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The synthesis and analysis of KAu(CN)4.3/2 H2O and its proposed separation from KAu(CN)2.2H2O

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The Synthesis and Analysis of $KAu(CN)_4 \cdot 3/2 \ H_2O$
and
Its Proposed Separation From $KAu(CN)_2 \cdot 2H_2O$

by

George Edgar Hartwell Jr. UC 1962   UC/p

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

By *[signature: George Hartwell Jr.]*

Approved by *[signature: Prof. C. F. Weick]*

May 22, 1962

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Illustrations and Graphs

Introduction

The increasing use of radioactive tracers in chemistry
has lead to many investigations of the rate of exchange
between two different oxidation states of a single element
in solution. These studies lead to a more basic understanding
of the structure of certain ions and their chemical reactions.

One element that has not been studied in this manner
is gold. The lowest oxidation state, Au(I), is such a powerful
oxidizing agent that Au^+ ion is nonexistant in aqueous solution,
oxidizing itself to the Au(III) oxidation state.

$$3Au^+ \longrightarrow Au^{+3} + 2\underline{Au} \quad ; \text{ self oxidation}$$

$$6Au^+ + 3H_2O \longrightarrow Au_2O_3 + 6H^+ + 4\underline{Au} \text{ ; in aqueous solution}$$
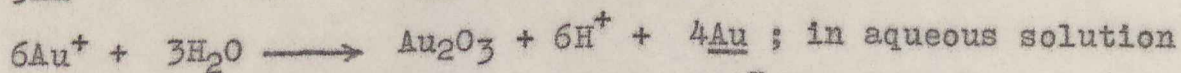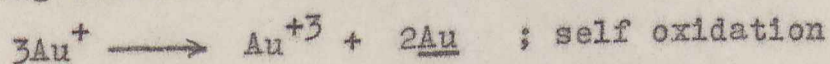
The latter equation shows that the Au^{+3} ion is also
nonexistant in aqueous solution and forms an insoluble
compound or complex.

Although the Au(II) oxidation state has been reported
as in AuS, an insoluble black compound, its existence is
doubted. It is more likely that this compound represents
an equimolecular combination of unipositive and tripositive
materials having the same stoichiometry. The intense black
color is also characteristic of the presence of two oxidation
states.

The oxidation potential for the reaction:

$Au(s) \rightleftharpoons Au^+ + e^-$ is 1.7 volts, thus Au^+ can be considered
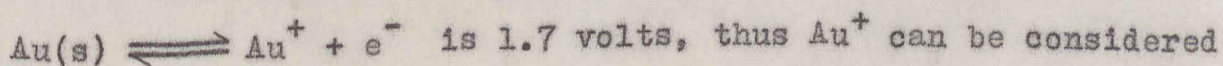
as strong an oxidizing agent as the permanganate ion. However,
the Au(I) oxidation state can be stabilized in aqueous
solution by complexing with cyanide ions to form $Au(CN)_2^-$.

$$Au(s) + 2CN^- \rightleftharpoons Au(CN)_2^- + e^- \quad ; \quad +0.060 \text{ volts}$$
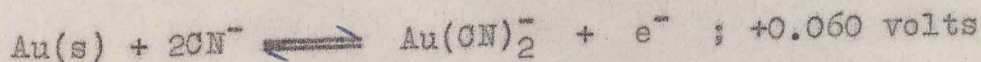
The corresponding ionization constant according to
Sneed[12] is:

$$\frac{[Au][CN^-]^2}{[Au(CN)_2^-]} = 2.5 \times 10^{-29}$$

The cyanide complex of the Au(III) oxidation state,
$Au(CN)_4^-$, which is also stable in aqueous solution, has no
published ionization constant. Its stability is noted
during attempted reduction of the complex to gold, as will
be mentioned later.

In a study of the exchange between $Fe(CN)_6^{-3}$ and
$Fe(CN)_6^{-4}$ in aqueous solution, Cobble and Adamson[2] found
100% electron transfer between the two oxidation states of
iron. They concluded that since the external nitrogen atoms
in cyanide complexes bear a negative formal charge and the
central atom is therefore surrounded by a sheath of electron-
rich atoms, it is possible that this higher electron density
is responsible for the anomalous rapid exchange. In the
exchange between the gold cyanide complexes one might expect
an analogous situation.

To proceed with such an investigation of electron
transfer it is necessary that:

1). A synthesis for one of the gold cyanides should
be available so that it can be labeled with a radioactive

species. In the particular case under study $KAu(CN)_2$ is
readily available commercially, but $KAu(CN)_4 \cdot 3/2\ H_2O$ must
be synthesized and subsequently analysed.

2). A method for determining quantitatively the degree
of separation achieved in the preparation for the decay
counting of one of the anions to measure exchange has to
be developed.

3). A method of separation of the anions from their
water solution should be developed once a detection procedure
has been perfected. This procedure should be fairly rapid,
yet if at all possible a physical method avoiding any
electron transfer that might occur during a chemical separation,
such as precipitation, should be sought. In this particular
case speed is even more important since the isotope that
would be used for labeling, Au^{198}, has a 2.7 day half life,
allowing about 27 days in which to synthesize and separate
the two anions.

Further comparison of the two gold cyanide ions shows
their similarities and suggests a method of separation:

$Au(CN)_2^-$ is a linear complex anion with a sp configur-
ation, the carbons directly attached to the gold central
atom[5].

$Au(CN)_4^-$ is square planar with a dsp^2 configuration.
The differences in the two cyanide ions are in charge distri-
bution and anion size. In aqueous solution the water of
hydration may give the two very similar hydration spheres.

Chemi. Chemical methods of separation are to be avoided for this particular study, since the reactions may catalyze the exchange. No precipitating reagents are known that will differentiate between the two, due to their similarities. Both anions are from potassium compounds and are highly ionic in character, thus separation by solvent extraction is highly unlikely. Electrophoresis and electroosmosis, both dependent upon charge differences, are ruled out because of the slowness of these processes.

Ion exchange chromatography, taking advantage of a possible hydration sphere difference and differing charge distributions, amy offer a solution to this separation problem. The high affinity of a resin for complex cyanide ions is generally due to high polarizability. Jones and Penneman[6] show that a strong base, quaternary amine, anion exchange resin will hold metallic complexes with varing degrees, which makes such a separation appear possible.

Before this separation can be investigated a method for the quantitative determination of the two gold cyanide complexes in aqueous solution must be found. It would also be convenient to have a qualitative method of detection for each complex, such as a spot test.

One might expect, since the complexes are of transition metals, that they would appear colored in solution. Although neither complex is colored it is quite possible that the absorption peaks have been shifted into the ultra violet

part of the spectrum. If so, it is possible that the spectra
of the two complexes may be different enough to merit both
qualitative and quantitative determination in aqueous solution
by absorption measurements in the ultra violet.

As a solid $KAu(CN)_2$ has a cyanide stretching frequency
at 2141 cm^{-1}[7], it is quite possible that this frequency
may be shifted enough in the $KAu(CN)_4$ compound to offer
identification using infrared spectra.

Other methods of identification open for investigation
include polarography and the use of conductance measurements,
since the equivalence conductances differ significantly[14].

The Synthesis of $KAu(CN)_4 \cdot 3/2\ H_2O$

The following procedure has been adopted from a synthesis presented by Wogrinz[13] for the preparation of alkali cyanides of gold.

In a 50ml round bottom flask 5.00 grams of $HAuCl_4 \cdot 4H_2O$ were dissolved. In a 50ml Erlenmeyer flask 3.95 grams of KCN were dissolved in 14ml of water. This cyanide solution was then added dropwise to the chloro-auric acid solution while under a hood. The mixture was stirred vigorously to remove the HCN formed.

$$HAuCl_4 + 5KCN \longrightarrow KAu(CN)_4 + 4KCl + HCN \uparrow$$
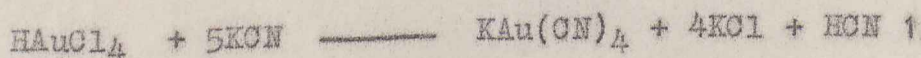
Three milliliters of water were used to wash the flask; the washings were added to the reaction mixture.

As the mixture was stirred the color of the $AuCl_4^-$ complex slowly changed from dark orange through yellow to a colorless solution. The color changes depended upon the extent to which $AuCl_4^-$ was being depleted in the formation of the colorless anion $Au(CN)_4^-$. (See equation above.)

The flask, warm from the reaction, was kept above $25.7^\circ C$ in the hood for between fifteen and twenty minutes after the color change had ended. This allowed for a complete removal of the HCN formed.

The flask was then suspended, undisturbed, in a $15^\circ C$ water bath for 24 hours. Because of the temperature

dependance of the solubility of $KAu(CN)_4$ and the lack of such great dependance for KCl, $KAu(CN)_4$ was precipitated in colorless leaflets leaving KCl in solution. It was important to keep the volume of water present constant. The above procedure has adjusted the volume properly.

The mother liquor was decanted and a second recrystallization was attempted. The yield was poor and complicated by precipitating KCl, whose solubility product was then exceeded. The $KAu(CN)_4$ formed was then dissolved in the minimum amount of boiling water, mixed with animal charcoal, and filtered through a previously warmed filter. The animal charcoal adsorbs impurities and any gold formed through decomposition. (Sneed reports that gold is often reduced in the course of dissolution.[12]) The recrystallization purifies the precipitate by releasing any coprecipitated compounds such as KCl or unreacted chloroauric acid. It is advisable to keep the product away from light as much as possible to avoid photodecomposition. The results are listed below:

Theoretical yield	4.46 grams of $KAu(CN)_4 \cdot 3/2\ H_2O$
purified yield	2.12 grams
percentage of ideal	47.7%

The change in color of the solution containing $AuCl_4^-$ during its reaction with cyanide, an unusual dilution phenomenon, was investigated in the following manner.

Three dilutions of $HAuCl_4$ were made and the spectrum of each solution was followed with the Beckman DU Spectrophoto-

Fig 1

Spectra of HAuCl₄·3½ H₂O at Various Dilutions
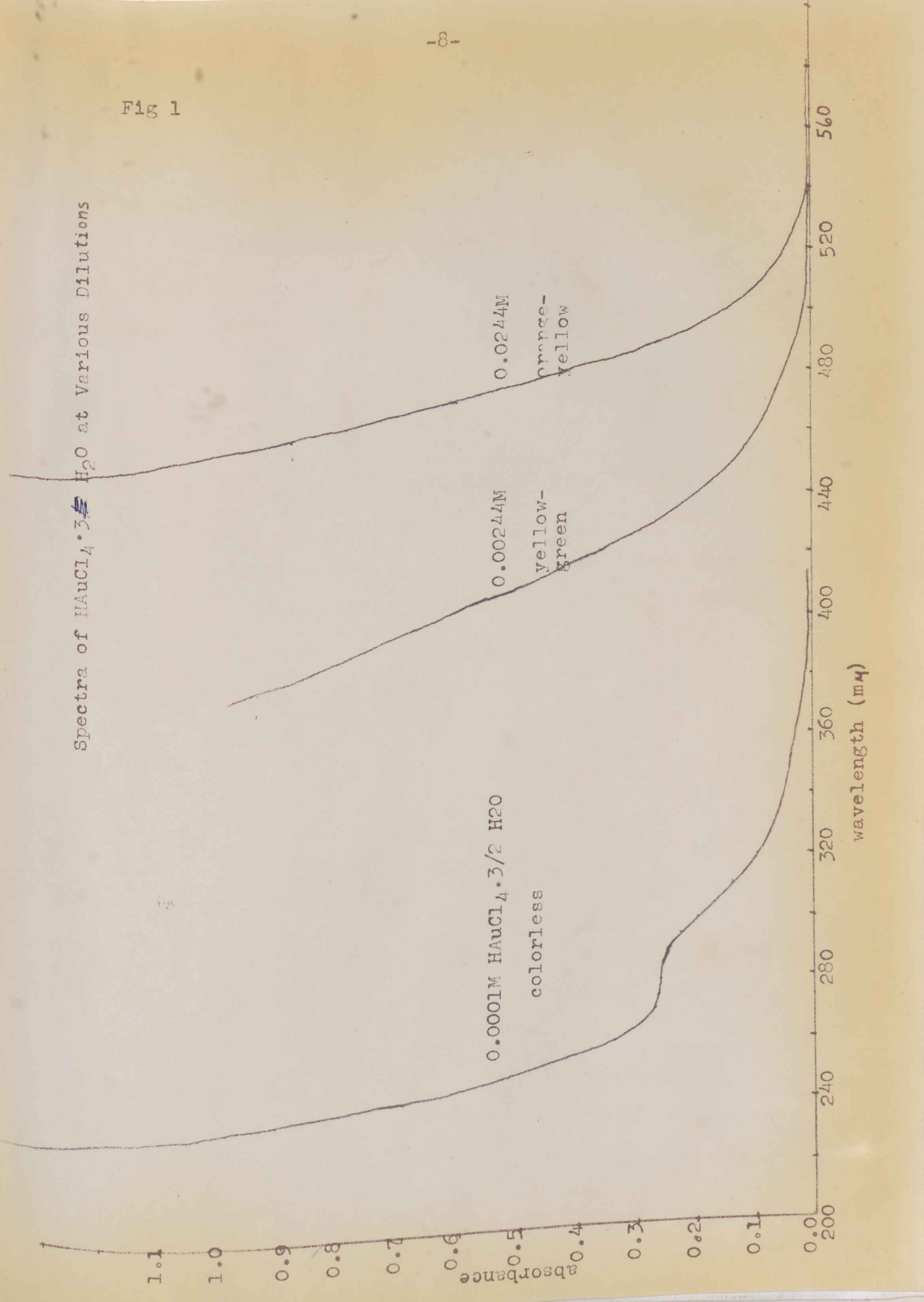
meter from the visible through the near ultra violet.

The resulting spectra (figure 1) can be summarized
as follows:

solution number	manner of dilution	concentration of $HAuCl_4 \cdot 3/2\ H_2O$	color of solution	average wavelength
1	--	0.0244 M	orange-yellow	480mμ
2	1:10	0.0024 M	yellow-green	420mμ
3	use #2; 1:25	0.0001 M	colorless	310mμ

It can be seen that concentration produces the color
rather than an assigned absorption peak. The color seen is
the average wavelength perceivable by the eye within the
given range. The presence of a shoulder at 280mμ suggests
the possibility that further dilution would result in an
absorption peak at this wave length.

Analysis of KAu(CN)$_4$·3/2 H$_2$O

Determination of Gold

Standard procedures for the analysis of gold involve either photometric[9] or gravimetric methods[10]. The former involving the formation of a gold colloid; the latter the quantitative reduction of gold to a weighable precipitate.

Those involving the formation of color through complexing were found to be inapplicable to the gold cyanide complexes, because of their stability. Both rhodamine B (an xanthone dyestuff) and benzidine were tried unsuccessfully.

Using reagents such as SnCl$_2$ to reduce the gold to a colloidal suspension which then is used for quantitative analysis by photoanalysis presents many difficult problems. The reaction involving the formation of the colloid is dependent upon both acid concentration and ion concentration. The size, and therefore the color, of the colloid is very dependent upon these two concentrations, and in order to properly use a standard curve from spectrophotometric readings it is best to first reduce the gold to a precipitate, wash it, and then put it into colloidal suspension.

Reduction to a collectable mass was tried with various precipitating reagents including aluminum (in strong OH$^-$), zinc, hydroquinone, and hydrogen peroxide. Without exception the resulting precipitate was only about 80% of the total

amount expected, and never reproducible. Apparently a
certain amount was lost in filtering due to the small size
of the gold precipitated, while some remained complexed
with the cyanide, further illustrating the stability of these
complexes. A certain amount was also lsot as a colloidal
suspension.

The gold plating industry often requires an accurate
determination of the amount of gold remaining in the plating
solution. From this analytical need has evolved a procedure
for the electrical deposition of gold from cyanide solutions.
Smith[11] presents such a method. An adoption of this
procedure follows.

$$4KAu(CN)_4 + 6H_2O \xrightarrow[E]{CN^-} 4KCN \uparrow + 12HCN + 4\underline{Au} + 3O_2 \uparrow$$
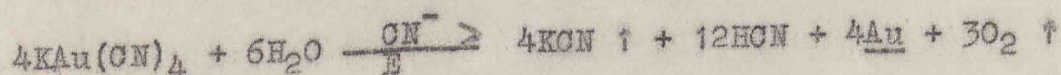
To a 180ml electrolytic beaker were added 1.50 grams
of KCN, 150ml water and 0.1402 grams of KAu(CN)$_4$. (0.0753g gold).
To neutralize any HCN formed 0.0640 grams of KOH were also
added. (Figure 2).

The temperature was elevated to 60°C to prevent the
formation of any decomposition products reported by Smith[11]
and to hasten the plating process. The power was maintained
at three volts-0.3 amps for about two hours. Gold metal
was plated out on the cathode, 0.0756 grams. Although KOH
was added to neutralize HCN, the experiment was done in a hood
for further precaution. The results are sumarized in the
following table.

gold in complex	gold plated on cathode	KCN	KOH	H_2O	volts	amps	time
0.0753g	0.0756g	1.5g	0.064g	150ml	3.0v	0.3a	2hrs

The gold is easily removed from the platinum elctrodes by a dilute solution of KCN and hydrogen peroxide, (100 ml water, 3 grams KCN, 5ml H_2O_2), for 2-3 minutes.

Determination of Potassium

The method used for the determination of potassium was suggested by Samuelson[8] who determinaed Na^+ and K^+ in various metal cyanides using cation exchange resins. The cyanide complexes are stable enough to be passed through a bed of cation exchange resin without decomposition. The potassium ions exchange with the hydrogen ions from the strong acid resin yielding the acid solution of the cyanide compound. This acid can then be titrated with standard base.

Jones, Penneman and Startizky[7] produced $HAu(CN)_2$ using a Dowex 50 resin. The potassium content of the synthesized salt was obtained as follows:

Using Dowex 50W x 8; 50/100 mesh, of the styrene type sulfonic acid in the hydrogen form, 2.491×10^{-4} moles of $KAu(CN)_4 \cdot 3/2\ H_2O$ were added and the acid formed was washed from the column. (Figure 3 shows apparatux). The acid was then titrated with standard NaOH using methyl orange as the indicator. The base was standardized with $KHC_8H_4O_4$, the results appear in the following table.
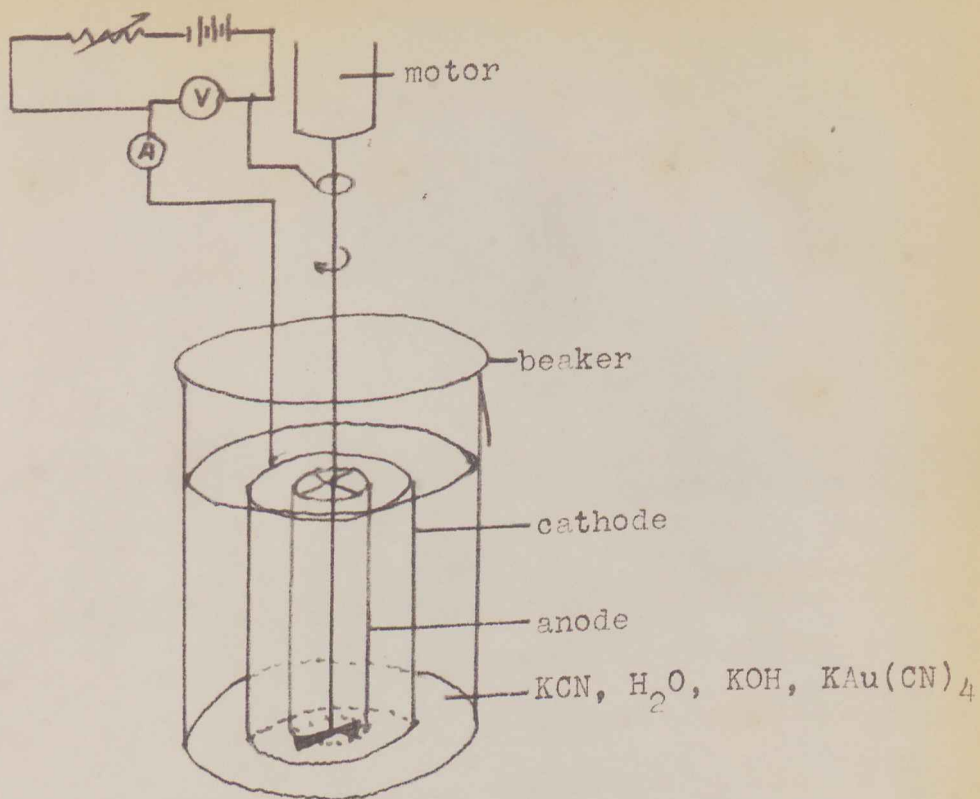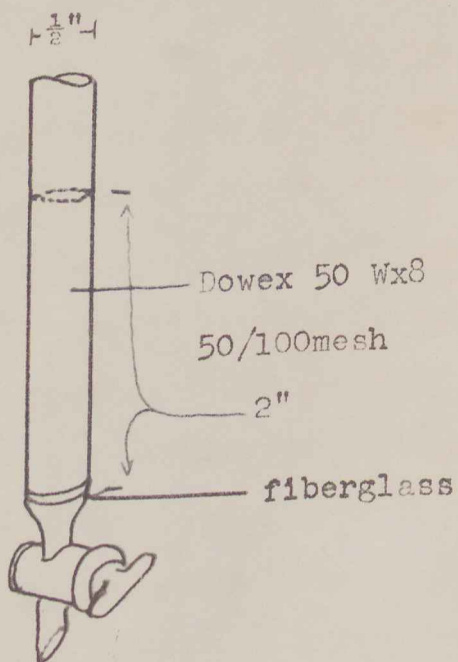
Fig 2. Apparatus for gold determination

Fig 3. Apparatus for potassium determination

Standardization of the NaOH solution

1)   0.03306N
2)   0.03288N
3)   0.03333N
average normality: 0.03309N NaOH

Titration of $HAu(CN)_4 \cdot 3/2 H_2O$

1)   7.50ml NaOH
2)   7.60ml
average of two titrations: 7.55ml NaOH, equivalent to 2.5×10^{-4} moles
theoretical moles 2.49×10^{-4}

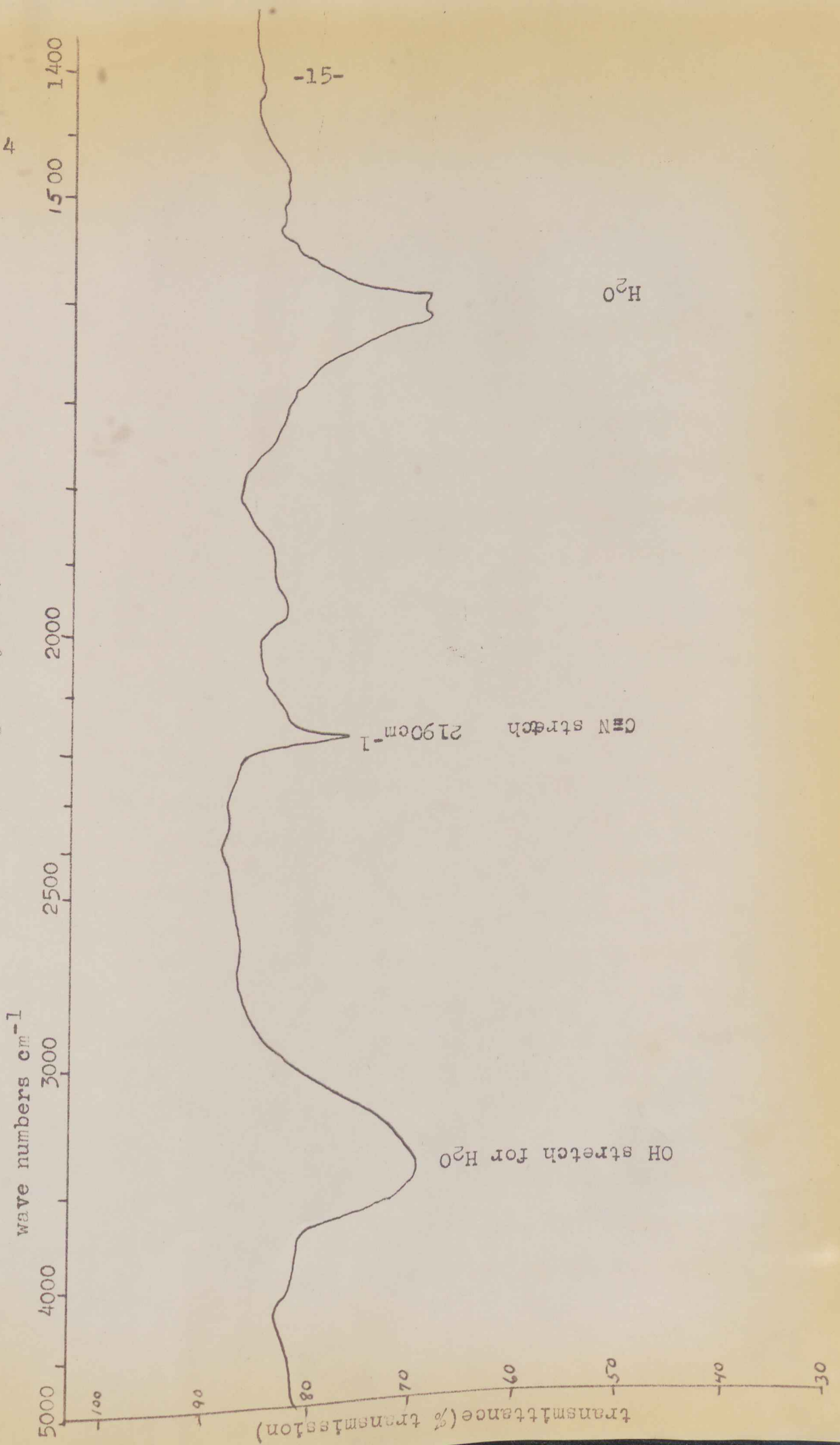## Determination of Cyanide and Water of Crystallization

Both cyanide and the water of crystallization offered greater problems in their quantitative analysis than the other two determinations. Since the other two agreed so well with the theoretical composition of the synthesized salt, it was necessary only to verify the presence of cyanide and water.

Using a Perkin-Elmer Model 210 Infrared Spectrophotometer a single crystal was used to obtain a spectrum in the infrared. The resulting spectrum, figure 4, shows water absorption peaks, and a sharp band at 2190 cm^{-1} due to the cyanide stretching. This compares to 2141 cm^{-1} reported for $KAu(CN)_2$ as a solid[7], and 2146 cm^{-1} for $HAu(CN)_2$ [7].

The transmittance scale is relative to air, the instrument was able to operate by closing down the opening for the control beam of the instrument.

Infrared Spectrum of KAu(CN)$_4$·3/2 H$_2$O

(a single crystal)

Fig 4

wave numbers cm^{-1}

transmittance (% transmission)

C≡N stretch 2190cm^{-1}

OH stretch for H$_2$O

H$_2$O

An Method For the Identification of
Gold Cyanide Ions in Solution

As mentioned before, a spot test for either of the cyanide complexes in the presence of the other would be very convenient. No spot test is available[4] for this type of detection due to the great stability of the cyanide complexes. One test that is of use tests for the presence of gold in solution making no differentiation between the oxidation state or the complexing ligands.

Feigel[4] mentions the use of thermodecomposition of the complex to native gold. The solution in question is sampled by immersion of a small capillary tube and the tube is heated gently to evaporate the liquid. Then the temperature is increased until the tube melts around the remaining gold salt. The salt is decomposed to elemental gold which appears red and is magnified by the glass of the capillary tube which acts as a lens. This test is valid to dilutions of 1:50,000, the red colloid forming if less than one microgram of gold is present in the sample taken. The colloid forms down to 0.05 micrograms in the sample, and above one microgram the resulting gold appears gold in color.

Although the two complexes offer different cyanide stretching frequencies the use of the infrared spectrograph with water solutions was not possible because of the soluble nature of the NaCl sample cells.

The ultra violet spectra, taken on the Beckman DU Spectrophotometer, of $KAu(CN)_2$, $KAu(CN)_4$, and $HAu(CN)_2$ were investigated for a possible significant difference. (Figure 5).

The spectra of $KAu(CN)_2$ and its acid form (formed in the manner described in the determination of potassium) are identical and have a characteristic spectra near the cut off point due to water absorption in the ultra violet. Two peaks were located, 230.0 and 239.5mμ and a shoulder at ca. 225mμ for concentrations below 1×10^{-3}M. The steady rise beginning at about 220mμ is due to the cyanide and water absorptions.

For $KAu(CN)_4$ these peaks are entirley missing, leaving only the cyanide absorption and water absorption below 220mμ. From these results it may be concluded that this complex will not interfere with the $Au(CN)_2^-$ absorption peaks until about 0.002M concentration, when the cyanide absorption band is spread to higher wavelengths by concentration.

The two peaks obtained with $Au(CN)_2^-$ were measured at varying concentrations and a resulting calibration curve was plotted. This (figure 6) revealed negative deviation from Beer's Law. Thus, the $Au(CN)_2^-$ anion can be quantitatively determined in the presence of $Au(CN)_4^-$ within the range indicated in figure 6, if the $Au(CN)_4^-$ concentration is below 0.002M.

The cyanide ion dependence of the peaks was measured

Figure 5

Ultra violet spectrum of $Au(CN)_2^-$
(0.00018M)
and $Au(CN)_4^-$ (0.00185M)

figure 6

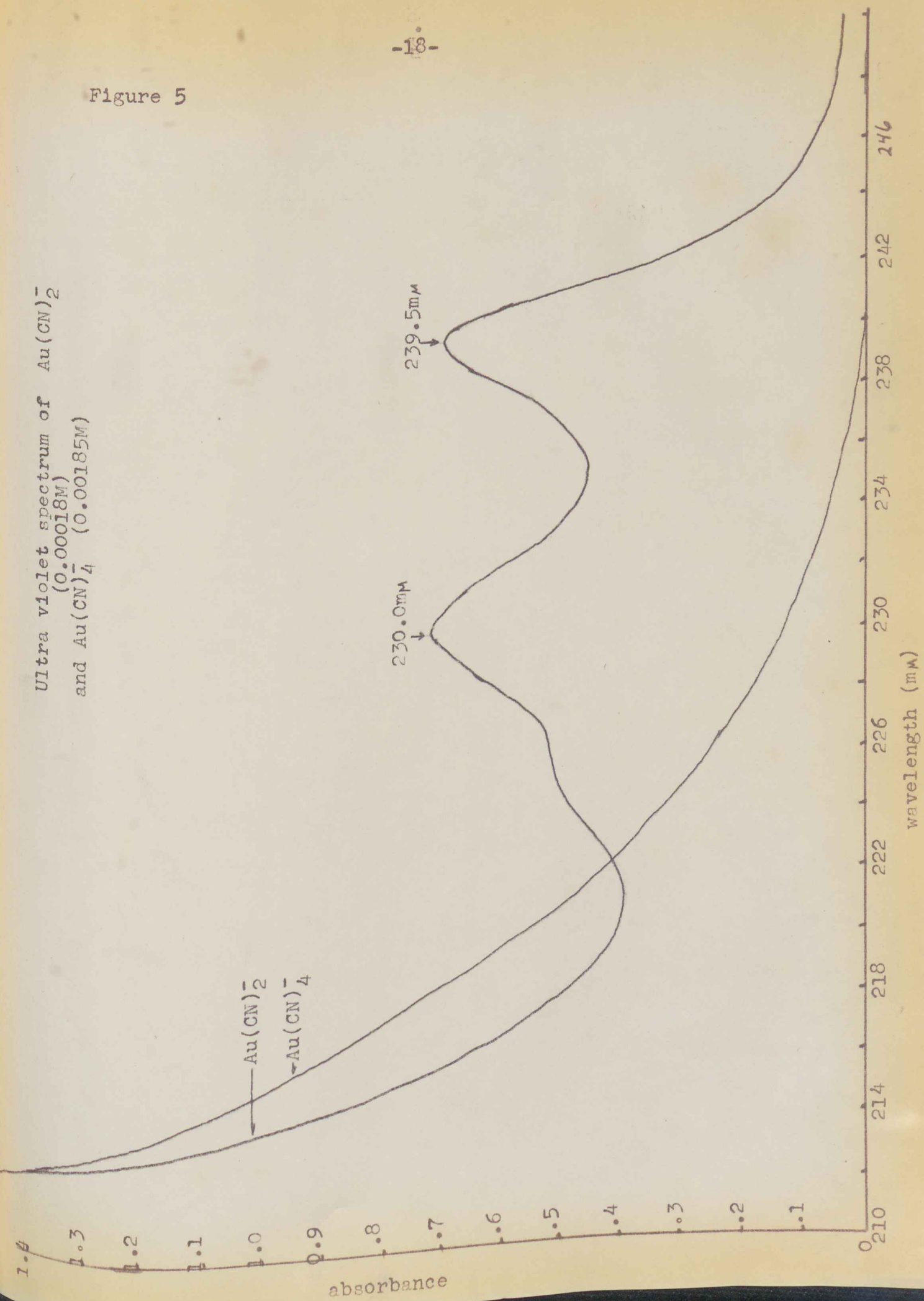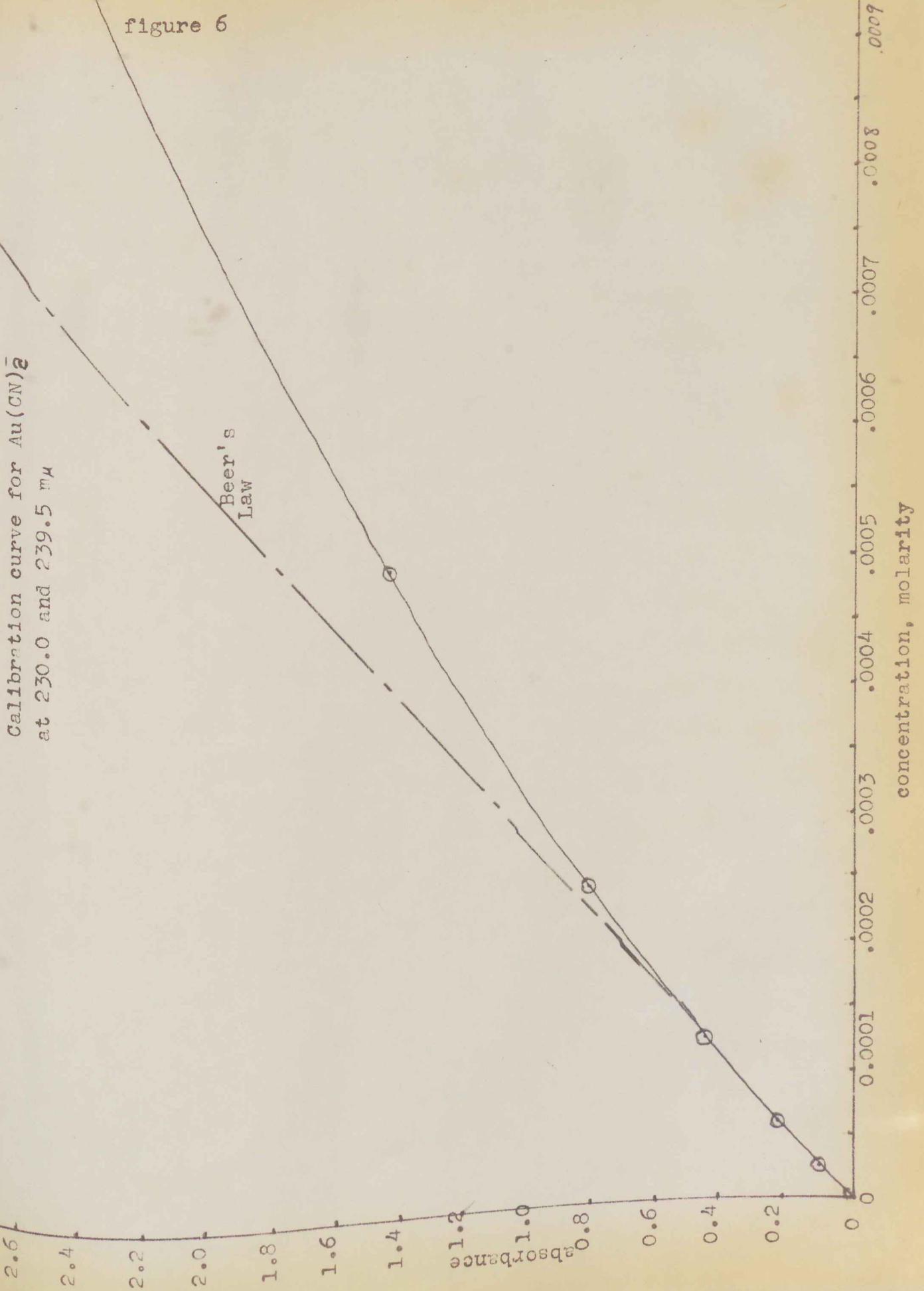Calibration curve for Au(CN)$_2^-$
at 230.0 and 239.5 mμ

Beer's
Law

absorbance

concentration, molarity

by subtracting from the spectra of KAu(CN)$_2$ plus o.1610g

KCN per 25ml water a blank of o.1610g KCN per 25ml water.

A curve identical to the original (figure 5) resulted,

showing independence of CN$^-$.

For the quantitative analysis of both anions in the

presence of each other in aqueous solution the following

procedure is proposed.

First the presence of gold can be detected by the

capillary tube method of thermo decomposition. Then by

proper dilution the sample is examined in the ultra violet

at the 239.5mμ. If only KAu(CN)$_4$ is present there will be

no absorption. Electroplation of the solution after the

addition of KCN will then give the quantity of gold complexed

in the Au(III) oxidation state. If absorption occurres the

amount of gold in the Au(CN)$_2^-$ complex can be determined, and

the electrodeposition will now give the total amount of gold

in both oxidation states. By subtraction the amount in

each oxidation state can be determined.

Attempted Separation of
the Gold Cyanide Complexes

Aveston, Everest, and Wells[1] showed the high affinity Amberlite IRA 400 has for complex cyanides. This resin is a strong base quaternary amine type. With this information available along with suggested elutriants a column was set up to attempt a separation of the two gold cyanides by ion exchange chromatography. The column was essentially the same as that shown for the potassium determination (figure 3) except that the resin was added to a height of about 30cm.

The resin was Amberlite IRA 400 in the chlorine form and a mesh of 20/50. The rate of flow through the column can be controlled by the stopcock, which gave 23 ml per minute as a maximum. The rate is very important and should be slow for the best separation. The column should be fairly long, the mesh small (ca. 100) and the packing should have no captured air. This latter may be avoided by mixing the resin with water before addition to the column, thus allowing for the resin to swell, and any air to escape.

With the column properly set the $Au(CN)_2^-$ and $Au(CN)_4^-$ solutions were added and the column rinsed with water. The effluent was collected in thirty test tubes each holding 5 ml of solution. By the addition of a drop of $AgNO_3$ to each, a colloidal suspension of AgCl was formed. The reaction in the column was the replacement of Cl^- by the gold cyanide

complex anions. Therefore the number of moles of complex added can be checked by coagulatinf the AgCl in the tubes and weighing the precipitate. The main reason for the addition of the AgNO$_3$ to each tube was to find the point at which the amount of Cl$^-$ being eluted reached background, that before the addition of the gold cyanides. Background was reached after 65ml had been collected.

The column at this time contained both complexes ready for the addition of an elutriant. If all worked well the complexes would move down the column at different rates and exit separated. Aveston, Everest, and Wells[1] suggested a HCl-water-acetone elutriant for Au(CN)$_2^-$, but this solution absorbs in the ultra violet and masked the method set up for determination of the two anions.

As a second choice dioxane was substituted for acetone and used as the elutriant. This solution also absorbed in th e ultra violet region, therefore by using a solution of dioxane-water and HCl to set 100% transmittance on the instrument the absorption peak for Au(CN)$_2^-$ was found although shifted from 239.5 to 237.0mμ.

The series of thirty test tubes were filled with effluent after which the column was shut off and each solution was analyzed for Au(CN)$_2^-$. After 190 ml had been collected it was evident that the complex was beginning to exit much more diluted.

Because the column was stopped while each thrity sample series was being analyzed the results are not very revealing. Each time the column had a chance to approach an equilibrium which would upset the separation of the complexes upon the column, if such was progressing.

It is suggested that a column be constructed that can give a continuous flow with a constant pressure so that the separation might be accomplished. A smaller mesh is also recommended as well as other elutriants such as SCN^-. The original acetone-water-HCl solution (90-5-5%) might also be rerun using a different method of detection.

For detection it would be interesting to follow the effluent conductivity as suggested by Samuelson on page 111. [8]

Although the separation wasn't completed, and the solutions weren't tested for the presence of $Au(CN)_4^-$ when $Au(CN)_2^-$ was detected it can be concluded that the resin used will hold both complexes and $Au(CN)_2^-$ can be eluted with a HCl, water, dioxane mixture.

Conclusions

The procedure for the synthesis of $KAu(CN)_4 \cdot 3/2\ H_2O$ can be considered as correct in view of the analysis of the salt. The "false" color present with $AuCl_4^-$ ions has been shown to be due to the absorption of light having an average wavelength to give the color perceived. It is interesting to note that none of the complexes studied, although complexes of transition metals, offer visible color due to absorption peaks.

The electrodeposition of gold from the cyanide complex and the exchange determination of potassium each gave very close agreement with the theoretical composition of $KAu(CN)_4 \cdot 3/2\ H_2O$. Cyanide and water of crystallization were shown to be present by using the infrared spectrum of the salt.

With this method of preparing one of the two oxidation states of gold it is now possible to label the complex for exchange study.

The use of ultra violet spectra of the two complexes shows that this is a very quick method for the determination of $Au(CN)_2^-$ in aqueous solution, with both peaks remaining constant in excess CN^- and independent fo the $Au(CN)_4^-$ complex within limits adjustable by dilution. There is now available a method of quantitative determination for each complex when occurring together in aqueous solution. The determination

of the $Au(CN)_4^-$ complex by electrodeposition is not very convenient, but will give accurate results.

It has been suggested that anion exchange resins will probably bring about a chromatographic separation of the two anions, when properly adjusted. A start was made toward such a separation but difficulty was found in the apparatus which called for refinement.

It is possible to follow the effluent by ultra violet spectra, determining the first gold to be eluted by the capillary method. It might be worthwhile to investigate a different method of following the effluent, such as with conductivity measurements.

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