) used extraction with chloroform to measure the composition of complexes and applied it to nickel ammonia sulfate. They determined the amount of ammonia extracted by shaking a known volume of an aqueous solution with a known volume of chloroform. The concentration of ammonia in water divided by the concentration in chloroform is constant. When this procedure was followed with nickel ammonia sulfate in the solution, a higher value was obtained for the constant. The amount of ammonia in combination with the salt can be deduced. Nickel ammonia sulfate, he decided, probably containes four ammonias.

Gensch (10) studied ammonia concentrations in complexes by conductimetric titrations. He stated that the ammonia can be determined by conductimetric titration by titration with excess hydrochloric acid and back titrating with sodium hydroxide.

Wijs (23) found the stability constants of some of the complexes by assuming that there were only three ammonias present. She determined the ammonia pressure above the solution and

substracted this from the total ammonia to give the combined
ammonia and from these the constants could be calculated. Derr
and Vosburgh (7) determined the instability constants of solutions
of the mono, di, and triammine complex. They found the solubility
of silver iodate in water and ammonia solution and then in a
solution of nickel ion and ammonia. From these they calculated
the concentration of free ammonia and the combined nitrate and
then calculated the constants. This work agrees with Bjerrum (4)
who decided that the ammonias added one at a time from the mono-
ammine through the hexammine complex. Wijs work could just as
well have been interpreted this way. Motola (18) also used about
the same method to show the ratio of nickel to ammonia to be 1
to 3.8.

Yatsimirskii and Grafova (24) disagreed with Bjerrum's (4)
statement that the ammonias are added one at a time thus giving
six complexes. He showed that from thermochemical data the
tetrammine adds two ammonias to form the hexammine instead of one
at a time. He also calculated the entropies, change in free
energy, and enthalpy for these two compounds.

These complexes have also been investigated spectrophoto-
metrically. Shibata et al (21) varied the concentration of a
solution of two ions and from the peak in the spectra the
composition of the compound could be found. This method is now
called "continuous variations". It has been used by Job (12)
on nickel ammonia complexes. However he used only one wave length
to measure the complex and therefore got inconclusive results

with nickel. He decided that the method was not appliable if more than one complex was present. Vosburgh and Cooper (22) tried to apply this method to more than one complex. They showed that if the peak in the "continuous variations" shifted with different wave lengths then different complexes were present. They measured the absorption spectra of various ratios of the complexing reagent to a fixed amount of the metallic ion. The shift in wave length peaks could be followed and a wave length picked so that the other complexes would not interfere. This wave length was then used for the "continuous variations" to find the composition of the complex. They tried to use this method on nickel ammonia complexes but stated that due to the instability of the complexes no positive results could be obtained.

Method

As previously stated Vosburgh and Cooper (22) investigated complexes by preparing solutions of fixed concentrations of the metallic ion and varying the ratios of the complexing agent. They tried to pick wave lengths to use to prove the complexes present by the method of continuous variations from the absorption spectra of these solutions so that the other complexes would not interfer. By choosing the place where two curves intersected the extinction coefficients would be equal and thus the higher complex would not interfere, and the rest of the complexes were enough lower in their absorbancies so they would not interfere either.

It was decided to repeat their work and see if modifications could be made which would enable the determination of complexes which are largely dissociated. Nickel nitrate was found to have a maximum in absorbancy at 395, 720, and 1130 millimicrons (Plate I). Ammonia caused the wave length maxima to shift toward shorter wave lengths (also shown in Plate I). The middle peak was picked for most of the study since it had a fairly sharp peak. At the lower wave length the nitrate ion started to absorb. For this run it was assumed that six ammonias was the maximum that combines with the nickel, and the literature supports this. The absorbancy curve continued to shift up and to the lower wave lengths with increasing ammonias until about a twelve to one ratio was reached. The continuous variations run was made at wave lengths picked according to Vosburgh and Cooper's method. Therefore it was decided to try to obtain the six to one complex at 590, the five to one at 600, the four to one at 615, the three to one at 635, the two to one at 680, and the one to one at 735 millimicrons. The results were inconclusive and agreed therefore with the statement of Vosburgh and Cooper.

The method of Vosburgh and Cooper is based on the complexes present being stable. However with an unstable complex there will be dissociation to give other complexes in equilibrium with it. The absorption spectra of each solution made up for choosing the wave length to use is, therefore, not one of a single complex. It is also true that because of the numerous complexes present the concentrations of the complexes represented by the different

EXPLANATION OF PLATE I

Absorbancy curves for one ml. of one molar nickel
nitrate and varying ratios (0, 1, 2, 3, 4, 5, and 6) of
one molar ammonium hydroxide—three molar ammonium nitrate
solution diluted to seven ml. with three molar ammonium
nitrate.

PLATE I
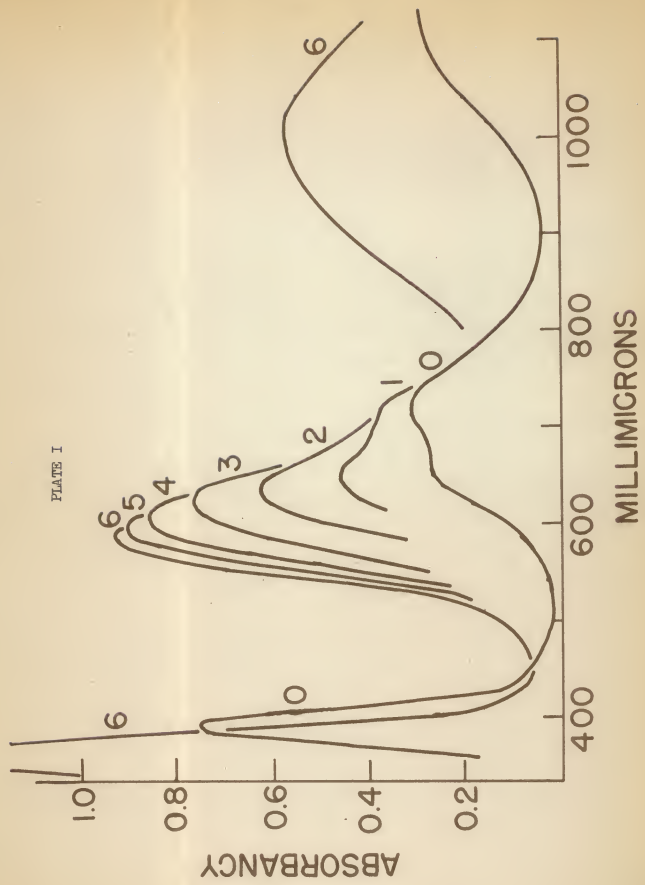
solutions can not be assumed to be equal. Therefore the intersection of the absorption curves has little chance of being that where the extinction coefficients are equal.

It was then noticed that there seemed to be a continuous shift in the wave length peaks. It was decided to run the method at numerous wave lengths. It was hoped that several wave lengths would correspond in their peaks and, it was assumed that if they did, this would be proof for the existance of the corresponding complex. This was done and several places seemed to check. It was decided to investigate this method further and the run was repeated adding new wave lengths where it seemed necessary until a series was obtained with a curve at every five millimicrons. The wave lengths that were found to correspond to the complex positions were not in agreement with those from Vosburgh and Cooper's method.

A method was then sought which would give an indication of what wave lengths could be used to indicate the complexes present. Absorption spectra were run on solutions containing the same amounts of nickel and ammonia as those in the method of continuous variations which would correspond to a ratio where a complex could be present. After substraction of the nickel absorption the curves obtained indicated the wave lengths sought.

It was decided to attempt to verify the presence of some of the complexes and also to try to calculate stability constants by making saturation curves. This was done in two ways. First, maximum saturation curves were made in which the concentration of

the nickel was kept constant and the ammonia varied. Readings
were made at several wave lengths, and it was hoped to pick up the
absorbancy due to one complex. Then minimum saturation curves
were run. The concentration of the nickel was varied and that
of the ammonia kept constant. In this way it was hoped to pick
up the lower complexes.

Experimental

The following stock solutions were prepared: a one molar
solution of $Ni(NO_3)_2 \cdot 6H_2O$, a three molar solution of ammonium
nitrate, and a one molar solution of ammonium hydroxide in three
molar ammonium nitrate. All had an ionic strength of three. All
the solutions used were made from these. The Beckman D. U.
Spectrophotometer was used to determine the absorption curves.
It was connected to a water bath so that the temperature of the
cell compartment was kept at about 23°C.

The absorption spectrum of nickel was made on a solution of
one ml. of the nickel nitrate solution diluted to seven ml. with
the ammonium nitrate solution. The absorption curves, with
increasing ratios of ammonia, were obtained from solutions
containing one ml. of the nickel nitrate solution and one to six
ml. of ammonia-ammonium nitrate solution. The solutions were
diluted to seven ml. with ammonium nitrate and the absorption
spectra made on them (Plate I). Absorption spectra were obtained
also on ammonia and ammonium nitrate solutions. Neither the

ammonia nor the ammonium nitrate interferred above 400 millimicrons. Somewhat below this range nitrate ion started absorbing and went to infinitive at about 340 millimicrons. Runs were also made to see if there was any difference in the absorbancy of nickel nitrate and nickel nitrate with ammonium nitrate. No difference could be detected above 400 millimicrons. Therefore it was reasoned that no complex is formed between the two.

For the continuous variation experiment ten ml. of the one molar nickel nitrate solution was used for the first point. For other points less and less nickel was used and more and more one molar ammonia-three molar ammonium nitrate solution. The final volume was kept constant at ten ml. until the solution of only ammonia-ammonium nitrate was reached. Readings were made at every five millimicrons from 510 to 750 millimicrons. A few sample runs representing the complexes believed to be present are shown in Plate II. Readings of a few wave lengths were obtained near the other two absorption peaks of nickel but with less satisfactory results. The dotted lines on the graph on Plate II represent the absorbancy of nickel nitrate diluted with ammonium nitrate which had no ammonia in it. This nickel was substracted from that of the nickel plus ammonia to give the curve of the excess absorbancy due only to the complex present (Plate III). The series of curves obtained showed fairly well the complexes present. However to show a better relationship the peak absorbancies of the curves at different wave lengths were plotted (Plate IV). Plate V was made by plotting wave lengths with the ratio of

EXPLANATION OF PLATE II

A continuous variations curve of solutions
containing the mole fraction indicated of one molar
ammonium hydroxide in three molar ammonium nitrate
solution and one minus this fraction of one molar
nickel nitrate. The letters refer to the curves
with ammonia present and the primes to the absorb-
ancies of the nickel solution without ammonia.

The wave lengths (millimicrons) indicated are:

A. 695
B. 660
C. 620
D. 585
E. 530

PLATE II

EXPLANATION OF PLATE III

The same continuous variations curves as in Plate
II with the absorbancy of the nickel alone (straight lines
on Plate II) substracted from the total absorbancy. The
mole fractions indicated are of one molar ammonium hydroxide
in three molar ammonium nitrate, and one minus this is the
mole fraction of one molar nickel nitrate.

The wave lengths and complexes the letters refer to
are:

A. 695 monoammine
B. 660 diammine
C. 620 triammine
D. 585 tetrammine
E. 530 hexammine
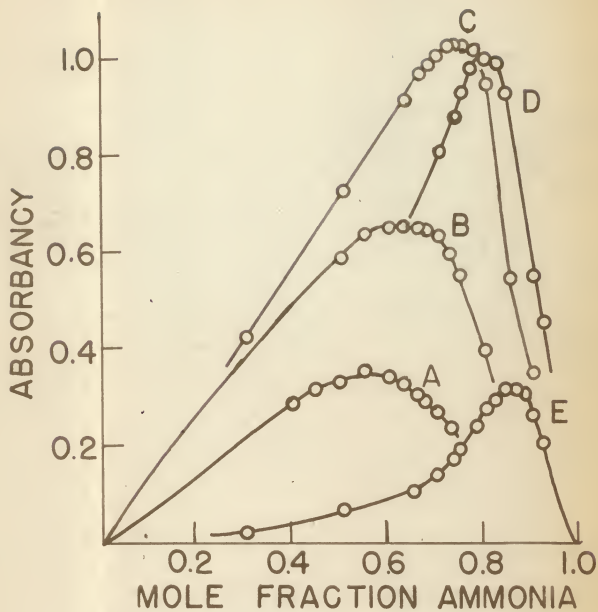
PLATE III

EXPLANATION OF PLATE IV

Plot of the maxima of the continous variations
plots at the different wave lengths with absorbancy.
Starting at the lower left side the wave lengths are
(millimicrons) 750, 735, 725, 715, 705 then every
five on up. Starting on the lower right side they
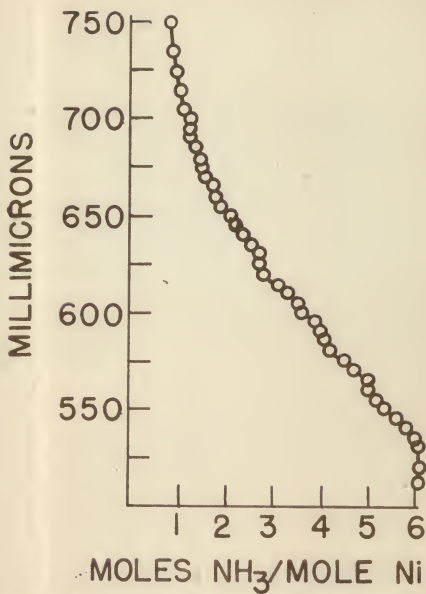are 510, 520, 530, 540 then every five on up.
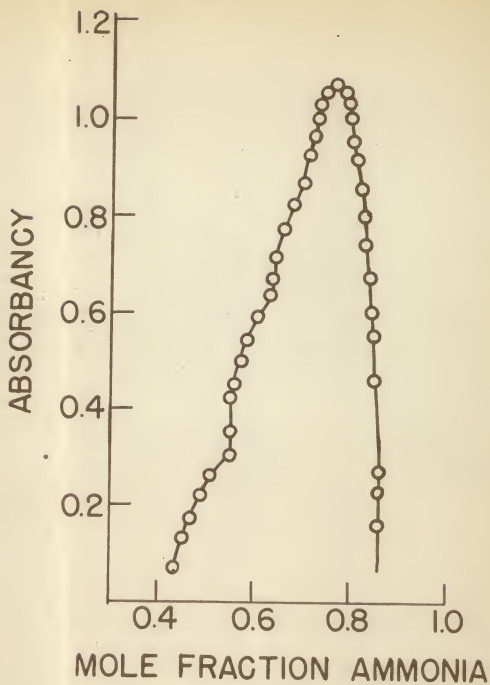
PLATE IV

Plot of wave length with the ratio of ammonia
to nickel corresponding to the peaks in the continuous
variations plots.

PLATE V

ammonia to nickel corresponding to the peaks of the continuous variations plot.

Then absorbancy spectra were made for the ratio of ammonia to nickel that represented the complexes possible. For example, for the one to one complex five ml. of nickel nitrate were mixed with five ml. of ammonia-ammonium nitrate solution and for the two to one complex 6.7 ml. of nickel nitrate were mixed with 3.3 ml. of ammonia-ammonium nitrate solution etc. Results are shown in the curves on Plate VI. The absorbancy of nickel nitrate solutions of the same concentrations as in the solutions above were subtracted from the absorbancy of the former to give results as shown in Plate VII.

Next maximum and minimum saturation curves were run to find the maximum and minimum complexes present. For the maximum saturation curves one ml. of the nickel nitrate solution was mixed with one to nine ml. of ammonia-ammonium nitrate solution and then diluted to ten ml. with ammonium nitrate solution. The absorbancies of these solutions were run at every five millimicrons from 350 to 375 and at every ten from 520 to 700 millimicrons. Results of some of the runs are shown in Plate VIII.
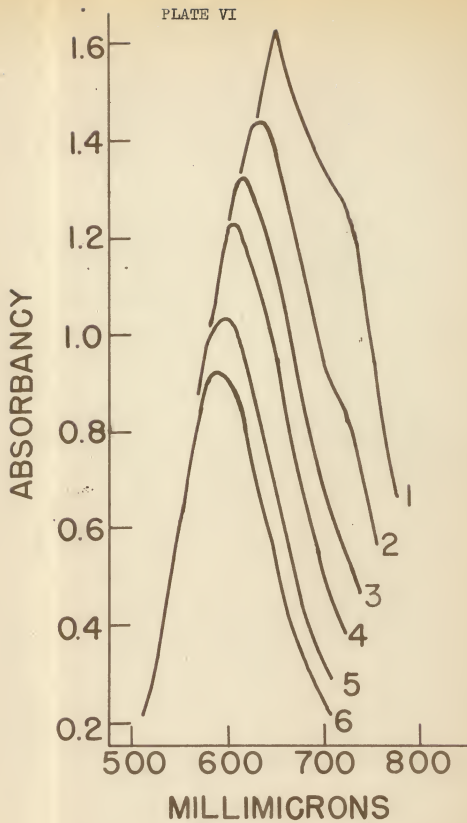
For the minimum saturation curves one ml. of the one molar ammonia-three molar ammonium nitrate solution was mixed with 0.1-1.4 ml. of one molar nickel nitrate solution and absorbancy readings taken at several wave lengths. Results of one at 650 and 386 millimicrons are shown in Plates IX and X. The straight lines represent the absorbancy on nickel nitrate diluted with solutions

EXPLANATION OF PLATE VI

Absorbancy curve of each concentration used in
the method of continuous variations where the maximum
amount of each complex should occur. The numbers
correspond to the ratio of the moles of ammonia to
nickel which gives the complex that should be at
maximum.

The ml. actually used were:

| number	ml. M Ni(NO$_3$)$_2$	ml. M NH$_4$OH in 3M NH$_4$NO$_3$
1	5.0	5.0
2	3.3	6.7
3	2.5	7.5
4	2.0	8.0
5	1.6	8.4
6	1.4	8.6

PLATE VI

EXPLANATION OF PLATE VII

Absorption curves of each concentration used in
the method of continuous variations where the maximum
amount of each complex should occur (Plate VI), minus
the absorbancy of nickel without ammonia at each
concentration and wave length.

The numbers again correspond to the ratio of the
moles of ammonia to the moles of nickel which gives
the complex which should be at maximum in its concen-
tration here. The actual volumes used are the same
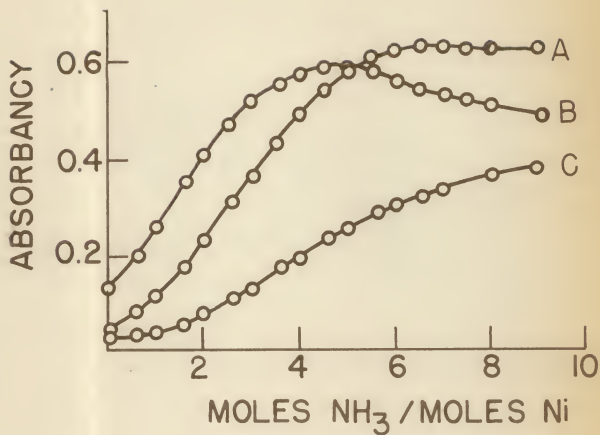as in Plate VI.

PLATE VII
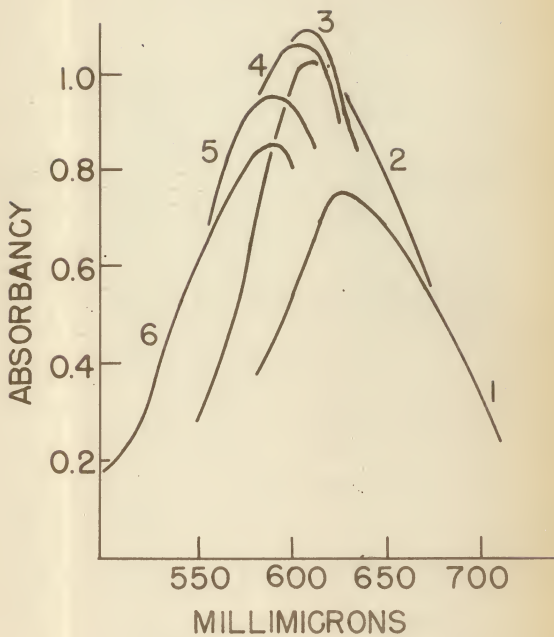
EXPLANATION OF PLATE VIII

Maximum saturation curves on solutions containing
one ml. of one molar nickel nitrate and varying ratios
of one molar ammonia in three molar ammonium nitrate
solution diluted to ten ml. with three molar ammonium
nitrate.

These were at wave lengths (millimicrons):

A. 580
B. 620
C. 540

PLATE VIII

EXPLANATION OF PLATE IX

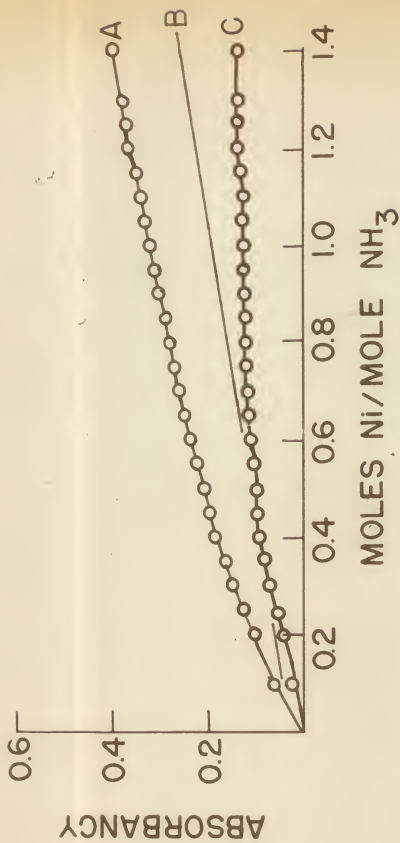Minimum saturation curve on solutions containing one
ml. of one molar ammonium hydroxide in three molar ammonium
nitrate solution and varying ratios of one molar nickel nitrate
and diluted to ten ml. with three molar ammonium nitrate.
The wave length used was 650 millimicrons.

A. Total absorbency curve of solution
B. Absorbency of nickel without ammonia
C. Difference between the two

PLATE IX

EXPLANATION OF PLATE X

Minimum saturation curve similar to Plate IX on solutions containing one ml. of one molar ammonium hydroxide in three molar ammonium nitrate solution and varying ratios of one molar nickel nitrate and diluted to ten ml. with three molar ammonium nitrate. This run was at 386 millimicrons.

A. Total absorbancy of solution
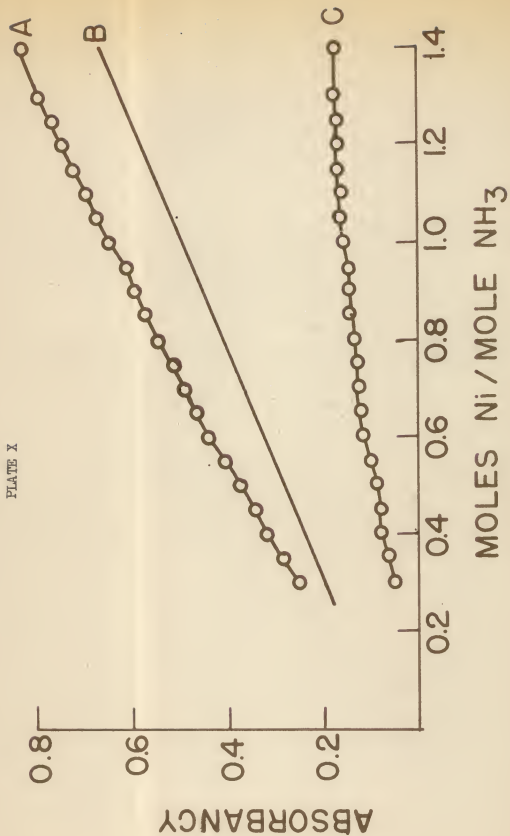B. Absorbancy of nickel without ammonia
C. Difference between the two

PLATE X

containing no ammonia and was substracted from the initial results
to obtain the lower ones.

A little work was done also with Ni^{III}. Ni^{II} was oxidized
with bromine then NaOH was added to precipitate $Ni(OH)_3$. Variable
amounts of this nickelic hydroxide were weighed corresponding
to the amounts desired for a continuous variations run and dissolved
in the desired amounts of ammonia-ammonium nitrate solution. The
results indicated at least the hexammine complex. The purple
solution seemed to be easier to form with Ni^{III} than Ni^{II} so its
hexammine may be more stable. It was assumed that the Ni^{III}
stayed Ni^{III} when dissolved. Absorption curves and polarograms
did not seem to indicate any difference between the two.

Discussion

When the peaks of all the curves obtained according to the
method of continuous variations were plotted (Plate IV) the peak
shift could be followed as the complexes shifted. Wherever
several occurred at the same concentration ratio this was taken to
indicate that a complex was present. Following the curve a shift
is seen to take place up to about 0.55. This would correspond
approximately to the one to one complex which should be at 0.5.
The next straight portion is at 6.4 which corresponds to the two
to one complex at 6.7. Then the peaks tend to straighten out at
7.3 (three to one is at 7.5) and now coming down the curve at 8.0
(four to one is at 8.0). Coming further down the shift is so

slight that it is impossible to tell if the five to one complex
is present or not. Toward the bottom the curve definitely tends
to straighten out at 8.6. This corresponds to the six to one
complex. The curve rises at first because the complexes with
more ammonias have a higher absorption than those with the lesser
amounts. The curve finally falls because the higher the complex
in the method of continuous variations the less concentrated it is,
and this effect finally overcomes the increased absorbancy of the
higher complexes.

In regard to the plot of wave length with the ratio of ammonia
to nickel corresponding to the peaks of the continuous variations
curves (Plate V) much the same results are indicated as in Plate
IV. An improvement is made however in that the possible confusion
of the bend at the top of the graph on Plate IV is eliminated.
Also this method exaggerates the presence of the higher complexes
which were previously hard to determine. By this method it appears
that the pentammine complex is also present.

Next the plots of the absorbancy spectra of the complexes
having concentrations as they appear in the method of continuous
variations will be considered. Plate VI shows the original plots
and Plate VII the same plots after substraction of the absorbancy
due to the nickel. The place where the absorbancy of the complexes
appears above the other complex curves gives some indication of
the wave length at which the different complexes are picked up.
For example the hexammine complex looks like it sho uld be picked
up from about 500 to 550 millimicrons, the triammine from 600-625,

and the monoammine from 675 on. This was approximately the way
it came out. The monoammine could not be picked up beyond 700
because the hexammine complex absorbs here less than the nickel
solution alone and therefore tends to cause the maximum peaks to
shift further to the left from the position of the one to one
complex. This method is one way of indicating, therefore, at what
wave lengths the different complexes will be at a maximum in the
method of continuous variations for dissociated complexes.

However for an actual determination of the complexes present
the easiest and most accurate method is to actually run continuous
variations with an entire series of wave lengths instead of trying
to pick out the proper ones according to the method just discussed.
By doing this the complexes present should be indicated. For
nickel all six complexes from the mono through the hexammine were
indicated to be present.

Not too much was shown in the study with the saturation curves.
In the maximum saturation curves (Plate VIII) there were no breaks
which might indicate the change from one complex to another. An
attempt was made to calculate equilibrium constants, but due to the
presence of large number of complexes consistent results could
not be obtained. One thing was noticed though, at around a wave
length of 540 the curve is still increasing at a ratio of nine
ammonias to one nickel. This probably would be the unstable
hexammine being formed. At around 580 the curve is flat on top
at a ratio of eight ammonias to one nickel. This curve is probably
due mainly to the tetrammine. At about 620 the curve reaches a

maximum at a ratio of five ammonias to one nickel, but then
absorption falls off with higher concentrations of ammonia showing
that another, higher, complex is being formed at its expense. This
could correspond to the triammine. All variations between these
types were found.

For the minimum saturation curves (Plates IX and X) absorptions
were run at the middle and lower absorbancy peaks of nickel. It
was hoped that the higher absorption for the lower complexes might
show more at the lower wave lengths. Actually this turned out to
be the case. In the curve at 386 millimicrons after subtraction
of the nickel two fluctuations were noted; one corresponded to
the two to one complex and one to the one to one complex. The
same fluctuations occurred in the curve at 650 millimicrons except
the fluctuations are less and seem to be shifted to the right.
Cell corrections and constant temperature were used for these runs
and the fluctuations although slight were also supported by a
duplicate run. They were also supported by the determinations
at the other wave lengths. Actually one would be more inclined
to expect breaks like this with the lower complexes since they
are supposed to be more stable. Thus the findings of the mono
and diammine nickel complex by the method of continuous variations
is supported by these saturation curves.

DETERMINATION OF ZIRCONIUM

History

The methods for the determination of zirconium are many and varied. However the prime interest of this work was a method for small amounts of zirconium using phthalic acid.

Green (11) determined up to 0.275 mg. of zirconium oxide colorimetrically with the pink lake formed by the zirconium alizarin sulfonate complex.

Kiefer and Boltz (14) determined it spectrophotometrically. They precipitated the zirconium by adding a standard phosphate solution. The concentration of the supernatant phosphate decreased in proportion to the amount of zirconium present. The phosphate was determined spectrophotometrically as the molybdiphosphoric acid complex. This method can be used for zirconium in the range of 1-80 p.p.m.

Purushottam and Raghava Rao (19) determined it by precipitation with phthalic acid and ignition to the oxide. They found that phthalic acid was fairly selective for zirconium in slightly acid media.

Method

It was known from Purushottam and Raghava Rao's work (19) that phthalic acid could be used as a reagent for precipitating

zirconium. It was decided to try to find an instrumental method
of analysis to replace their gravimetric method. Two methods were
developed, one turbidimetric using the inexpensive Bausch and
Lomb colorimeter and the other a spectrophotometric using the
Beckman D. U. Spectrophotometer.

Turbidimetric. It was noticed that the precipitate formed
by heating phthalic acid with zirconyl chloride was very finely
divided and tended to stay in suspension. This suggested a
turbidimetric method for small concentrations of zirconium.
The absorbancy of the turbid solution was measured on the Beckman
Spectrophotometer to find what wave length to use. It was found
that the lower the wave length the greater the optical density.
Therefore the lowest wave length available with the Bausch and
Lomb (430) was used to measure the percent transmittancy at
various concentrations and also the effect of variables.

Spectrophotometric. A curve of the absorbancy of phthalic
acid with wave length was made and it was found that absorbancy
peaks were present at 228 and 276 millimicrons (Plate XI). It
was decided to attempt a method similar to that of Kiefer and
Boltz (14) but with phthalic acid instead of phosphate solution.
The amount of zirconium could be determined by the loss in
absorbancy of the phthalic acid due to its precipitation with the
zirconium. The Beckman D. U. Spectrophotometer was used to measure
the absorbancies. It was found that the absorbancy of the phthalic
acid was so great that a known concentration of phthalic acid had
to be used as a reference instead of a water blank in order to

EXPLANATION OF PLATE XI

Absorbancy curve for 0.005 grams of potassium
hydrogen phthalate in 100 ml. of 0.15 N hydrochloric
acid.

PLATE XI
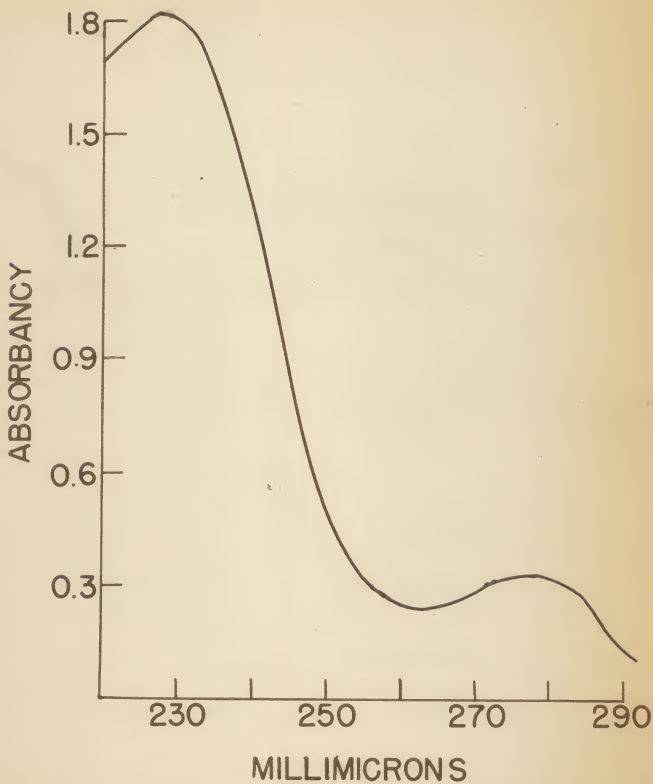
get satisfactory results for the unknown acid. Various concentrations were made up and the zirconium precipitated from a hot solution, centrifuged, the supernatant liquid decanted off and its absorbancy measured after dilution. The solution had to be fairly concentrated to start with to obtain a satisfactory precipitate. This method works for higher concentrations of zirconium.

Experimental

Turbidimetric. Procedure. Solutions were made up containing 7 grams of 99.38 percent pure potassium hydrogen phthalate in a liter of 0.15 N hydrochloric acid and twenty grams of c. p. $ZrOCl_2 \cdot 8H_2O$ also in a liter of 0.15 N hydrochloric acid. The latter was used as a stock solution from which all other concentrations were made for the turbidimetric and spectrophotometric determinations by diluting with 0.15 N hydrochloric acid.

A series of solutions of from 0.1-2.0 grams per liter of $ZrOCl_2 \cdot 8H_2O$ in 0.15 N hydrochloric acid were made. This range corresponds to 28-566 p.p.m. of zirconium. A beaker of boiling water was prepared. In the bottom of it a coil of wire was placed to prevent corked test tubes placed in it from touching the bottom of the beaker and becoming too warm. The volume of the boiling water was kept about constant. Ten ml. of the phthalic acid solution was added to five ml. of the zirconium solution in a test tube. The solution was mixed by inverting the tube and then lightly corked and placed in the beaker of boiling water. After

about one minute of heating the corks were firmly pushed into the
test tubes. This was to prevent evaporation of the solution which
would change the transmittancy. At first this evaporation caused
considerable variations in the readings. The solutions were
allowed to remain in the beaker of boiling water for a total time
of ten minutes after which they were placed in a beaker of cool
water. After cooling the solutions were shaken vigorously for
a few seconds to break up any precipitate or settling that had
taken place and then allowed to stand about three or four minutes
to allow air bubbles to escape. The solutions were then placed
in a square cell of the Bausch and Lomb Colorimeter with a 430
millimicron filter and the percent transmittance measured with
water as a blank. A curve of the percent transmittance with
concentration of zirconium was plotted (Plate XII).

Variables. The measurements of variables were made on
solutions of 0.2 grams of $ZrOCl_2 \cdot 8H_2O$ per liter (57 p.p.m. of
zirconium). This seemed to be the best place on the curve for a
determination.

Several concentrations and ratios of phthalic acid solution
were used and the transmittancy was found to vary with changes
in the amount of phthalic acid. It was found that about a two to
one ratio of phthalic acid solution to zirconyl chloride solution
gave the lowest transmittancy. It was also true that the higher
the concentration of the stock phthalic acid the lower the trans-
mittancy. The concentration of potassium hydrogen phthalate used
was believed to be the highest concentration that could be easily

EXPLANATION OF PLATE XII

Transmittancy curve for the turbidimetric determination
of zirconium with a 430 millimicron filter on the Bausch and
Lomb Colorimeter.

PLATE XII

43
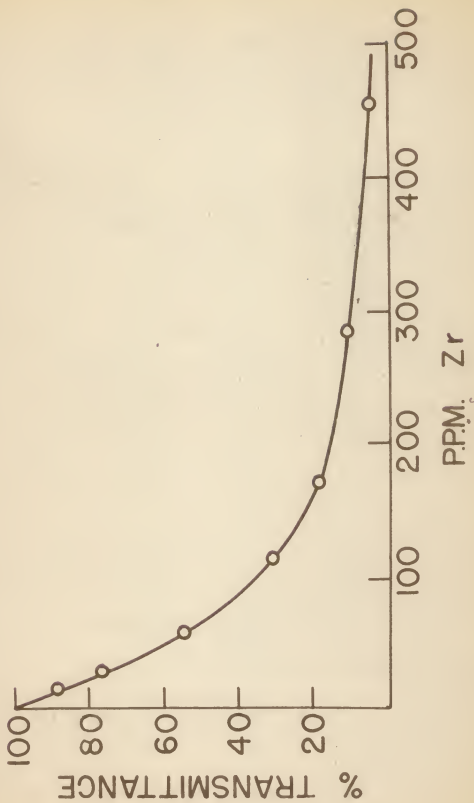
made. This had to be warmed to get it into solution.

The effect of time of boiling on the transmittancy is shown graphically in Plate XIII. It was found that the transmittancy decreased rapidly at first but later became constant in about five minutes. Ten minutes was chosen as the boiling time to insure a complete reaction. Although small variations from this time do not seem to affect the results, this time of boiling should not be increased to maintain a minimum evaporation. With continued heating a precipitate is usually formed. However a constant value for the transmittancy was reached before the precipitate was formed so this does not affect the results.

Determinations made using different order of mixing showed that this caused no variation. Determinations were made in which the heated solutions were cooled by placing in water kept at 20°C and 30°C, but this did not affect the results either. There also seemed to be no variation due to the length of cooling as long as a reasonably cool solution resulted.

The turbid solution also seemed quite stable. No variations in readings were noticed a half an hour after the cooled solutions had been shaken. However some interfering ions may cause the precipitate to settle out faster so it would be better to take the readings a few minutes after shaking. If the solutions stand long enough a precipitate will form. Solutions were read and allowed to stand overnight. This caused the precipitate to come down. However when shaken up again the same readings were obtained.

The final hydrochloric acid concentration of a solution was

Rate of formation of turbidity for a 57 p.p.m. solution of zirconium.

PLATE XIII
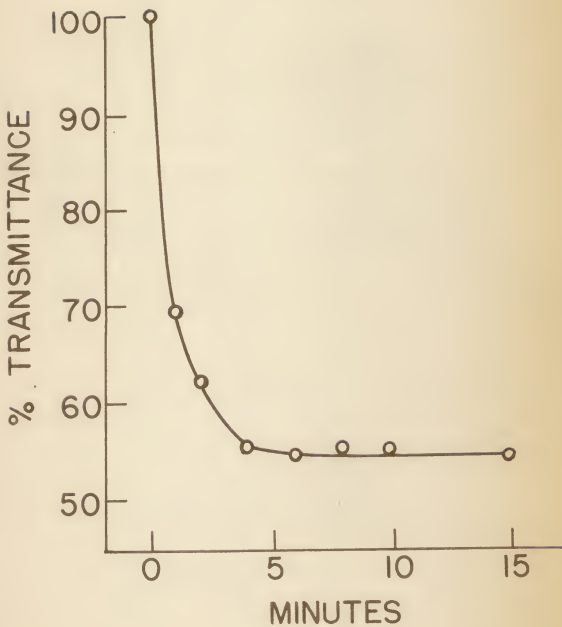
varied from 0.1-0.3 N with no appreciable change in the readings.
Hydrochloric acid was used since Purushottam and Raghava Rao (18)
noted that the phthalic acid was more specific for zirconium in
acid. Since smaller concentrations of zirconium were present we
employed a less acid solution in the determination. If the
hydrochloric acid is too strong the precipitate will not form.

Tests on the effect of interfering ions were made also with
the same concentration of zirconium (57 p.p.m.). These tests
were made with one ml. of a solution of zirconium five times the
strength of the concentration desired plus four ml. of the inter-
fering ions. The concentrations of the impurities is actually
that of the four ml. added. The results obtained are shown in
Table 1.

Table 1. Effect of interfering ions on the turbidimetric
determination of a 57 p.p.m. solution of zirconium.

Compound used	Calculations based on	Concentration at which no interference was noted (p.p.m.)
NaCl	Cl	1000
NaNO$_3$	NO$_3$	1000
Na$_2$SO$_4$	SO$_4$	1000
MnSO$_4$	Mn	600
Ni(NO$_3$)$_2$	Ni	600
Al$_2$(SO$_4$)$_3$	Al	300
V$_2$O$_5$	V	100
FeCl$_3$	Fe	60
Cr(NO$_3$)$_3$	Cr	50
SnCl$_2$	Sn	10
NaF	F	1

Spectrophotometric. Procedure. A solution of five grams of
potassium hydrogen phthalate in a liter of 0.15 N hydrochloric
acid was made. A series of solutions were made from the stock
zirconyl chloride solution (20 grams $ZrOCl_2 \cdot 8H_2O$ per liter of
0.15 N HCl) containing from 1-20 grams $ZrOCl_2 \cdot 8H_2O$ per liter of
0.15 N HCl (0.283-5.66 grams of zirconium per liter).

Five ml. of the zirconium solutions and five ml. of the
phthalic acid solution were placed in 15 ml. conical centrifuge
tubes. These solutions were mixed by inverting the tubes. The
tubes were lightly corked and placed in a beaker of boiling water.
after about a minute the corks were pushed in firmly to lessen
evaporation. The solutions were allowed to heat for twenty
minutes. A precipitate formed in about 5-10 minutes and continued
heating caused it to become more flocculent. Twenty minutes
seemed to be sufficient for most of the solutions. However the
concentrations of from 15-20 grams per liter of zirconyl chloride
required a longer heating period. In fact when solutions of 20
grams per liter were heated over two hours the reaction was still
incomplete. Concentrations above 15 grams of zirconyl chloride
(four grams of zirconium per liter) are therefore impractical and
inaccurate.

After boiling the solutions were centrifuged for five minutes.
This should cause the precipitate to be packed so firm that the
supernatant liquid can be decanted off without disturbing the
precipitate. Five ml. of the decantate were placed in a 25 ml.
volumetric flask and diluted to the mark with distilled water.

Dilutions made with water and with 0.15 N HCl gave the same absorbancy.

A solution containing 0.2 grams of potassium hydrogen phthalate per liter was made. This solution was placed in a quartz cell in the Beckman D. U. Spectrophotometer and used as a reference. The absorbancies of the prepared solutions were read at 276 millimicrons and corrected for cell differences. A curve showing the results is plotted on Plate XIV. When the absorbancies of the prepared solutions fell below that of the reference then the solutions were reversed and the optical density of the reference was measured with the unknown solutions as a reference.

Variables. No variations were noted due to order of mixing or in boiling time as long as a flocculent precipitate was formed. However lowering the acid concentration of the initial solution to 0.1 N seemed to lower the absorbancy of the final solution. Therefore the initial acid concentration should be kept constant.

Fairly high concentrations of solutions had to be used and later diluted to cause a precipitate to form. More dilute solutions were tried but little or no precipitate was formed.

The effect of interfering ions was determined on the four grams per liter zirconyl chloride solution (1.13 grams of zirconium per liter). This seemed to be the most ideal place to study an unknown. A solution for studying interfering ions was made by taking one ml. of a zirconium solution of a concentration five times that desired and adding four ml. of the impurity. The

EXPLANATION OF PLATE XIV

Spectrophotometric determination of zirconium
plot at 276 millimicrons on the Beckman Spectro-
photometer with a reference solution of 0.2 grams
per liter of potassium hydrogen phthalate showing
the decrease in the absorbancy of the phthalic
acid due to its precipitation with zirconium.

PLATE XIV
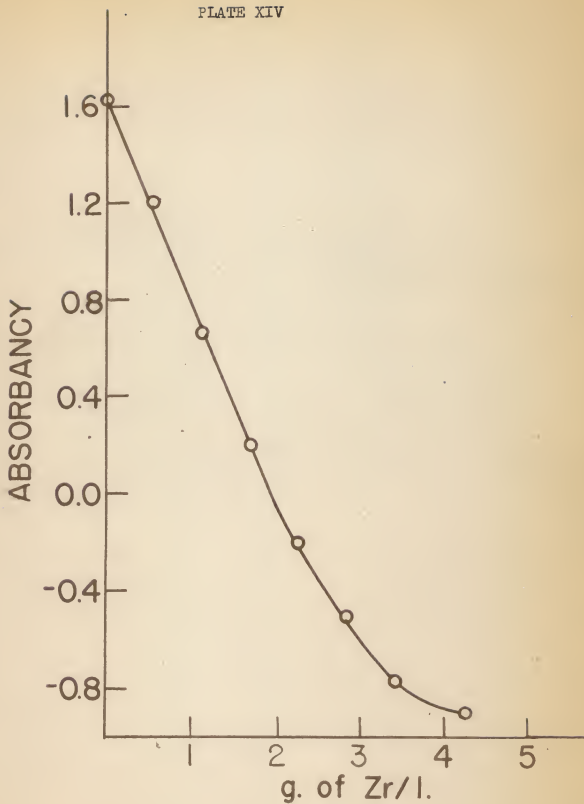
concentration of the impurities given is that of the four ml. added. The results are shown in Table 2.

Table 2. Effect of interfering ions on the spectrophoto-
metric determination of a solution of 1.13 grams
per liter of zirconium.

Compound used	Calculations based on	Concentration at which no interference was noted (g./l.)
$NaNO_3$	NO_3	0.6
$NaCl$	Cl	0.3
Na_2SO_4	SO_4	0.01
$Mn(NO_3)_2$	Mn	0.6
$Ni(NO_3)_2$	Ni	0.6
$Cr(NO_3)_3$	Cr	0.5
$Al(NO_3)_3$	Al	0.3
$SnCl_2$	Sn	0.1
$FeCl_3$	Fe	0.006
V_2O_5	V	0.005

Next an investigation of the composition of this precipitate formed between zirconium and phthalic acid was made. A sample of it was made by heating a solution of 6 grams per liter of $ZrOCl_2 \cdot 8H_2O$ with a solution of 5 grams per liter of potassium hydrogen phthalate mixed in the ratio of one to two ml. The centrifuged precipitate was washed with 0.15 N HCl and dried at room temperature in a calcium chloride desicator. Another sample was dried at 100°C. The latter product did not look as nice, but its results did not differ appreciably. When carbon hydrogen analyses were run the results indicated 21.2 percent carbon, 3.2

percent hydrogen, and 32.2 percent zirconium. Assuming a multiple of the eight carbon atoms found in phthalic acid this percentage corresponds to 16 carbons, 29 hydrogens, and 3 zirconium atoms. Since the two phthalic acids have eight oxygens this would add 14.2 percent to the total percent giving a total of 70.8 percent. Apparently the rest of the compound is made of oxygens or chlorides combined with the excess hydrogens found. Another sample of the precipitate was made using a higher concentration of phthalic acid. This time the precipitate was made by heating a solution of 10 grams of $ZrOCl_2 \cdot 8H_2O$ per liter with a solution of 7 grams of potassium hydrogen phthalate per liter mixed in the ratio of two to ten ml. This precipitate was yellower than the first and carbon hydrogen analyses showed 24.6 percent carbon, 3.3 percent hydrogen, and 29.7 percent zirconium. This would correspond to 16 carbon, 26 hydrogen, and 2.6 zirconium atoms. Since the amount of zirconium differs from the first run the precipate appears to be a mixture of at least two complexes. It appears reasonable that these could contain one complex with one zirconium to one phthalic acid and another complex with two zirconiums to one phthalic acid.

Discussion

These methods seem to be very good for determining zirconium. There seems to be little effect due to variables, and the analysis can be run in a short time.

In the turbidimetric method there were occasional variations from the average transmittancy. The reason was not found but was probably due to evaporation while heating or perhaps the rate of boiling of the heating water. However as a check a known sample can be run with the unknown. Several samples run at the same time always gave results that checked with each other. Any variations were with a previous batch.

Of the various ions added to the solution only a few seemed to affect the results. The concentration of the ions about all had to be considerably greater than that of the zirconium to cause interferences. Most of the interfering ions studied can be present at a higher concentration than indicated.

When the logarithm of the transmittancy curve is plotted with concentration, a straight line is obtained up to about 125 p.p.m. of zirconium. The ideal concentration range is therefore up to this concentration and naturally the higher concentrations give a larger percent accuracy. Of ten determinations made on a concentration of 57 p.p.m. of zirconium the average amount found was 59, the average deviation was 1.4, the maximum deviation 4.2, and the standard deviation 2.3 p.p.m.

Determination by the spectrophotometric method is not as fast as the turbidimetric method but gives satisfactory results in the higher concentration range. Different concentrations of phthalic acid and different final dilutions were tried, but this one used gave the most satisfactory results. The main disadvantage is that in the lower concentrations of zirconium the absorbancy

is so high that repeated checks need to be made on the readings
of the Beckman in order to obtain a satisfactory value.

The concentrations of the interfering ions can be higher
than those given. Upon the basis of the amount of zirconium
present interferences seem to be greater in the spectrophotometric
method than in the turbidimetric. However the results are at
least as good if not better than many of the other means of
determining zirconium. The sulfate ion had the most variation
between the two methods. The maximum allowable concentration
was less in the spectrophotometric than in the turbidimetric
method. Higher concentrations of chromic and stannous ions but
lower concentrations of ferric ion and vanadium could be allowed
in the spectrophotometric than in the turbidimetric method.

The spectrometric determination curve (Plate XIV) followed
a straight line up to two grams of zirconium per liter. This
is therefore the maximum concentration for an ideal determination.
Actually this straight line did curve slightly in the more dilute
region (less than 0.5 gm. per liter of zirconium). Of ten
determinations on a zirconium concentration of 1.13 grams per
liter the average amount found present was 1.11, the average
deviation was 0.015, the maximum deviation 0.028, and the standard
deviation 0.015 grams of zirconium per liter. The accuracy of
this spectrophotometric determination is sufficient for many
determinations.

SUMMARY

1. The method of continuous variations has been extended to include dissociated complexes by using a series of wave lengths, and the results obtained were further clarified.

2. A study of ammonia complexes with nickel nitrate by the improved method of continuous variations indicated the presence of the complexes containing from one to six ammonias.

3. A study of the nickel ammonia complexes with saturation curves indicated the mono and diammine complexes. Certain results could not be obtained for the higher complexes.

4. A turbidimetric method for determining zirconium was developed using phthalic acid for a concentration range from 3-125 p.p.m. The method had an accuracy of 3 p.p.m., and foreign ions or variable conditions caused little interference.

5. A spectrophotometric method for determining zirconium was developed for a concentration range up to 2 grams per liter with an accuracy of 0.03 grams per liter. The method used the loss in absorbancy of phthalic acid due to its precipitation with zirconium.

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A STUDY OF NICKEL AMMONIA COMPLEXES IN SOLUTION
AND
THE DETERMINATION OF ZIRCONIUM WITH PHTHALIC ACID

by

LEROY EDWIN SWIM

B. S., Kansas State College
of Agriculture and Applied Science, 1952

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AN ABSTRACT OF A THESIS

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This work includes an investigation of nickel ammonia complexes and also the use of phthalic acid for determining zirconium.

The method of continuous variations was used to study the nickel ammonia complexes. This had been tried before but with little success because the technique used in selecting the wave lengths was, in this case, in error. The accepted method for selection of the wave lengths is dependent upon a plot of absorbancies for solutions each with a constant concentration of nickel but with varying concentrations of ammonia. The assumption is then made that at the wave length where the absorbancy curves of two of the solutions cross that the extinction coefficients of the corresponding complexes are equal. This is not true for a dissociated complex because the measured absorbancy is the sum of the absorbancies of all the complexes in equilibrium with the one being determined. However by using the method of continuous variations at a series of wave lengths the different complexes could be identified. By this method all the complexes with one to six ammonias were indicated to be present.

The complexes were also investigated by determining saturation curves. The curves obtained by using constant nickel but varying ammonia were of little value because of the numerous complexes present. However the curve obtained with constant ammonia but varying nickel showed two breaks corresponding to the mono and diammine.

The analysis of zirconium with phthalic acid was investigated.

A turbidimetric method was developed using $ZrOCl_2 \cdot 8H_2O$ and potassium hydrogen phthalate. It was found that if a solution containing 3-125 p.p.m. of zirconium was added to phthalic acid and the solution heated, cooled, and shaken a turbid solution was obtained. The transmittancy of this solution was measured with the Bausch and Lomb Colorimeter. It was found that results checked within 3 p.p.m. and there was no variation due to small changes in the heating time, final temperature, acid concentration, order of mixing, or in length of time of standing. The concentration of phthalic acid affected the results some. Chloride, sulfate, nitrate, manganous, nickel, and aluminum ions caused only small interferences. Larger but not bad interferences were obtained with ferric and chromic ions and vanadium. Stannous and fluoride ions were the only ions that had to be in smaller concentration than the zirconium.

A spectrophotometric method was also developed using the Beckman Spectrophotometer. This method can be used on solutions containing up to two grams of zirconium per liter. To use this method a mixture of solutions of phthalic acid and zirconium ions was heated until there was complete precipitation. The solutions were centrifuged and the liquid portion diluted and its absorbancy measured. A known concentration of phthalic acid of 0.2 gm. per liter must be used as a reference. This method gives checks within 0.03 gm. per liter of zirconium.

Less interfering ions could be tolerated, in proportion to the amount of zirconium present, than in the turbidimetric method

although many of the allowable concentrations were about the same. Nitrate, chloride, manganous, nickel, chromic, and aluminum ions caused little interference. A more concentrated solution of stannous ions could be tolerated than in the turbidimetric method. The tolerable allowance for the sulfate ion was still less and in this respect differed from the turbidimetric method. Ferric ion and vanadium could be present only in small amounts.