CHARACTERIZATION OF CHLORIDE COMPLEXES OF NIOBIUM (V)

by

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CHARACTERIZATION OF CHLORIDE COMPLEXES OF NIOBIUM (V)

INTRODUCTION

In recent years interest in niobium has increased tremendously. This has been due largely to two major factors. With the advent of the Atomic Energy Commission and the problems involved in the analysis and separation of niobium in complex mixtures of fission products, it has become necessary to know more about the chemistry of this metal. Another factor in the increased interest in niobium chemistry is the use of the metal in high temperature and corrosion resistant alloys which are becoming very important in the development of jet and rocket engines. Because of the complexity of niobium containing ores, the separation of the niobium from other constituents is very difficult.

Niobium and tantalum are rather unique in their lack of stable water soluble compounds and in the difficulties involved in preparing solutions of them. This and the fact that the two are chemically very similar and occur together results in the great difficulty in separation and analysis of mixtures containing them (17, p.337). Because of this lack of water soluble compounds, early workers have concerned themselves primarily with the preparation and study of water insoluble compounds.

In aqueous solutions which are neutral or slightly acid, niobium and tantalum are hydrolyzed to give hydrated oxides of varying composition and high adsorptive powers. These metals do
not form simple ions and in order to produce water soluble compounds complexing agents must be used (1, p.478). To eliminate non-reproducibility inherent in systems which involve hydrolysis, colloid formation, and coprecipitation, analytical and separative techniques should be based on systems which are ionic in nature.

One of the few systems in which niobium appears to be present in an ionic form, at least over certain concentration ranges, is the solution of niobium in hydrochloric acid. In this the niobium appears to be in the form of an ionic complex at the higher hydrochloric acid concentrations. At lower mineral acid concentrations niobium tends to hydrolyze rapidly. The system involving a solution of niobium in concentrated hydrochloric acid has been used by Kanzelmeyer and Freund (9, pp.1807-9) in developing a method for the spectrophotometric determination of niobium. In this system the absorbance of a chloride complex showing a maximum at 281 m\textmu; is measured. It is apparent then that a more thorough knowledge of the chloride systems of niobium is of value.

Previous Work on Chloride Systems. The anhydrous chlorides of niobium (V) are quite well known. These are the pentachloride (\textit{\textbf{NbCl}}_5) and the oxychloride (\textit{\textbf{NbOCl}}_3). Both of these materials are made by chlorination procedures. Several methods are available for preparing these compounds starting either with niobium metal or with niobium pentoxide and a reducing agent. These may be chlorinated either with chlorine or some volatile compound containing chlorine
that will act as a chlorinating agent. When either niobium pentachloride or niobium oxychloride is put in water immediate and complete hydrolysis takes place whereas they dissolve in hydrochloric acid of fairly high concentration. This has been one method that has been used to produce hydrochloric acid solutions of niobium.

Renz (16, p.103) reported the preparation of a compound with the formula NbCl₅·C₅H₅NHC₁. This was prepared from a concentrated hydrochloric acid solution of niobium. The basis for assigning the above formula was an analysis for carbon, hydrogen, and nitrogen. Weinland and Storz (24, p.223) later proved this analysis to be in error. Smith and Hall (20, p.204) reported that niobium pentachloride was soluble in carbon tetrachloride and inferred that "double chlorides" could be prepared in this solvent but gave no examples. Several later workers have attempted this but have not succeeded.

In solutions which were high in niobium and saturated with hydrochloric acid, Weinland and Storz (23, pp.3056-9) (24, pp.223-43) reported the preparation of the salts: NbOCl₃·2CsCl, NbOCl₃·2RbCl, NbOCl₃·2NH₄Cl, NbOCl₃·C₉H₇NHC₁, and NbOCl₃·C₅H₅NHC₁. By using alcoholic solutions of niobium oxychloride and containing hydrochloric acid, they claim to have prepared NbOCl₃·2C₉H₇NHC₁, NbOCl₃·C₅H₅NHC₁·H₂O, and NbOCl₃·2C₂H₅NHC₁·H₂O. These compounds were reported to be moderately stable in dry air, and their formulas were determined by precipitating them from solutions, filtering out of solution, drying and analyzing for niobium;
chloride; and nitrogen, cesium, or rubidium with other constituents determined by difference or valence requirements.

Kraus and Moore studied the system of niobium in hydrochloric-hydrofluoric acid mixtures using anion exchange resins and postulated that in this media there are species present "with a probable negative charge of minus two or greater" (10, p.3855). They did not however state their reasons for believing this to be true. They made further studies in this system in an attempt to establish the fluoride dependence of the species present (11, pp.9-13) (12, pp.2900-2) and from this they postulated the presence of three species of niobium in the HCl-HF systems in which the hydrochloric acid was nine molar. These species differ by two fluoride atoms each. They did not establish the formula of any one species but stated that two of them were probably oxygenated. This system is complicated by the use of a mixed HCl-HF solvent, and due to the very strong complexing power of fluoride it is probable that chloride does not enter into the complexes except at zero or extremely low hydrofluoric acid concentration.

Gruben and Gruben (5, pp.771-80) measured electrode potentials in Nb(III)-Nb(V) systems in hydrochloric acid. In order to obtain constant values of $E^0$ from the Nernst equation, they postulated the ion $\text{NbO}^{4+}$ under these conditions. When they used the equation

$$\text{Nb}^{4+} + \text{H}_2\text{O} \rightarrow \text{NbO}^{4+} + 2\text{H}^+ + 2\text{e}^-$$

and substituted into the Nernst equation values for the observed
EMF, hydrogen ion activity, and values for Nb(III) and Nb(V), they obtained nearly constant $E^\circ$ values. It might be pointed out that this equation may be changed to

$$\text{NbX}_2^{2-n} + H_2O \rightarrow \text{NbOX}_2^{2-n} + 2H^+ + 2e^- \text{ or to}$$

$$\text{NbX}_2^{2-n} + 2H_2O \rightarrow \text{Nb(OH)}_2\text{X}_2^{2-n} + 2H^+ + 2e^-$$

where $X$ is any complexing anion of minus one charge. This change could be made without affecting the constancy of the $E^\circ$ value as obtained from the Nernst equation.

Elson (3) studied the absorption spectra in the range 210-400 $\text{m} \mu$ for solutions of niobium in perchloric acid of varying hydrogen ion and chloride ion concentration. He reported finding peaks at 212, 219, and 280 $\text{m} \mu$ in low acid levels and at 261, 280, and 230 $\text{m} \mu$ at higher acid levels to which he qualitatively assigned the species $\text{NbO}_2\text{Cl}$ or $\text{Nb(OH)}_4\text{Cl}$, $\text{NbO}_2\text{Cl}_2$ or $\text{Nb(OH)}_4\text{Cl}_2$, and $\text{NbO}_2\text{Cl}_3$ or $\text{Nb(OH)}_4\text{Cl}_2$ respectively in low acid levels and in higher acid levels $\text{NbO}_2\text{Cl}^{++}$ or $\text{Nb(OH)}_2\text{Cl}^{++}$, $\text{NbOCl}_2^+$ or $\text{Nb(OH)}_2\text{Cl}_2^+$, and $\text{NbOCl}_3$ or $\text{Nb(OH)}_2\text{Cl}_3$ respectively. No account was taken of the fact that a single species might show an adsorption curve having more than one peak. Also the lack of anionic species in high acid and high chloride appears quite unreasonable in view of anion exchange data on niobium in various hydrochloric acid concentrations (7, pp.4474-5).

Wernet (25, pp.213-37) in studies on possible methods for the
precipitation separation of mixtures of niobium, tantalum, and
titanium proposed the ions NbCl$_5^-$, NbCl$_7^-$ or NbOCl$_5^-$ in solution
in concentrated aqueous hydrochloric acid. No attempt was made to
prove these.

Ellenburg, Leddicotte, and Moore (2, pp.1045-7) extracted
niobium in the presence of tantalum with chloroform-tribenzylamine
from hydrochloric acid solutions above six molar. The tantalum
did not extract and this was qualitatively attributed to the
presence of complexes of the type HNbOCl$_4^-$ or H$_2$NbOCl$_5^-$ and to the
lack of such complexes in the case of the tantalum.

By means of batch equilibrium experiments, Huffman, Iddings,
and Lilly (7, pp.4474-5) determined the distribution coefficients
of niobium and tantalum in various hydrochloric acid concentrations
on the anion exchange resin Dowex-2. In solutions 9-12 molar in
hydrochloric acid, the distribution coefficient is almost constant
at a value of about 1200. In this the distribution coefficient is
defined as

$$K_D = \frac{M_r}{M_o} \times \frac{\text{volume of solution}}{\text{mass of resin}}$$

where $M_r$ = fraction of niobium on the resin and $M_o$ = fraction of
niobium in the liquid. Below about nine molar hydrochloric acid
this distribution coefficient drops off rapidly to a value of about
20 in the range four to six molar in hydrochloric acid. At lower
acid levels this value slowly increases again. It was reported
that on the low acid side (below about six molar), equilibrium
was established very slowly between the solution and the resin and that normal elution characteristics were not followed but that instead the niobium was very rapidly washed off the resin.

It is apparent that the marked decrease of the distribution coefficient in the range 6–9 molar hydrochloric acid must indicate a decrease in the negative charge of the niobium species involved. The anomalous behavior of the exchange below six molar hydrochloric acid might be taken to indicate the absorption of colloidal "anions" such as colloidal "anions" of niobic acid. Such species could be expected to yield rather high absorption on the resin yet rather weak binding to the resin. This would be due to the fact that an entire colloidal particle could be held by one or two exchange points yet the binding would be very weak due to the size of the so-called "anion".

In later work these authors (6, pp. 471–5) found that if carrier free niobium was absorbed on an anion exchange column from ten molar hydrochloric acid and eluted with seven molar hydrochloric acid, three peaks were obtained in the elution curve. A repeat of this experiment also yielded three peaks but the shapes and relative heights were different. This was explained on the basis of moderately slow establishment of equilibrium between species. It is quite possible here that overlap of two peaks can produce an intermediate peak. The interpretation of these observations is complicated by the mixing effect between the ten molar and seven molar hydrochloric acid and also by the extremely low
level of niobium used.

Schubert and Richter (18, pp. 376-85) used cation exchange resins to study niobium and zirconium in solutions which were one molar in hydrochloric acid and with the addition of various complexing agents. They found that in one molar hydrochloric acid the distribution coefficient does not follow the behavior expected for cationic exchange when the mass of resin or volume of solution is varied. Instead it follows the behavior to be expected for the adsorption of a colloid on the surface of a substance with large surface area. From this they conclude that niobium in one molar hydrochloric acid is present mainly as a colloid.

Kanzelmeyer (8) (also Kanzelmeyer and Freund (9, pp. 1907-9)) found that in solutions high in both hydrogen ion and chloride ion concentration niobium shows a very distinctive spectrophotometric absorption peak at 281 mp. In hydrochloric acid this peak is found to decrease slowly in the concentration range from twelve molar down to about ten molar, and rapidly below ten molar having disappeared completely at six molar. This is in the range in which a rapid decrease was found by Huffman, Iddings, and Lilly, in the anion exchange distribution coefficient. This and electro-migration work by Kanzelmeyer indicate that the species responsible for this absorption at 281 mp is an anion.

Kanzelmeyer also measured the absorption curves of niobium in solutions containing mixtures of perchloric and hydrochloric acid in which the hydrogen ion was kept at 10.5 molar and the
chloride was varied. Another set of curves was obtained for 10.5 molar chloride in which hydrogen ion was varied. Both sets of curves were obtained with constant niobium level. The curve obtained for the highest chloride ion and hydrogen ion activity was considered to represent a pure species. When the contribution of this species absorbing at 281 m\(\mu\) was subtracted from the curves in the manner of that used by Newman (14, pp.2611-5) for the antimony-hydrochloric acid system, the resulting curves obtained represent all other species present. This procedure gave resulting curves in the case of hydrogen ion variation and in the case of hydrochloric acid variation which show no pronounced peaks above 210 m\(\mu\) but rather a gradual decrease in absorbance with increasing wavelength. The resulting curves in the case of chloride ion variation show a distinct absorption peak at 260 m\(\mu\) in about the range 0.02 to 0.3 molar chloride ion. At lower chloride ion concentration the resulting curves are similar to the resulting curves for hydrogen ion variation.

The general equation \(\text{II} + n\text{Cl}^- + m\text{H}^+ \rightleftharpoons \text{I}\) was set up for the reaction of a species \(\text{II}\) with hydrogen ion and chloride ion to produce species \(\text{I}\) absorbing at 281 m\(\mu\). The logarithm of the equilibrium constant equation would be:

\[
\log K_c = \log a_\text{I} - \log a_\text{II} - m \log a_{\text{H}^+} - n \log a_{\text{Cl}^-}
\]

Assuming the activity coefficients of the niobium species to be nearly constant, a plot of \(\log\) absorbance at 281 m\(\mu\) was made versus
chloride ion activity at constant hydrogen ion concentration, and a plot of log absorbance at 281 μm was made versus hydrogen ion activity at constant chloride ion concentration in order to determine values for n and m. The absorbance at 281 μm was first corrected for the absorbance of the other species at this wavelength.

Examination of the logarithmic equation above reveals that this is not the proper method of plotting since both species I and species II vary with hydrogen ion and chloride ion activity. Also it must be pointed out that species II in the chloride ion variation is not necessarily the same as species II in the hydrogen ion variation.

If we hold hydrogen ion constant and vary chloride ion, the equilibrium equation becomes:

$$\log \text{constant} = \log a_I - \log a_{II} - n \log a_{Cl^-}$$

Since the total niobium was known and the corrected absorbance at 281 μm is a measure of species I, a plot of log a_I - log a_{II} versus log a_{Cl^-} can be made which will have a slope of n. When this was done a value of n = 0.95 was obtained. Applying this same procedure to hydrogen ion variation, a value of m = 1.24 is obtained. This could indicate that more than two species were present in the case of the hydrogen ion variation. This type of investigation only gives evidence of the relation between species and does not indicate the true nature of any of the species.
The Problem. As is seen in the previous discussion, little is actually known about the nature of niobium chloride complexes in aqueous solution. Some of the previous work has indicated possible species. Some rather valuable data have been obtained which do not prove any certain species but narrow the field of possibilities. Other work has shown the relationship between species. None of the work, however, has presented any definite proof for the existence of any particular species or for the number of species which may be present over a varying range of hydrogen ion and chloride ion concentration.

It is then the purpose of this thesis to characterize, in so far as possible, the nature of the various chloride systems of niobium, and to identify the complexes involved. Due to the nature of these systems spectrophotometric methods offer by far the greatest possibility as a method for studying the species present. This is then a continuation of the work by Kanzelmeyer (8) with the aim of identifying and characterizing the chloride containing species involved.
Apparatus. All absorbance measurements were made by use of a Beckman Model DU Spectrophotometer. For all measurements below 340 μm a hydrogen discharge lamp was used as the source of radiation and for measurements above 340 μm a tungsten lamp was used. The absorbance measurements were made using matched 1.00 cm. silica cells unless otherwise specifically stated. A reagent blank was used for all measurements and net absorbances were recorded. Wherever there was possibility that the blank might be different than the solution, this fact was noted.

Cesium Chloride. This was obtained from two sources. The first belonged to the U. S. Bureau of Mines in Albany, Oregon. It had been used by L. S. Leonard and was known to contain organic acid-base indicators as well as other possible impurities such as calcium and iron. Organic material was removed by fusing the compound for several minutes at the full heat of a Meker burner. The compound was then dissolved and ammonium hydroxide and ammonium carbonate were added to remove possible cationic impurities as hydroxides or carbonates. The solution was then passed through a chloride form anion exchange column (IRA 400) and was evaporated. It was found that organic material from the resin had been picked up by the solution so the cesium chloride was fused twice dissolving, filtering, and evaporating it each time. Cesium compounds recovered
during the course of the work were treated in similar manner. Eimer and Amend C.P. cesium chloride was also used.

**Hydrogen Chloride Gas.** During the earlier part of the work this was prepared by allowing concentrated sulfuric acid to drop on a mixture of calcium chloride and concentrated aqueous hydrochloric acid. Later Matheson compressed anhydrous hydrogen chloride was used.

**Niobium Pentoxide.** The pure compound was obtained as "Columbium Pentoxide" from A. D. MacKay, 198 Broadway, New York, 7, New York. A spectrographic analysis (8, p.127) shows no impurity present to greater than 0.1%.

**Niobium Solutions.** Niobium solutions were made up according to the procedure of Wernet (25, pp.213-37). A ratio of one gram of niobium pentoxide to three grams of potassium pyrosulfate was fused at a low temperature to give a clear melt. This was cooled, ground to a fine powder, and added to 1:1 sulfuric acid with constant stirring. A milky solution resulted which was neutralized with 25% ammonium hydroxide in an ice bath. The resulting precipitate was washed by centrifugation until peptization prevented further washing without considerable loss.

The freshly precipitated hydrous oxide then was shaken up in cold concentrated hydrochloric acid and placed in an ice bath. Hydrogen chloride was bubbled through the solution at a rapid rate.
until saturation was reached. Most of the hydrated oxide went into solution as soon as the solution was saturated at 0°C, but considerable cloudiness remained which disappeared after passing hydrogen chloride through at a slow rate for about two to three days. At this time any residual insoluble material was removed by centrifugation or by pressure filtering on sintered glass.

The solution was analyzed by allowing a portion to come to room temperature, pipetting an aliquot, diluting with water, neutralizing with NH₄OH, filtering, igniting and weighing as niobium pentoxide. The highest concentration obtained was about 20 grams of niobium per liter. These solutions are stable at room temperature for a few hours, but on longer standing about half of the niobium precipitates out. If this precipitate is removed, the solution is then stable at room temperature.

**Organic Solvents.** Diethyl ether was reagent grade and was dried and stored over freshly cut sodium metal.

1,4-Dioxane was obtained from Matheson Coleman and Bell, Inc. It was dried and peroxides were removed by refluxing for 48 hours over sodium metal. It was then distilled discarding the first and last fractions and stored over freshly cut sodium metal.

All other chemicals used were reagent grade.
Methods. Since the species absorbing at 281 m\(\mu\) is by far the most prominent of all possible species as far as a characteristic absorption peak is concerned and since it is the basis of the previously mentioned spectrophotometric method of analysis for niobium, it was considered to be the most logical species to study first. The fact that niobium is much more soluble in the hydrogen ion and chloride ion levels in which it shows the 281 m\(\mu\) peak shows that it is probably in the form of an ionic complex in this range.

Previously mentioned anion exchange work by Huffman, Iddings, and Lilly and electromigration work by Kanzelmeyer indicate that the 281 m\(\mu\) species is an anion. An experiment was designed to further prove this. A solution of niobium in 11.9 molar hydrochloric acid showing the 281 m\(\mu\) peak was passed through a 30 cm column of Amberlite IRA 400 anion exchange resin. The resin had first been washed with 11.9 molar hydrochloric acid and the last of this wash liquid saved as a spectrophotometric blank. It was found that the absorbance of the niobium solution after passing through the column was essentially zero at all wavelengths indicating complete removal of the 281 m\(\mu\) species. The same type of experiment was repeated using the cation exchange resin Dowex 50. The absorption curve of the resulting solution indicated absolutely no removal of niobium. This then was taken as proof that the species absorbing at 281 m\(\mu\) is an anion.
A most promising method of identification of a species in solution is to isolate a compound which can be analyzed and compare its absorption spectrum to that of the solution containing the species. This is usually done by one of two methods. The most important of these is to dissolve the isolated compound in an inert solvent, usually organic, and obtain the spectrophotometric curve of the solution. The limitation of the method is that a solvent must be found which will not react with the compound and in which the compound is sufficiently soluble. Also the solvent must not be opaque to light of the desired wavelength. The other method is to obtain the spectrophotometric curve of a thin film of the compound. In order to lend itself to this treatment, the compound must have a low melting point and be stable to slightly above its melting point.

Both of these methods were used by Friedman (4, pp.5-10) in showing that ferric iron exists in concentrated hydrochloric acid solution as the ion FeCl₄⁻. In doing this he showed that the spectrophotometric curves for solid films of KFeCl₄, solutions of KFeCl₄ in organic solvents, and solutions of FeCl₃ in concentrated hydrochloric acid were the same. This procedure was also used by Neuman (14, pp.2611-5) to show that the SbCl₅ ion was the species present in concentrated hydrochloric acid solutions of antimony (V). The compounds used here were H₂OＳbCl₆·H₂O and MgSbCl₇. The MgSbCl₇ had been shown independently (19, p.300) to contain the SbCl₅ ion. The spectrophotometric curves of solutions of these were shown to
be the same as spectrophotometric curves of solutions of SbCl5 in concentrated hydrochloric acid.

The procedure was then to attempt to prepare a niobium compound which could be analyzed and which would show an absorption curve similar to the curve of the 281 μ species. As was previously mentioned Weinland and Storz (23, pp.3056-9) (24, pp.223-43) reported chloride compounds with cesium, rubidium, ammonium, pyridine, and quinoline. Pyridine and quinoline were eliminated since they absorb in the wavelength region desired. Wernet (25, pp.213-37) attempted to prepare an ammonium compound and was not successful. Since the cesium compound had been reported originally to be the most stable, it was selected for this work.

Cesium Compound. This compound was made under four different conditions. This was done to show that it was the 281 μ species and not some other species in equilibrium with it that was causing the reaction with cesium chloride. Use of the different conditions might possibly produce other compounds than that which had been reported. All four of these involve the mixing of a highly concentrated solution of niobium in hydrochloric acid with a solution of cesium chloride in hydrochloric acid.

Batch number 1 was prepared by the addition of 1.5 grams of cesium chloride dissolved in 5 ml. of hydrochloric acid saturated with hydrogen chloride gas at 0°C. to 30 ml. of niobium solution containing 0.6 grams of niobium also saturated with hydrogen chloride gas at 0°C. An immediate dense, light yellow precipitate formed,
and hydrogen chloride gas was passed through the mixture for ten minutes in an ice bath. The solid compound was separated by suction filtering on a medium porosity sintered glass filtering crucible. It was washed with hydrochloric acid saturated with hydrogen chloride at 0°C. and excess liquid was drawn off. The moist compound was transferred to a small weighing bottle and dried in a desiccator over anhydrous magnesium perchlorate. The filtrate and washings were found to contain both cesium and niobium indicating appreciable solubility of the compound.

Batch number 2 was prepared in exactly the same manner except that the order of mixing was reversed. The niobium solution was added to the cesium chloride solution.

Batch number 3 was made from a niobium solution which had been kept at 45°C. for one hour and which was saturated with hydrogen chloride at 45°C. 1.0 grams of cesium chloride in 5 ml. of hydrochloric acid saturated at 45°C. was added to 20 ml. of this solution. The precipitate formed slightly more slowly than at the lower temperature and settled out more rapidly. The precipitate was visibly crystalline. The compound was washed in this case with 11.8 molar hydrochloric acid. The yield was lower than at 0°C. indicating greater solubility.

Batch number 4 was prepared in a similar manner from hydrochloric acid solutions saturated with hydrogen chloride at -20°C. At this temperature the solution was in equilibrium with frozen hydrochloric acid. The temperature was maintained by use of a
dry ice-acetone mixture and by keeping the system in contact with frozen solution. The material was filtered out and washed with hydrochloric acid saturated with hydrogen chloride at -20°C, and in contact with the frozen acid. The compound was drawn moderately dry, transferred to a weighing bottle, and dried over magnesium perchlorate. This was the highest possible hydrochloric acid concentration obtainable at atmospheric pressure. This batch was probably the most impure of the four due to the difficulties involved in filtering and washing at this temperature.

An attempt was made to prepare a similar compound using another cation. For this LiCl, NaCl, KCl, CaCl₂, BaCl₂ and NH₄Cl were used. No insoluble compound was formed with any of these. Furthermore, KCl, NaCl, and BaCl₂ were too insoluble in concentrated hydrochloric acid to be of value.

The analysis of the compound was carried out in the following manner. Niobium and cesium were run on the same samples. The sample was dissolved rapidly in 100 ml. of cold water resulting in a solution which was only slightly cloudy. This was then brought to boiling and adjusted to neutral with hydrochloric acid after first making basic with ammonium hydroxide. The resulting hydrated niobium pentoxide was filtered on ashless filter paper, washed with 1% NH₄Cl, ignited in a platinum crucible at full heat of a Meker burner to constant weight, and weighed as niobium pentoxide. The filtrate was made acid with hydrochloric acid, 10 ml. of concentrated nitric acid was added, and the solution was evaporated.
to dryness to destroy ammonium chloride. Five ml. of 70% perchloric acid was added and fumed to dryness. The resulting cesium perchlorate was dissolved, evaporated to dryness, dried at 350°C. (21, pp. 774-8) and weighed as cesium perchlorate.

In the chloride determination separate samples were used. The compound was dissolved in cold water and an excess of standard silver nitrate added. The solution was then heated to complete the hydrolysis and the determination completed by the standard Volhard method.

The results of the analysis along with the theoretical values for several possible compounds are listed in Table I. A separate average was calculated for batches 1, 2, and 3 because number 4 was much more difficult to wash and therefore less pure. It is seen from the table that the results of the analysis correspond most closely to Cs$_2$NbOCl$_5$. This is in agreement with the results reported by Weinland and Storz. It must be pointed out that the compound was probably somewhat impure because of its rapid precipitation during formation. Also in the analysis of the compound some error is probably introduced by trapping and coprecipitation in the precipitation of the hydrated niobium pentoxide. For these reasons it is difficult to be certain whether the compound is Cs$_2$NbOCl$_5$ or Cs$_2$Nb(OH)$_2$Cl$_5$.

An attempt was made to find a solvent for this compound which would not be opaque to the radiation at which the niobium species in concentrated hydrochloric acid shows its characteristic
### TABLE I

**ANALYSIS OF CESIUM-NIOBIUM-CHLORIDE COMPOUND**

<table>
<thead>
<tr>
<th>Batch Number</th>
<th>% Cs</th>
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<td></td>
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<tr>
<td>3</td>
<td>47.49</td>
<td>17.12</td>
<td>31.70</td>
</tr>
<tr>
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<td>46.03</td>
<td>17.75</td>
<td>32.76</td>
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<tr>
<td></td>
<td>45.72</td>
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<td>32.63</td>
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<tr>
<td></td>
<td>45.09</td>
<td>17.63</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>46.60</td>
<td>17.44</td>
<td>32.12</td>
</tr>
<tr>
<td>Average (batch 1, 2, and 3)</td>
<td>47.34</td>
<td>17.31</td>
<td>31.83</td>
</tr>
<tr>
<td>Reported by Weinland and Storz</td>
<td>48.0</td>
<td>17.2</td>
<td>32.3</td>
</tr>
<tr>
<td>Theoretical</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs$_2$NbOCl$_5$</td>
<td>48.16</td>
<td>16.83</td>
<td>32.12</td>
</tr>
<tr>
<td>Cs$_2$Nb(OH)$_2$Cl$_5$</td>
<td>46.63</td>
<td>16.30</td>
<td>31.10</td>
</tr>
<tr>
<td>CsNb(OH)$_2$Cl$_4$</td>
<td>33.1</td>
<td>23.1</td>
<td>35.3</td>
</tr>
<tr>
<td>CsNbCl$_6$</td>
<td>30.3</td>
<td>21.1</td>
<td>48.5</td>
</tr>
</tbody>
</table>
absorption curve. To be of any value this solvent must dissolve enough of the compound to show the characteristic absorption curve and it must also not react with the compound. To meet these prerequisites, the solvent should be non-polar and should preferably be an organic compound such as ether.

Since only a very low solubility would be required to produce a spectrophotometric curve, the absorption at several wavelengths in the ultraviolet including 281 mp of a solution which had been shaken with the compound was taken as a qualitative measure of its solubility. Organic solvents tried and found by this method either not to dissolve the compound or to be opaque to ultraviolet light were diethyl ether, dibutyl ether, carbon tetrachloride, chloroform, tributyl phosphate, diisopropyl ketone, diethyl ketone, butyraldehyde, acetic acid, 1,4-dioxane, ethyl acetate, and isobutyl alcohol. Acetic acid appeared to react with the compound giving a white suspension. Various other organic solvents were tried in which the compound was not visibly soluble. In general, then, no organic solvent was found in which even a trace of solubility was detectable. The compound was found to decompose below its melting point so that there was no possibility of obtaining an absorption curve for a solid film.

Since there appears to be no non-aqueous solvents for this compound, there is one alternative providing that equilibrium is established slowly between species. The possibility is to dissolve the compound in an aqueous solution in which niobium would
not be stable in the form of the species showing a maximum at 281 μ
or at least the major portion of it would not be in this form. If
equilibrium between species is established slowly, it should be
possible to observe the decay of the spectrophotometric curve of
the solid compound in aqueous solution and from this obtain an
idea of the appearance of the curve for this compound.

The most obvious possibility of this method is to dissolve the
compound in various concentrations of hydrochloric acid and to
observe the spectrophotometric curve as soon as possible. This
was done with 12, 10, 8, 6, and 4 molar solutions of hydrochloric
acid. In every case the spectrophotometric curve obtained was the
same as would be expected of a simple niobium solution in that
concentration of acid. The curves did not change by more than
about one percent on standing for four hours. The time interval
between dissolving and obtaining the first absorbance value was
in the neighborhood of one minute. From this it is seen that in
hydrochloric acid the equilibrium between species is quite rapid
at least for acid levels above four molar.

Another possibility is that the compound could be dissolved
in perchloric acid solution and the change of the absorbance curves
with time could be measured. Above about six molar perchloric
acid the solvent reacted with the compound liberating hydrogen
chloride. Below six molar acid the curves immediately after mixing
showed no maxima in the range of the instrument but rather an
increasing absorbance with decreasing wavelength.
Further Studies of Niobium in Concentrated Hydrochloric Acid.

At this point in the work it was decided that there was little chance of obtaining an absorption curve for the cesium compound. It was then considered important to show that the 261 μm species was the predominant species in solutions from which the cesium compound was precipitated. It is to be noted that the niobium concentration in the solutions from which the compound was prepared were in the order of 0.02 g. Nb/ml, whereas the solutions in which spectrophotometric studies had been made and in which the 261 μm peak had been observed were in the range 1-10 μg. Nb/ml. This corresponds to a concentration factor of 2000. It is apparent that in order to obtain a spectrophotometric curve for such a concentrated solution a cell with an extremely short path length must be used.

A cell holder was built which would hold two flat quartz plates clamped together. Since the quartz plates obtainable were not matched and were not extremely uniform, it was necessary to use the same two plates clamped in the same position for both the blank and the niobium solution. The instrument and the hydrogen lamp were allowed to warm up for one hour to insure as stable a condition as possible. A drop of 11.9 molar hydrochloric acid was placed between the two plates as a blank and the slit widths required for zero absorbance were measured at the various wavelengths. The drop of hydrochloric acid was then replaced with the concentrated niobium solution and the absorbance values were immediately measured using
the slit widths just determined with the blank. The absorption curve produced appears in Figure 1 along with a curve for a solution of approximately 8 µg. Nb/ml. in 11.9 molar hydrochloric acid. Absorbance was plotted on a logarithmic scale since the shapes of the curves are the points of interest.

It is seen from the plot that the general shapes of the curves are very similar. Both curves show a maximum at 281 µm and a minimum at about 250 µm. The fact that the two curves are not exactly the same shape can be attributed to two factors. The first of these is that the method of obtaining the absorption curve of a thin film between two plates is not highly accurate especially at shorter wavelengths where light scattering becomes an important factor and greater differences between slit widths from one wavelength to the other are required. The other factor is that it is difficult to expect Beer's law to hold exactly over such a great concentration range. It is also probable that Beer's law would not be followed to the same degree at different wavelengths. This curve then is taken as proof that the same species is present in both the high and low niobium levels in concentrated hydrochloric acid.

Since there is little change in the absorption curve for niobium from about ten to twelve molar in hydrochloric acid, it had been assumed that all the niobium was present in the form of one species in twelve molar hydrochloric acid. In order to further establish this, or to see if other species appeared at higher
hydrochloric acid concentration, the absorption curve of a more concentrated hydrochloric acid solution was obtained. The first attempt at this was made by saturating the solution and blank at 0°C and keeping them cool in the cell holder with dry ice. So much fogging of the cell faces resulted that reproducible results could not be obtained. By allowing the room temperature to drop to a low value it was possible to obtain the absorption curve of a solution of niobium 13.4 molar in hydrochloric acid. The hydrochloric acid was determined by titration on a sample removed from the cell after the absorption measurements had been made. The curve is shown in Figure 1 and comparison with the curve for 11.9 molar hydrochloric acid in which the niobium content was the same shows that no change in the nature of the niobium occurred in going from 11.9 to 13.4 molar.
FIGURE 1
ABSORPTION OF NIOBIUM SOLUTIONS IN CONCENTRATED HCl

- 0.02 g. Nb/ml.
- 11.9 M HCl

- 7.85 µg. Nb/ml.
- 11.9 M HCl

- 13.4 M HCl

Graph showing absorbance vs. wavelength for niobium solutions in concentrated HCl.
Quaternary Ammonium Compounds. Since no solvent could be found for the cesium compound, an attempt was made to find a cation which would produce an insoluble salt with the niobium anion and which would be expected to promote solubility in organic solvents. To promote solubility in organic solvents the possibilities are limited almost entirely to organic cations. In order to be of value in this respect, the cation must not absorb in the ultraviolet region at the concentrations to be used. Also it must act as a simple ion and not as a complexing agent, and it should be the cation of a strong base which forms as much as possible quite ionic salts. The quaternary ammonium cations fit all these requirements far better than any other organic cations. Both water solubility and organic solvent solubility can be varied by changing the length of the aliphatic chains present in these quaternary amines.

For this purpose tetramethyl ammonium chloride was first used. This compound was dissolved in 0°C. saturated hydrochloric acid and added to a niobium solution also saturated with hydrogen chloride at 0°C. No precipitate appeared so more of the tetramethyl ammonium chloride was added in the solid form. When a considerable excess had been added a precipitate slowly formed. This was filtered and washed with a small amount of concentrated hydrochloric acid in which a large percent of it dissolved. Only a small amount was prepared and no further work was done with it.

In order to attempt to decrease the water solubility and at
the same time probably enhance the solubility in organic solvents, tetraethyl ammonium chloride was used next. To 25 ml. of the concentrated niobium solution saturated with hydrogen chloride at 0°C. was added 1.0 grams of tetraethyl ammonium chloride dissolved in the minimum required amount of hydrochloric acid saturated with hydrogen chloride at 0°C. A white solid slowly separated out in the form of fine white crystals. The solution was allowed to stand in an ice bath for 30 minutes. The solid was then filtered out on a medium porosity sintered glass crucible and washed thoroughly with hydrochloric acid saturated with hydrogen chloride at 0°C. It was then dried over magnesium perchlorate. It appears to be much less soluble than the tetramethyl compound and is much less dense than the cesium compound.

The compound was analyzed for niobium, chloride, and nitrogen. Since the compound contained no metals other than niobium, it was possible to analyze for niobium by merely moistening the compound in a crucible, drying, igniting, and weighing as niobium pentoxide. One run was made by hydrolyzing, filtering, and igniting in the same manner as for the cesium compound. The same value was obtained by both methods. The chloride was determined by the Volhard titration in the same manner as for the cesium compound. The nitrogen was determined by the micro-Dumas method (15, pp.79-99). The results of the analysis and the theoretical values for several possible compounds are given in Table II. It is important to note that in this compound a much more accurate analysis can be obtained
than in the case of the cesium compound since no other metal is present which could be trapped or coprecipitated with the hydrous niobium pentoxide. The completely ignited oxide should then be almost completely free of impurities. Also since the compound formed much more slowly than the cesium compound it probably contains less impurity.

TABLE II
ANALYSIS OF TETRAETHYL AMMONIUM COMPOUND

<table>
<thead>
<tr>
<th></th>
<th>% Nb</th>
<th>% Cl</th>
<th>% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>23.66</td>
<td>35.03</td>
<td>3.40</td>
</tr>
<tr>
<td></td>
<td>23.62</td>
<td>35.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>23.51</td>
<td>34.92</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>23.59</td>
<td>35.00</td>
<td>3.40</td>
</tr>
<tr>
<td>Theoretical:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C$_2$H$_5$)$_4$NNb(OH)$_2$Cl$_4$</td>
<td>23.29</td>
<td>35.54</td>
<td>3.51</td>
</tr>
<tr>
<td>(C$_2$H$_5$)$_4$NNbOCl$_4$</td>
<td>24.45</td>
<td>37.32</td>
<td>3.69</td>
</tr>
<tr>
<td>$\text{L(C}_2\text{H}_5)_4\text{NbOCl}_5$</td>
<td>16.00</td>
<td>30.53</td>
<td>4.82</td>
</tr>
</tbody>
</table>

From the results of the analysis it is apparent that the formula of the compound produced in this case is (C$_2$H$_5$)$_4$NNb(OH)$_2$Cl$_4$. This can also be written as (C$_2$H$_5$)$_4$NNbOCl$_4$.$\text{H}_2$O but the former is the more probable. There is little if any possibility of distinguishing between the two.

This compound was found to be insoluble in both diethyl ether
and n-butyl ether. The compound was then found to be soluble in 1,4-dioxane. When a small amount of the solid salt was placed in undried dioxane, it dissolved immediately but the solution became cloudy in about two minutes. During this period of time, the absorption of the solution at 281 mp decreased rapidly.

When dry dioxane was used, a clear solution was obtained which remained stable if kept protected from atmospheric moisture. The solubility of the compound appears to be in the order of a few tenths of a gram per liter. Since dioxane is transparent to ultraviolet light down to about 260 mp, this solvent was used for spectrophotometric work and no attempt was made to find other solvents in which the compound might be soluble.

3.836 milligrams of the tetraethyl ammonium compound was weighed out on a microbalance and dissolved in 40.00 ml. of dioxane. It was found that this much dioxane was required to dissolve the compound in a reasonable amount of time. Twelve ml. of this solution was diluted to 37.00 ml. By use of the theoretical percent niobium in the compound, the concentration of niobium in this solution was calculated to be 7.24 µg./ml. The absorption curve of this solution was measured and is shown in Figure 2 along with the absorption curve of a solution containing 7.85 µg. Nb/ml. in 11.9 molar hydrochloric acid. Absorbance is plotted on a logarithmic scale in order that the shape of the curves will not be affected by concentration. The data for this curve are shown in Table III.
FIGURE 2
COMPARISON OF TETRA ETHYL AMMONIUM SALT WITH SPECIES IN CONCENTRATED HCl

Et₄NNb(OH)₂Cl₄ in DIOXANE
(7.34 ug Nb/ml)

Niobium in 1.9 M HCl
(7.85 ug Nb/ml)
### TABLE III

**ABSORBANCES OF (Et)$_4$Nb(OH)$_2$Cl$_4$ IN DIOXANE AND NIOBIUM IN 11.9 M HCl**

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Absorbance</th>
<th>Wavelength (nm)</th>
<th>Absorbance</th>
<th>Wavelength (nm)</th>
<th>Absorbance</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>7.34 µg. Nb/ml. as (Et)$_4$Nb(OH)$_2$Cl$_4$ in Dioxane</td>
<td></td>
<td>7.34 µg. Nb/ml. as (Et)$_4$Nb(OH)$_2$Cl$_4$ in Dioxane after 35 minutes standing</td>
<td></td>
<td>7.85 µg. Nb/ml. in 11.9 M HCl</td>
</tr>
<tr>
<td>265</td>
<td>0.270</td>
<td>265</td>
<td>0.243</td>
<td>265</td>
<td>0.365</td>
</tr>
<tr>
<td>270</td>
<td>0.366</td>
<td>270</td>
<td>0.327</td>
<td>270</td>
<td>0.549</td>
</tr>
<tr>
<td>275</td>
<td>0.513</td>
<td>275</td>
<td>0.732</td>
<td>275</td>
<td>0.822</td>
</tr>
<tr>
<td>279</td>
<td>0.616</td>
<td>279</td>
<td>0.551</td>
<td>279</td>
<td>0.840</td>
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<tr>
<td>281</td>
<td>0.643</td>
<td>281</td>
<td>0.579</td>
<td>281</td>
<td>0.830</td>
</tr>
<tr>
<td>282</td>
<td>0.650</td>
<td>282</td>
<td>0.840</td>
<td>282</td>
<td>0.830</td>
</tr>
<tr>
<td>283</td>
<td>0.650</td>
<td>283</td>
<td>0.590</td>
<td>283</td>
<td>0.830</td>
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<tr>
<td>284</td>
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<td>0.780</td>
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<tr>
<td>286</td>
<td>0.628</td>
<td>286</td>
<td>0.491</td>
<td>286</td>
<td>0.654</td>
</tr>
<tr>
<td>290</td>
<td>0.538</td>
<td>290</td>
<td>0.470</td>
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<tr>
<td>295</td>
<td>0.379</td>
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<td>0.315</td>
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<td>300</td>
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<tr>
<td>305</td>
<td>0.148</td>
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<tr>
<td>310</td>
<td>0.097</td>
<td>310</td>
<td>0.065</td>
<td>310</td>
<td>0.065</td>
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<tr>
<td>320</td>
<td>0.064</td>
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<tr>
<td>330</td>
<td>0.047</td>
<td></td>
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<td>340</td>
<td>0.024</td>
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</tr>
<tr>
<td>350</td>
<td>0.013</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It is seen that \((\text{Et})_4\text{NNb(OH)}_2\text{Cl}_4\) shows an absorption peak between 282 and 283 \(\text{m}\) and further examination of the absorption curve shows that it is almost identical to the absorption curve of niobium in concentrated hydrochloric acid. The major difference here is that the curve for the dioxane solution is shifted by about two \(\text{m}\). It is well known that change of solvent causes small shifts in absorption curves so this small shift is not surprising.

If the molar extinction coefficient is assumed to be the same in dioxane as in concentrated hydrochloric acid, the absorbance at 282 \(\text{m}\) for this solution corresponds to about 6.3 \(\mu\text{g. Nb/ml.}\) instead of 7.24 \(\mu\text{g. Nb/ml.}\) which the solution should have contained. This difference is probably due to pickup of moisture and resulting hydrolysis of the compound during weighing and dissolving of the sample and during the time required for measuring the absorption curve. In order to determine how great this moisture pickup might be, the solution was allowed to stand in the spectrophotometer cell in the instrument for 35 minutes. At this time the absorption curve was run again. The results are shown in Table III. This was approximately the same amount of time required for dissolving the compound and measuring its absorbance. The apparent concentration of niobium was then about 5.5 \(\mu\text{g./ml.}\). This indicates that the extinction coefficient for the \((\text{Et})_4\text{NNb(OH)}_2\text{Cl}_4\) is the same as the extinction coefficient for niobium in concentrated hydrochloric acid.
In order to show that the tetraethyl ammonium ion was not contributing to the absorption curve, a solution of tetraethyl ammonium chloride in water was prepared and its absorption curve was measured. The absorbance in the ultraviolet was found to be negligibly small even in solutions of fairly high concentration.

This very close similarity in the absorption curves in Figure 2 shows that the ionic niobium species present in concentrated hydrochloric acid is Nb(OH)$_2$Cl$_4$. If the acid of this anion is a weak acid, the niobium will be present almost entirely in the form HNb(OH)$_2$Cl$_4$ in this extremely high hydrogen ion concentration.
OTHER CHLORIDE SPECIES OF NIOBiUM

The 281 μm species which has been identified as Nb(OH)$_2$Cl$_4^-$ is no doubt the most important chloride species in aqueous solution, but it is also of considerable interest to determine the nature of other chloride species of niobium. As was pointed out earlier, there is a considerable amount of data showing the relationship of one species to another. It should then be possible to predict some of the species present from knowledge of the 281 μm species and from previous work which gives an indication of the relation between species.

Species Not Showing Absorption Peaks Above 210 μm. Kanzelmeyer (8, pp.45-53) measured the absorption curves of niobium in various hydrochloric acid concentrations. These curves show that the 281 μm peak does not disappear completely until the hydrochloric acid concentration is lowered to about six molar. At this concentration the curve shows a gradual decrease in absorbance from the lower wavelengths toward the higher wavelengths. This range in which the 281 μm peak is disappearing is exactly the same range in which the data of Huffman, Iddings, and Lilly (7, pp.4474-5) show a very marked decrease in the anion exchange distribution coefficient indicating a decrease in the negative charge of the niobium species present. Since the species absorbing at 261 μm has been shown to have a minus one charge it is probable that the species being produced, as the hydrochloric acid is decreased from twelve to six
molar, has a zero or positive charge.

In order to further understand the change between species, a short study of the system of antimony (V) in hydrochloric acid was made. Neuman (14, pp. 261-11-5) studied the system of antimony (V) in hydrochloric acid solutions by spectrophotometric methods. In this system he showed the presence at high hydrochloric acid concentration of the species \( \text{SbCl}_3^- \). As the hydrochloric acid level was lowered \( \text{SbOHCl}_2^- \) was formed and on further lowering \( \text{Sb(OH)}_2\text{Cl}_4^- \) was produced. All three of these species show the minus one charge and all three of them show similar shaped absorption peaks although each peak is displaced further toward the short wavelengths in the order of decrease of chloride. The highest concentration of the species \( \text{Sb(OH)}_2\text{Cl}_4^- \) was found in about 5.8 molar hydrochloric acid. No further study of the nature of species occurring at lower acid level was made.

In order to compare the niobium system to the antimony system and to further explain the results of Huffman, Iddings, and Lilly (7, pp. 4474-5), anion exchange studies were made with antimony. A stock solution of antimony was made up by dissolving 30 ml. of antimony pentachloride in concentrated hydrochloric acid and diluting to 500 ml. with this acid. This solution was analyzed by evaporating 10 ml. portions to dryness with nitric acid, igniting at 830°F. and weighing as \( \text{Sb}_2\text{O}_4 \). The solution was found to contain 0.0250 g. \( \text{Sb/ml} \). From this stock solution 100 ml. solutions were made up in 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, and 1 molar hydrochloric acid
with 0.250 g. Sb in each. These solutions were allowed to stand for 48 hours to establish equilibrium. A precipitate formed in solutions one and two molar in hydrochloric acid and these solutions were discarded. To 50 ml. portions of each of these solutions was added 5.0 grams of Dowex-1 anion exchange resin. The mixtures of solution and resin were then equilibrated for 24 hours at 25°C. by constant agitation in a constant temperature bath. The resin was removed by filtering on sintered glass. The hydrochloric acid concentration was determined on the original solutions by titration with standard NaOH. The antimony content of the solutions from which the resin had been removed was determined by precipitating the antimony with hydrogen sulfide and comparing to standards. The procedure was to take 20 ml. aliquots, neutralize with solid NaOH, add sufficient concentrated hydrochloric acid to make the final acidity two molar, dilute to 50 ml. with water, add 0.1 g. gum arabic as a protective colloid, and saturate with hydrogen sulfide. The lower antimony concentrations were visually compared to standards in 50 ml. volumetric flasks. The higher concentrations were compared with a Duboscq colorimeter.

The distribution coefficient, $K_D$, is defined as

$$K_D = \frac{M_R \times \text{volume of solution}}{M_e \times \text{mass of resin}}$$

where $M_R$ and $M_e$ are the fractions of an ion on the resin and in the liquid respectively. The distribution coefficients for antimony at these various hydrochloric acid concentrations were
calculated and are given in Table IV. These values are shown plotted against hydrochloric acid concentration in Figure 3. The larger values of the distribution coefficient are somewhat inaccurate since this indicates an antimony content very near the lower limit of measurement by the hydrogen sulfide method.

TABLE IV

DISTRIBUTION COEFFICIENTS OF ANTIMONY IN HYDROCHLORIC ACID SOLUTIONS ON ANION EXCHANGE RESIN DOWEX-1

<table>
<thead>
<tr>
<th>Molarity HCl</th>
<th>K_D</th>
<th>Molarity HCl</th>
<th>K_D</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.9</td>
<td>7.7 x 10^3</td>
<td>7.0</td>
<td>9.1 x 10^3</td>
</tr>
<tr>
<td>11.0</td>
<td>2 x 10^4</td>
<td>5.96</td>
<td>4.12 x 10^3</td>
</tr>
<tr>
<td>10.0</td>
<td>1.3 x 10^4</td>
<td>5.00</td>
<td>2.69 x 10^3</td>
</tr>
<tr>
<td>9.0</td>
<td>1.3 x 10^4</td>
<td>4.12</td>
<td>4.95 x 10^2</td>
</tr>
<tr>
<td>8.0</td>
<td>1.55 x 10^4</td>
<td>2.96</td>
<td>49.0</td>
</tr>
</tbody>
</table>

It is to be expected that as long as a minus one charged complex is present the distribution coefficient will remain very nearly constant. It is quite apparent that this is true in the case of antimony. As was previously cited, Neuman showed antimony to be present in the form of a minus one charged anion from 12 molar down to 5.8 molar hydrochloric acid. Below this the distribution coefficient drops off rapidly indicating disappearance of an ionic species. The distribution coefficient curve for niobium obtained by Huffman, Iddings, and Lilly (7, pp.4474-5) is also
FIGURE 3

DEPENDENCE OF DISTRIBUTION COEFFICIENT ON HCl CONCENTRATION

Huffman, Iddings & Lilly
J.A.C.S. 73, 4474 (1951)
shown in Figure 3. Comparison of these two curves shows that the
distribution coefficient is about the same for antimony and niobium
in the acid ranges where the Sb(OH)$_2$Cl$_4$ and the Nb(OH)$_2$Cl$_4$ ions pre-
dominate. It is also apparent that the distribution coefficient
drops off sharply in each case at acid levels below those in which
these species are present. This shows that a non-anionic form is
produced in each case at lower hydrochloric acid concentration than
those at which the M(OH)$_2$Cl$_4$ predominates.

It is to be expected that if an uncharged species is formed
in solution it would very likely be NbOCl$_3$ or some hydrate of it.
In order to check this theory some NbOCl$_3$ was prepared. This was
prepared by two distinctly different methods.

If the cesium compound which was discussed earlier is heated
in a vacuum, a white or very light yellowish solid is sublimed off.
The expected reaction here would be Cs$_2$NbOCl$_5$ $\rightarrow$ NbOCl$_3$ + 2CsCl.
The fact that some of the niobium remains behind and cannot be
sublimed tends to support the earlier thought that the compound
is actually Cs$_2$Nb(OH)$_2$Cl$_5$. Some of the sublimate obtained in this
reaction was dissolved in diethyl ether and the absorption curve
was measured. This appears in Figure 4. If hydrogen chloride is
passed through the solution and blank for 30 seconds, a 261 m$\mu$ peak
begins to appear. The small peak at 260 m$\mu$ is probably due to
overlap of the 261 m$\mu$ peak and the high absorption at low wave-
lengths. When the hydrogen chloride is passed through the solution
and the blank for five minutes, the absorption curve was changed
to one showing predominantly a peak at 283 mp. Both of these curves appear in Figure 4. It is important to note here that the ether reacts with hydrogen chloride making it opaque to ultraviolet light upon continued addition of hydrogen chloride or upon standing after addition of hydrogen chloride. This reaction eliminates any possibility of quantitative interpretation of these curves.

According to Süe (22, pp. 530-7) niobium oxychloride can be prepared by heating a mixture of niobium pentoxide and carbon in a stream of chlorine. This is formed along with a small amount of niobium pentachloride. By passing niobium pentachloride over hot niobium pentoxide it was found to be converted to the oxychloride with the pentoxide disappearing. The oxychloride was then made by chlorinating, with chlorine, a mixture of niobium pentoxide and finely powdered sugar charcoal at about 400°C. The resulting vapor was passed over hot niobium pentoxide to convert any of the pentachloride formed to the oxychloride. The chlorination tube was then flushed out with nitrogen dried by passing through concentrated sulfuric acid. The niobium oxychloride was sublimed down the tube into smaller side tubes which were sealed off leaving the niobium oxychloride under a nitrogen atmosphere.

It was found that the niobium oxychloride was quite soluble in diethyl ether and that the solution produced is perfectly clear and free of Tyndall effect. The absorption curve of a dilute solution of niobium oxychloride in ether is shown in Figure 4.
FIGURE 4

$\text{NbOCl}_3$ IN DIETHYL ETHER

Dry HCl 5 min.  
Dry HCl 30 sec.  
Sublimate from thermal decomposition of $\text{Cs}_2\text{NbOCl}_5$
From this curve it is seen that the sublimate from the thermal decomposition of the cesium salt is NbOCl₃. Addition of hydrogen chloride to this solution results in curves similar to those obtained upon addition of hydrogen chloride to an ether solution of the thermal decomposition product of the cesium salt.

It was noticed that the absorption curve for NbOCl₃ in diethyl ether was very similar to the absorption curve obtained by Kanzelmeyer (8, p.49) for a solution of niobium in six molar hydrochloric acid. It would appear then that the species formed in hydrochloric acid as the 281 μ peak disappears is NbOCl₃. As the hydrochloric acid is decreased below six molar, the general appearance of the absorption curves for niobium remain similar but the slope becomes more negative. Thus the solutions absorb more at lower wavelengths. This trend continues to below one molar at which concentration Schubert and Richter (18, pp.376-85) showed the niobium to be colloidal. This same general shape of curve was obtained by Kanzelmeyer (8, pp.106-109) by subtraction of the 281 μ peak for solutions 10.5 molar in chloride with varying hydrogen ion activity.

In order to further identify the species present, a solution of niobium was prepared in constant boiling (6.1 molar) hydrochloric acid. The absorption curve is shown in Figure 5 as curve 1. Curve 2 is the absorption curve for NbOCl₃ in ether. Curve 3 shown in Figure 5 is a curve for niobium in 4.2 molar hydrochloric acid. A solution of niobium in hydrochloric acid was made slightly basic
with ammonium hydroxide. Curve 4 in Figure 5 is the absorption curve for this colloidal solution. A Tyndall effect can be observed in this solution if a very strong beam of light is used. Curve 5 in Figure 5 is a curve obtained by Kanzelmeyer (8, p.108) by subtracting the contribution of the 281 \( \mu \) species from the absorption curve of a solution 10.5 molar in chloride and 1.8 molar in hydrogen ion.

Careful observation of Figure 5 shows the marked similarity between the absorption curve of the niobium in 6.1 molar hydrochloric acid and the absorption curve of NbOCl\(_3\) in ether. Because no distinguishing peaks are present the slopes of the curves must be compared in this case. Since there is no great difference in the general shape of the colloidal curve and the NbOCl\(_3\) curve, it is difficult to study the change from one to the other. It is quite apparent though that the curve obtained by the subtraction of the contribution of the 281 \( \mu \) species for a solution 10.5 molar in chloride and 1.8 molar in hydrogen ion is the curve produced by a colloid. It appears from these results that as hydrochloric acid concentration is decreased from 12 molar the Nb(OH)\(_2\)Cl\(_4\) is first converted to NbOCl\(_3\) or a simple polymer or hydrate of it. Below about four molar this is gradually hydrolyzed and colloidal formation takes place. It is extremely probable that no soluble ionic species of niobium exists to any appreciable degree in hydrochloric acid systems other than the one showing the characteristic absorption peak at 281 \( \mu \) which has been shown to be Nb(OH)\(_2\)Cl\(_4\).
FIGURE 5
NIOBium SOLUTIONS SHOWING NO ABSORPTION MAXIMA ABOVE 210 m\mu.
Species Showing Absorption Maximum At 260 μm. In solutions of niobium 10.5 molar in perchloric acid and 0.02 to 0.3 molar in chloride Kanzelmeyer (8, pp.100-110) obtained a distinct absorption peak at 260 μm by subtracting the contribution of the 281 μm species from the total absorption curve. As was mentioned in the earlier part of this thesis, the chloride ion dependence for the reaction of a lower species to form the 281 μm species was found to be 0.95 or essentially one. At first glance then it would seem that since one chloride ion is lost in decreasing the chloride ion concentration from the concentration range showing the 281 μm species, the reaction would be \( \text{Nb}(\text{OH})_2\text{Cl}_4 \rightarrow \text{Nb}(\text{OH})_2\text{Cl}_3 + \text{Cl}^- \). This species would essentially be a hydrated niobium oxychloride and as such could be expected to show an absorption curve similar to that of niobium oxychloride. Since niobium oxychloride shows no absorption peak in the range of the instrument, this reaction cannot explain the 260 μm peak. Also as has previously been mentioned, the absorption curve of niobium in six molar hydrochloric acid appears to be the same as the absorption curve of niobium oxychloride and shows no sign of the 260 μm peak.

It must be emphasized that although the chloride dependence data show a change of one chloride it does not eliminate the possibility of other changes at the same time. Other changes taking place at the same time in no way affect the method of measuring this chloride dependence. It may well be that at the extremely high hydrogen ion activity found in 10.5 molar perchloric
acid the reaction

\[
\text{Nb(OH)}_2\text{Cl}_4^- + H^+ \rightarrow \text{NbOHCl}_3^+ + \text{Cl}^- + \text{H}_2\text{O}
\]

takes place. This may also be thought of as a stepwise process going through \(\text{Nb(OH)}_2\text{Cl}_3\). If, as is probably the case, \(\text{HNb(OH)}_2\text{Cl}_4\) is a moderately weak acid the reaction might be considered

\[
\text{HNb(OH)}_2\text{Cl}_4^- \rightarrow \text{NbOHCl}_3^+ + \text{Cl}^- + \text{H}_2\text{O}.
\]

In order to attempt to show whether or not this hypothesis was correct an experiment was designed to determine whether the species showing an absorption peak at 260 μm is a cation. A solution of niobium was prepared in 10.5 molar perchloric acid which was 0.025 molar in hydrochloric acid. The absorption curve of this solution versus a reagent blank appears as curve 1 in Figure 6. A 30 cm. cation exchange column was set up using Dowex-50 resin in the hydrogen form. The total volume of the empty column without the resin was 10 ml. About 70 ml. of the reagent blank was passed through the resin and the last 10 ml. coming through was saved as a spectrophotometric blank. The niobium solution was then passed through and a small portion was collected after 40 ml. of the solution had passed through. The absorption curve of this solution versus the blank that had been passed through the resin is curve 2 in Figure 6.

This experiment was repeated with the same solution but with a new bed of resin. This time 100 ml. of the blank was passed through before a spectrophotometric blank was collected. Eighty ml.
of niobium solution was then passed through before a sample was collected. The absorption curve of this sample is curve 3 in Figure 6.

It is apparent from the curves that a major portion of the niobium has been removed from this solution which had been composed of a mixture of the 260 μ species and the 281 μ species. Since the flow rate was quite rapid and since the 281 μ species is not a cation, it would be expected that not all the niobium would be removed by the column unless equilibrium between these two species is extremely rapid. It is important to note that these strong perchloric acid solutions pick up considerable organic material from the resin and that this absorbs in the ultraviolet region. This no doubt accounts for the appearance of a variable "background" absorbance for the niobium solutions which have passed through the resin. This is brought about by the non-reproducibility of this resin pickup.

This is considered very strong evidence for the existence of the ion NbOHC\textsuperscript{+} or some hydrate of it in 10.5 molar perchloric acid with 0.02 to 0.3 molar chloride. This is the species showing a characteristic absorption peak at 260 μ.
FIGURE 6

EFFECT OF CATION EXCHANGE RESIN ON NIOBIUM SOLUTIONS CONTAINING 260 m\(\mu\) SPECIES

WAVELENGTH m\(\mu\)

ABSORBANCE

220 230 240 250 260 270 280 290 300 310
SUMMARY

A study was made of the various chlorine containing species of niobium existing in aqueous solution. The principal object of this study was to identify the chloride complex of niobium which exists in concentrated HCl and shows an absorption peak at 281 m\(^\mu\). This species is of considerable interest since it is the basis for an important spectrophotometric method of determining niobium. A tetraethyl ammonium salt of this complex anion was prepared and found by analysis to be \((C_2H_5)_4NNb(OH)Cl_4\). A solution of this compound in dioxane was shown by spectrophotometric comparison to contain the same complex species as that present in concentrated hydrochloric acid solutions of niobium. It was then concluded that the species present in concentrated hydrochloric acid is \(\text{Nb(OH)}_2\text{Cl}_4^-\) or the unionized acid of this anion.

At lower hydrochloric acid concentrations it was shown that non-ionic species of niobium are present. At intermediate hydrochloric acid levels it appears that \(\text{NbOCl}_3\) or some polymer or hydrate of it is present. At low hydrochloric acid levels the niobium is in the form of a colloid.

In 10.5 molar perchloric acid containing a small amount of chloride a niobium species is present showing an absorption maximum at 260 m\(^\mu\). By use of cation exchange resin this species was shown to have a positive charge. Since earlier work indicated that it contained three chlorine atoms, it is assumed to be \(\text{NbOCl}_3^+\).
BIBLIOGRAPHY.


