A SPECTROPHOTOMETRIC STUDY OF NIOBIUM (V)
IN HYDROCHLORIC ACID SOLUTION

by

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FOREWORD

It is true that a system need not be completely described nor fully understood to be useful for limited purposes. Many practical analytical procedures are worked out with such systems. In these, the effects of such variables as appear to be significant are investigated over that region of the system which is thought to be useful. With no thought concerning the nature of the system, the analyst can make use of it within the region in which its behavior has been empirically measured.

The limitations of the empirical approach are obvious. Carried to the extreme it offers two major objections. First is the lack of any rational means of determining that all of the significant variables have been studied. The second objection is the lack of a basis for extrapolation of the system's behavior to values of the variables outside the region investigated. Extrapolation may be done only in the light of an understanding of the exact nature of the system in terms of known physical and chemical relationships. It is hardly necessary to point out that the accuracy of such extrapolation increases as the system is more accurately described.

Other reasons justify the time and effort expended in seeking an exact understanding of the nature of a system. For the most part, any particular problem has limited objectives. But the information obtained by an

investigation undertaken from a theoretical point of view
is often of great value for purposes other than for those
originally intended. This is not generally true of
empirically designed experiments.

Not of least importance is the satisfaction the
investigator may derive from filling in missing details in
the picture of knowledge. He may well do so haphazardly,
a stroke here or a line there. But the sense of accom-
plishment is greater if his contributions in themselves
make a significant pattern.

ACKNOWLEDGMENTS

DEDICATION

To my beloved wife, Evelyn, belongs the great-
est portion of credit for this thesis; save for her
selfless sacrifice and constant encouragement it
would have never been written. I therefore dedicate
this work to her and hope that it may honor her name.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd.)

A SPECTROPHOTOMETRIC STUDY OF NIOBIUM (V)
IN HYDROCHLORIC ACID SOLUTION

INTRODUCTION

Historical Background - Since the discovery of nio-
bium by Hatchett in 1801 its determination in minerals and
alloys has been the subject of much investigation and con-
troversy. The one point of nearly universal agreement was
the practical impossibility of precipitating quantitative-
ly any one of the elements - niobium, tantalum, titanium,
zirconium or tin - in the presence of an appreciable amount
of any of the others. Each element tends to "mask" the
reactions of the others in proportion to the relative
amounts of each present (22,pp.464-5; 42,p.77).

Modern Methods - Schoeller (52) has developed a
scheme of analysis for materials containing niobium and
tantalum based upon previous work (38,vol.9,pp.837-82) and
seventeen years of research by himself and his associates.
In his methods, the elements are separated by repeated
fractional crystallizations and leaching. While this
device leads to ultimate purity, it is achieved only by
the expenditure of large amounts of time and effort. The
results are highly dependent upon the skill and experience
of the analyst (2,p.478).

More recently, Atkinson, Steigman and Hiskey (2,
pp.477-80) published a critical discussion of the methods
available for the analysis of niobium and tantalum

materials. They quoted Schoeller's explanation of the difficulties inherent in the separations of niobium and tantalum. "Each individual constituent, more particularly a subordinate one, cannot behave quantitatively toward reagents as it would in the pure state because its molecules are too firmly interlocked with those of another constituent of different chemical reactivity." They further proposed that the effects are caused by colloid formation and "the formation of isomorphous mixtures not only in flocculated precipitates but also in colloidal solution parts."

The conclusion reached is that rapid, simple methods for the analysis of niobium must be based upon reactions which take place in solutions in which all of the elements are present in an ionic form. This eliminates the possibilities of adsorption and mixed crystal formation. Atkinson, Steigman and Hiskey (2,pp.480-8) chose a radical approach, the chlorination of the elements and the fractional distillation of their chlorides from anhydrous medium.

Other means have been used in attempts to perfect a rapid and accurate method of analysis. Most prominent were the volumetric, colorimetric, ion-exchange, chromatographic and solvent extraction procedures.

The volumetric methods employed the reduction of niobium (V) to niobium (III) and subsequent oxidation with a suitable reagent (6,pp.233-5; 12,pp.563-70; 31,pp.405-8; 39,p.818; 16,pp.129-33; 43,pp.115-9; 54,pp.215-20; 60,pp. 533-5; 65,pp.6-9).

Three essentially different spectrophotometric methods for the determination of niobium have been re-ported in the literature: methods based upon the peroxy complex, those which make use of the thiocyanate complex, and those employing the polyphenolic complexes.

The peroxy methods (44,pp.926-31; 59,pp.163-5) lack sensitivity and suffer from the inconveniences inherent in the hydrogen peroxide - concentrated sulfuric acid reagent employed - i.e., the corrosive nature of the solutions and the annoyance of oxygen bubble formation. The lack of sensitivity of these methods is aggravated by the limited solubility of many materials in concentrated sulfuric acid, for this often establishes a practical upper limit to the sample size.

The procedures utilizing the thiocyanate complex, while possessing adequate sensitivity, offer other dis-advantages. The complex is unstable in aqueous medium. Freund and Levitt (10,pp.1813-6) stabilized the complex by the addition of a miscible organic solvent, acetone. The resulting solutions showed increasing absorption with time,

making it necessary to specify accurately the time inter-
val from the addition of the reagent to the measurement of
absorbance. Lauw-Zecha, Lord and Hume (35,pp.1169-73)
extracted the colored species with ether, a process fur-
ther complicated by the necessity for accurate control of
the acidity. Hydroquinone in concentrated sulfuric acid
served as reagent for a colorimetric method for niobium
and titanium (26,pp.1340-4), either simultaneously or
separately.

Ion exchange techniques are primarily designed for
the separation of elements, either for preparative pur-
poses or as a preliminary step to more conventional
analyses. Zirconium and niobium have been separated on
the anion exchange resin Dowex 1 from oxalic acid solution
(61), from hydrochloric-hydrofluoric acid mixtures (33,pp.
9-13), and from concentrated hydrochloric acid solutions
(25,pp.4474-5). Zirconium, protactinium, niobium and tan-
talum were separated on anion exchange resins by succes-
sive elution with several solutions containing various
amounts of hydrochloric acid, hydrofluoric acid and
ammonium chloride (34,pp.2900-2).

While chromatographic procedures have not yet
become highly developed, niobium and tantalum have been
separated, though not quantitatively, by adsorption on
activated cellulose and elution with methylethyl ketone

containing hydrofluoric acid (5,pp.1497-1504; 66). Elec-
trochromatographic separation of many inorganic ions
including niobium and zirconium in various dilute organic
acids was briefly surveyed by Sato, Norris and Strain (50,
pp.267-71). Separation of niobium, tantalum and tungsten
on a silica column was utilized for a scheme of qualita-
tive analysis (56,pp.99-100).

Most recent investigations concerning the separa-
tion of niobium have employed liquid-liquid extractive
procedures. Tantalum and niobium have been separated in
mineral acid solutions containing hydrofluoric acid by
diisopropyl ketone (57,pp.1517-19), from hydrochloric acid
solutions by a five percent solution of methyldioctylamine
in xylene (36,p.1618) and from sulfuric acid solutions by
an eight percent solution of tribenzylamine in methylene
chloride (8,pp.1045-7). Scadden and Ballou (36,pp.1602-4)
surveyed the effectiveness of a number of organic com-
plexing agents in various organic solvents for the extrac-
tion of niobium, zirconium and rare earth elements from
mineral acid solutions.

Structural Studies - "Tantalum and niobium are dis-
tinguished from other elements by the very small number of
their stable water-soluble compounds, a fact which
accounts for most of the difficulties encountered in
earth-acid analysis" (53,p.337). It is not surprising,

then, that until very recently, investigators were pre-occupied with the discovery and characterization of water-insoluble crystalline compounds of niobium.

Niobium compounds hydrolyze rapidly in dilute aqueous solutions of mineral acids. However, highly concentrated mineral acids and moderately concentrated organic acids are known to form niobium solutions that are stable over long periods of time. This behavior has been attributed to the formation of stable complex ions with the anion of the acid involved. Early investigators paid little heed to the ionic species present, but some did suggest forms for the species based upon the structures of the precipitated solids obtained from solutions.

In highly saturated hydrochloric acid solutions Weinland and Storz (62,pp.3056-9; 63,pp.223-43) prepared insoluble halogen salts of the form $NbOCl_3 \cdot RCl$ and $NbOCl_3 \cdot 2RCl$ where R represents cesium, rubidium, quinoline and pyridine. From this they inferred the existence of $H(NbOCl_4)$ or $H_2(NbOCl_5)$. Russ (49,pp.42-91) claimed to have precipitated an oxalate whose formula he wrote as $Nb(HC_2O_4)_5$. Edmister and Albritton (7,pp.438-42) performed simple electromigration experiments and "expect a better form to be $H_5Nb(C_2O_4)_5$, to ionize to hydrogen ions and anions containing niobium."

With the advent of the Atomic Energy Commission and
the problems posed by fission products analysis and
separation, increased interest was shown, not only in the
development of workable procedures for complex mixtures
containing niobium, but also in the aqueous chemistry of
the element. Most of the papers mentioned above in con-
nection with ion exchange, chromatographic and solvent
extraction separation procedures had as a second objective
elucidation of the structures of the ionic species
involved.

Kraus and Moore have shown by anion exchange that
in solutions nine molar in hydrochloric acid and five
hundredths molar in hydrofluoric acid niobium and tantalum
form negatively charged complexes "with probable charge
minus two or greater" (32,p.3855). These authors extended
this work (33,pp.9-13), and interpreted their results as
requiring at least three ionic species of niobium differ-
ing by two fluoride ions each. They postulated that the
two species existing at low fluoride concentrations are
oxygenated. Both of these investigations suffered from
the use of a mixed HCl-HF solvent. This only further
complicated the already complex niobium (V) aqueous system.

Huffman, Iddings and Lilly (25,pp.4474-5) used
hydrochloric acid solutions of zirconium, hafnium, niobium
and tantalum in batch equilibrium exchange experiments to

demonstrate the existence of negatively charged chloro
complex ions of these elements. It is interesting to note
that with niobium and tantalum, exchange increased with
increase of hydrochloric acid concentration above about
five molar (a result to be expected with increased com-
plexing by chloride), but that exchange also increased
when the acid concentration was decreased. This means
that a minimum in the anion exchange of niobium and tanta-
lum occurred at a concentration of about four molar hydro-
chloric acid. The same behavior was not observed with
zirconium and hafnium. It was mentioned that equilibrium
was reached within four hours in high acid solutions but
that at least two days were required on the low acid side
of the curve. No explanation was given.

The same authors reported subsequently (24,pp.4714-
5) that the elution of carrier-free niobium from a column
of Dowex 2 anion exchange resin with seven molar hydro-
chloric acid resulted in an elution curve having three
peaks. There was no possibility of isotope separation,
and activity checks ruled out any foreign activity. A
repeat experiment also gave three peaks, but their shapes
and relative magnitudes were not the same as for the first
run. Elution with six molar hydrochloric acid gave the
usual symmetrical curve. The suggestion was made that
this unusual type of behavior could be attributed to the

slow establishment of equilibrium among various ionic species which are present.

Cation exchange resins, not usually considered of value in the case of such easily hydrolyzable elements as niobium, were employed by Schubert and Richter (55,pp.376-85) in studies on zirconium and niobium. They confirmed the colloidal character of these elements in solution. In fluosilicic acid solution they concluded that niobium was probably completely ionic, and that it was ionic in the presence of phosphate and oxalate. They listed the qualitative strengths of the complexes formed in the order: oxalic, phosphoric, sulfuric.

Burstall and coworkers (5,pp.1479-1504) inferred, from their chromatographic data, the presence of $R(TaF_6)$ or $R_2(TaF_7)$ and $R_2(NbF_7)$ or $R_2(NbOF_5)$ as the "commonest and most stable complexes in solution". They reasoned that only the non-oxygen-containing forms would be extractable by the methylethyl ketone. The observed fact that tantalum extracted at both high and low fluoride concentrations while niobium extracted only at high acid strengths indicated to them that at low fluoride the niobium species contained oxygen while at higher concentrations the fluoride replaced the oxygen to form an extractable species.

However, in the solvent extraction studies of
Ellenburg, Leddicotte and Moore (8,pp.1045-7) the exact
opposite behavior was observed with the chloride com-
plexes. Here, only the niobium extracted into the
chloroform-tribenzylamine layer and this occurred only at
hydrochloric acid concentrations above six molar. In the
same system, tantalum did not extract appreciably under
any circumstances. The explanation proposed was that the
niobium was thought to extract into the solvent phase as
a complex of the type $H(NbOCl_4)$ or $H_2(NbOCl_5)$ while the
tantalum was not presumed to form either chlorotantalates
or tantalum oxychloride species.

Wernet (64,pp.213-37) gave the solubility of
freshly precipitated niobium hydrous oxide as about four
grams Nb_2O_5 per hundred milliliters of solution saturated
at 0^oC. with hydrogen chloride. Niobium pentachloride
dissolved in highly concentrated hydrogen chloride to form
an unstable, but clear, solution containing the equivalent
of twenty grams of the oxide per hundred milliliters. The
latter decomposed slowly to yield a stable solution con-
taining about four grams of the oxide per hundred milli-
liters and a voluminous precipitate of the oxychloride
$NbOCl_3$. Wernet proposed the following ions in solution
$NbCl_6^-$, $NbCl_7^=$, or $NbOCl_5^=$ with the promise that subse-
quent work would appear to demonstrate this contention.

Measurements of electrode potentials in Nb(III)-Nb(V) systems in hydrochloric acid (1-6 $\underline{M}$) were interpreted by Grube and Grube (15,pp.771-80) as indicating the presence of NbO^{+++} ions under those conditions. They calculated the E^O values for solutions at various acid concentrations by substituting in the Nernst equation experimental values for the observed EMF, the activity of the hydrogen ions and the analyzed concentrations of Nb^{+3} and Nb^{+5}. The form of the Nernst equation which yielded nearly constant values for E^O was that one corresponding to the equation

$$Nb^{+++} + H_2O \longrightarrow NbO^{+++} + 2H^+ + 2e^-$$

throughout the range 2-6 $\underline{M}$ hydrochloric acid.

Elson (9) gave a qualitative description of the ultraviolet spectra (210-400 mμ) of niobium in perchloric acid and also in solutions of varying acid and chloride concentration. On the basis of qualitative correlation of the changes in absorbance with changes in the solution, he proposed forms for the complex species. At low acid with increasing chloride he postulated a series (NbO_2Cl), $(NbO_2Cl_2)^-$, $(NbO_2Cl_3)^{-2}$. In the intermediate and high acidities the species would be $(NbOCl)^{+2}$, $(NbOCl_2)^+$, and $(NbOCl_3)$. However, it is unlikely that such positive ions do in fact exist because of the previously mentioned

anion exchange data.

The Problem - There exists a need for new methods
of analysis for niobium which are rapid, accurate, and
suitable for routine use by personnel of ordinary skill.
It has been shown that this can be accomplished only in
ionic systems of the element. Therefore a need exists
for the investigation of those systems showing promise of
being ionic for the purpose of identifying the species
present and obtaining a measure of their stability.

The chloride system seems to be suitable for the
purposes mentioned. It exhibits an ultraviolet spectrum
that may be useful in determining its structure. This
thesis sets out to investigate that possibility and to
determine the suitability of the chloride complexes as a
basis for a spectrophotometric method of analysis.

APPARATUS AND SOLUTIONS

Apparatus - Absorbance measurements were made with
the Beckman Model D.U. Spectrophotometer. Matched 1.000
cm. Corex cells were used in all measurements of the
niobium-thiocyanate system. Matched 1.00 cm. silica cells
were employed in those cases where measurements extended
below 340 mμ.

All absorbance measurements were made with a
reagent blank in the null cell and the net absorbance was
recorded. Where the behavior of the reagent blank itself
was to be observed, measurements were made against a water
blank and this fact was noted.

The cell potentials were measured with a Leeds and
Northrup Model K1 potentiometer. The hydrogen electrodes
were of the Hildebrand type and were replatinized when the
E.M.F. fluctuated excessively with the bubbling of the
electrode. Six silver chloride electrodes were construct-
ed according to the directions of Brown (4,p.646). These
electrodes could be used about twice before requiring
replating and rechloridizing.

Measurement of the vapor pressure of the solutions
was accomplished with the isotensiscope (37,p.65).

E.M.F. and vapor pressure measurements were made
at 25 ± 0.1°C.

Niobium Pentoxide - This substance was obtained in a pure form as "Columbium Pentoxide" from A. D. MacKay, 198 Broadway, New York 7, New York (see Appendix A).

Niobium Solutions - During the first part of the investigation, prior to the discovery that concentrated hydrochloric acid solutions were permanently stable, niobium was prepared in soluble form by fusing Nb_2O_5 with potassium bisulfate and dissolving the melt in 0.5 $\underline{M}$ tartaric acid solution. Such solutions are reasonably stable, but the organic complexing acid must be destroyed by wet oxidation with sulfuric and nitric acids before being used to determine the stability of niobium in mineral acid. Once the stability of niobium in concentrated HCl was established, solutions of known niobium concentration were prepared as follows:

A weighed quantity of Nb_2O_5 was heated with 30-50 times its weight of fused potassium bisulfate in a porcelain crucible until a clear melt was obtained. This was cooled and dissolved in about 50 ml. of 1:1 sulfuric acid in a 400 ml. beaker by heating on the hot plate. The crucible was removed and carefully rinsed. The contents of the beaker were transferred to a 250 ml. centrifuge tube and placed in cold running water. The hydrous oxide of niobium was precipitated by the slow addition of 28% NH_4OH, keeping the solution as cool as possible. The

precipitate was centrifuged, decanted, stirred up with 200 ml. of distilled water, centrifuged and decanted again. The precipitate was taken into solution with a minimum amount of concentrated HCl, warming slightly to encourage solution of the precipitate. This clear solution was then transferred to a volumetric flask and diluted to the proper volume with concentrated HCl. Solutions of the order of 0.2 to 0.5 mg. Nb/ml. were easily prepared in this manner.

More concentrated niobium solutions were prepared according to the procedure of Wernet (64,pp.213-37). One gram of Nb_2O_5 was fused with about 3 g. of potassium bisulfate to obtain a clear melt. This was taken up in a small amount of sulfuric acid and transferred to a large centrifuge tube. The hydrous oxide was precipitated as before and, after separation by centrifugation, was slurried immediately with enough concentrated HCl to bring the volume up to 75-80 ml. The suspension was cooled in an ice bath while HCl gas was introduced at a rapid rate. The gas was prepared by dropping concentrated aqueous HCl into concentrated H_2SO_4. After the solution was saturated with hydrogen chloride at $0°C.$, the flow of gas was continued at a slow rate, until the opalescence of the solution disappeared. The length of time required for this varied with the conditions under which the hydrous

oxide was precipitated and the length of time the precipitate was aged before addition of the HCl. The solution sometimes cleared overnight but occasionally required 2-3 days to complete the process. This solution was transferred to a 100 ml. volumetric flask which was filled with concentrated HCl to a point 3-4 ml. below the mark. HCl gas was again passed into the solution in an ice bath until the saturation point was reached. The solution may then be diluted to the mark, if desired, with concentrated HCl, but the procedure followed consisted of standardizing the solution by removing a sample and determining the niobium content by gravimetric analysis with tannin (53, p.346). In any event, the solution was stored in an ice bath or other suitable storage place that kept it near 0°C. to prevent excessive loss of hydrogen chloride.

Zirconyl Chloride Hydrate - This solid zirconium compound was prepared by dissolving zirconium tetrachloride in water and crystallizing the product twice from 8.5 $\underline{N}$ HCl to eliminate iron[1]. It contained 31.20% zirconium by gravimetric analysis (see Appendix B).

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[1] The absence of iron was assumed when thiocyanate gave no color with an aqueous solution of the salt.

<u>Zirconium Solutions</u> - Solutions of known zirconium concentration were prepared by weighing out the amount of zirconyl chloride hydrate calculated from its analysis (see above) to give the required weight of zirconium. This was diluted to the proper volume with hydrochloric acid of the desired concentration.

PRELIMINARY EXPERIMENTS

Solubilizing Effects - It has been noted that early
workers were unable to obtain stoichiometric reductions of
niobium due, presumably, to the formation of a difficultly
reducible colloidal form of niobium. It was noted, with
no further explanation, that "concordant" results could be
obtained if titanium was present (60; 6; 12; 65). Other
investigators could reach no definite conclusion concern-
ing the effect of titanium or organic complexing agents.
Typical comments were: (31,p.408) "if not beneficial at
least exerts no harmful influence"; (43,p.118) the effect
was noticeable only when the weight of pentoxide reduced
was of the order of one milligram.

The difficulty experienced in precipitating niobium
by an acid hydrolysis when large amounts of zirconium are
present suggested that zirconium might be used to prevent
the precipitation of niobium in those analytical procedures
which depend upon an ionic species of the element.

In order to determine the magnitude of this effect,
an experiment was devised in which niobium was hydrolyzed
by a modification of the method of Geld and Carroll (14,
p.1098) in the presence of various amounts of zirconium.

The recovery of niobium pentoxide was complete in
the absence of zirconium, but as the ratio of zirconium to

TABLE I

EFFECT OF ZIRCONIUM ON THE
PRECIPITATION OF NIOBIUM

Sample No.	Milligrams Nb_2O_5	Milligrams $ZrOCl_2$	Weight ratio Zr/Nb	Milligrams Nb_2O_5 Found	Milligrams Nb_2O_5 Corr.
1	0	0	--	0.5	--
2	14.3	0	0	14.8	14.3
3	14.3	32.0	1	14.3	13.8
4	14.3	320.0	10	13.0	12.5
5	14.3	3200.	100	1.9	1.4

niobium increased, the amount of niobium recovered de-
creased. At a ratio of 100 parts of zirconium to one part
of niobium, the recovery amounted to only 10% of the
niobium present in the solution. It would appear that
even a 10 to one ratio of zirconium to niobium should have
a definite effect upon the hydrolysis of niobium in acid
solutions.

A series of experiments was undertaken to determine
the effect of various amounts of zirconium on the extent
and rate of hydrolysis of niobium in solutions of differ-
ent HCl concentrations. Susceptibility to determination
by the thiocyanate method of Freund and Levitt (10,pp.
1813-6) was taken as the criterion for the ionic state of
niobium.

By adding zirconium to samples containing the same amount of niobium and measuring the absorbance of the thiocyanate color developed, it was determined that a thousand-fold excess of zirconium did not cause an appreciable difference in color developed. The data are given in Table II.

TABLE II

INTERFERENCE OF ZIRCONIUM IN THE THIOCYANATE METHOD

Sample No.	µg. Zr	µg. Nb	Zr/Nb	Total Absorbance	Absorbance
1	10	1	10	0.195	0.184
A	10	0	--	.011	--
2	100	1	100	.198	0.187
B	100	0	--	.011	--
3	1000	1	1000	.195	0.183
C	1000	0	--	.012	--

An experiment was designed to determine the effect of various amounts of zirconium on the extent and rate of hydrolysis of niobium in solutions of various HCl concentrations. Several runs were conducted, differing only in the concentration of zirconium employed. Each run contained samples of various HCl concentrations, made up to contain the same concentration of niobium (10 µg./ml.).

The amount of niobium remaining in an ionic form was determined by removing a portion of each sample from time to time and applying the thiocyanate colorimetric method. The experiment was conducted at room temperature. Table III and Figures 1-3 show the variation of hydrolysis with time as both the HCl concentration and Zr/Nb ratio vary.

The experiment was repeated exactly as before except that the concentration of ionic niobium was measured after each sample had stood at room temperature exactly 16 hours, a length of time sufficient for most of the hydrolysis to take place. Table IV and Figure 4 display the results.

It should be pointed out that no visible evidence of hydrolysis was found except that in sample 1T (0.1 $\underline{N}$ HCl, Zr/Nb = 10) a slight haze appeared after two days, indicating the presence of a solid phase.

In Figure 4, the dotted line connects points representing the samples containing zirconium, the solid line those which contain no zirconium. These curves actually correspond to a cross-section of the previous curves at 16 hours. It is apparent that zirconium had a stabilizing effect in solutions of HCl concentration as low as 9 $\underline{N}$. This is of no practical advantage, since 9 $\underline{N}$ HCl is very nearly as obnoxious a solvent to use as is concentrated HCl.

TABLE III

ABSORBANCE VS. TIME FOR VARIOUS HCl CONCENTRATIONS

(All absorbances are total A − 0.006 blank)

Run 1 Zr/Nb = 10

Sample No.	HCl Concentration	Hrs.	A
1T	0.1	0.5	0.135
		1.5	.131
		3.5	.133
		7.5	.167
		13.5	.128
		48.0	.101
2T	1.0	0.5	0.176
		1.5	.146
		3.5	.132
		7.5	.145
		13.5	.107
		48.0	.073
3T	3.0	1.2	0.137
		2.7	.090
		8.0	.076
		45.5	.056
4T	6.0	1.3	0.137
		2.7	.090
		8.0	.086
		45.5	.044
5T	12.0	1.4	0.201
		2.7	.186
		8.0	.190
		45.5	.202

TABLE III (Cont'd.)

Run 2 Zr/Nb = 1

Sample No.	HCl Concentration	Hrs.	A
6T	0.1	0.7	0.152
		3.5	.145
		7.4	.150[a]
		15.4	.143
		29.8	.142
		42.6	.140
7T	1.0	0.7	0.143
		3.5	.094
		7.4	.096[a]
		15.4	.064
		29.8	.050
		42.6	.058
8T	6.0	2.5	0.088
		11.7	.056
		24	.047
9T	12.0	2.5	0.208
		11.7	.207
		24	.211

Run 3 Zr/Nb = 0

10T	0.1	0.17	0.155
		.8	.056
		4.2	.065
		12.2	.058
11T	1.0	0.17	0.188
		1.0	.121
		4.2	.092
		12.2	.084
12T	6.0	0.4	0.111
		2.3	.094
		10.3	.051
13T	12.0	0.4	0.196
		2.3	.203
		10.3	.203

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[a] Allowed color samples to stand slightly longer than 15 minutes. Noted that absorbance was increasing rapidl .

FIGURE I
HYDROLYSIS OF Nʙ-Zʀ SOLUTIONS
Zʀ / Nʙ RATIO = 10

FIGURE 2

HYDROLYSIS OF N_B-Z_R SOLUTIONS

Z_R / N_B RATIO = 1

9T   12 N

6T   0.1 N

7T   1 N

8 T   6 N

FIGURE 3

HYDROLYSIS OF Nʙ-Zʀ SOLUTIONS

Zʀ/Nʙ RATIO = 0
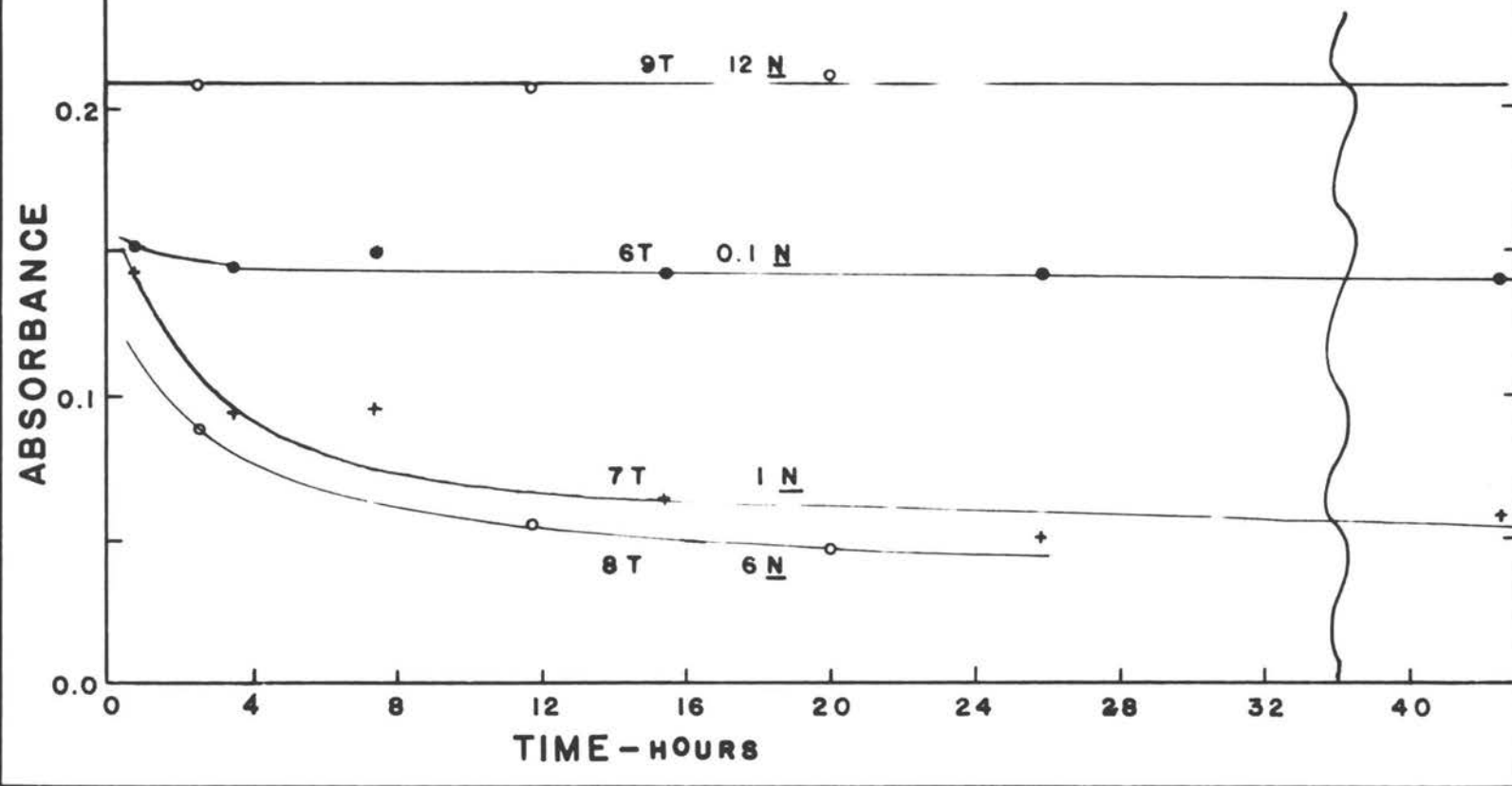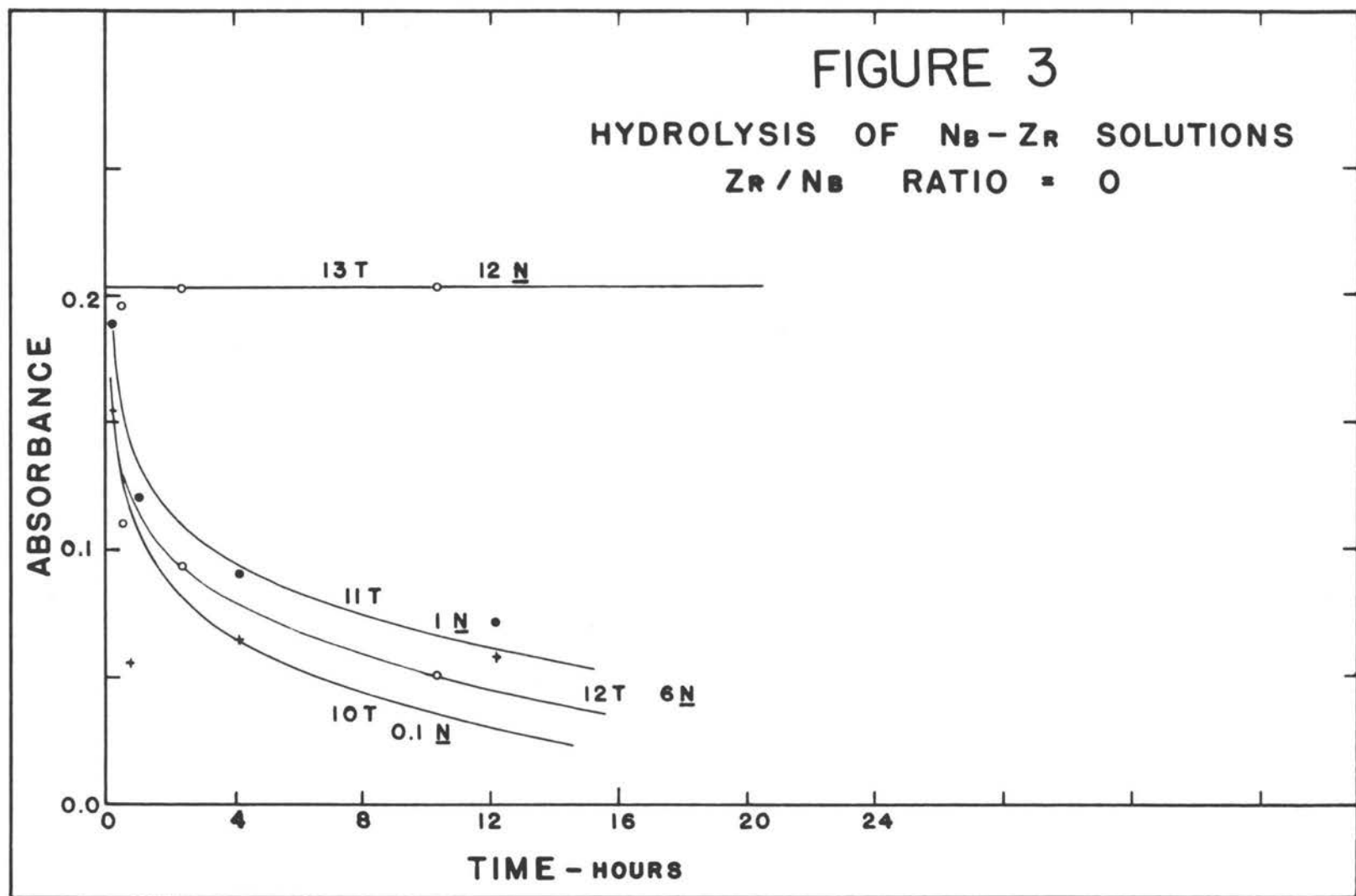
TABLE IV

VARIATION OF ABSORBANCE ACCORDING TO THE THIOCYANATE PROCEDURE FOR VARIOUS HCl CONCENTRATIONS AFTER HYDROLYSIS FOR 16 HOURS

Sample No.	Zr/Nb Ratio	HCl Concentration	Total A	A
1C	0	12	0.214	0.216
2C	0	11	.203	.201
3C	0	9	.163	.161
4C	0	6	.058	.056
5C	0	1	.077	.075
6C	0	0.1	.032	.030
BC1	--[a]	1	.002	--
7C	1	12	.211	.209
8C	1	11	.221	.219
9C	1	9	.224	.222
10C	1	6	.068	.066
11C	1	1	.061	.059
12C	1	0.1	.134	.132
BC2	--[a]	1	.013	--
13C	10	12	.225	.222
14C	10	11	.218	.215
15C	10	9	.215	.212
16C	10	6	.064	.061
17C	10	1	.055	.052
18C	10	0.1	.110	.107

TABLE IV (Cont'd.)

Sample No.	Zr/Nb Ratio	HCl Concentration	Total A	A
BC3	--[a]	1	.003	--
19C	0	12	.210	.206
20C	0	11	.195	.191
21C	0	9	.114	.110
22C	0	6	.058	.054
23C	0	1	.063	.059
24C	0	0.1	.034	.030
BC4	--[a]	1	.004	--

[a] Blank sample – contains all reagents and same weight of zirconium as companion samples but no niobium.

FIGURE 4

HYDROLYSIS OF NIOBIUM MEASURED
BY THE THIOCYANATE METHOD
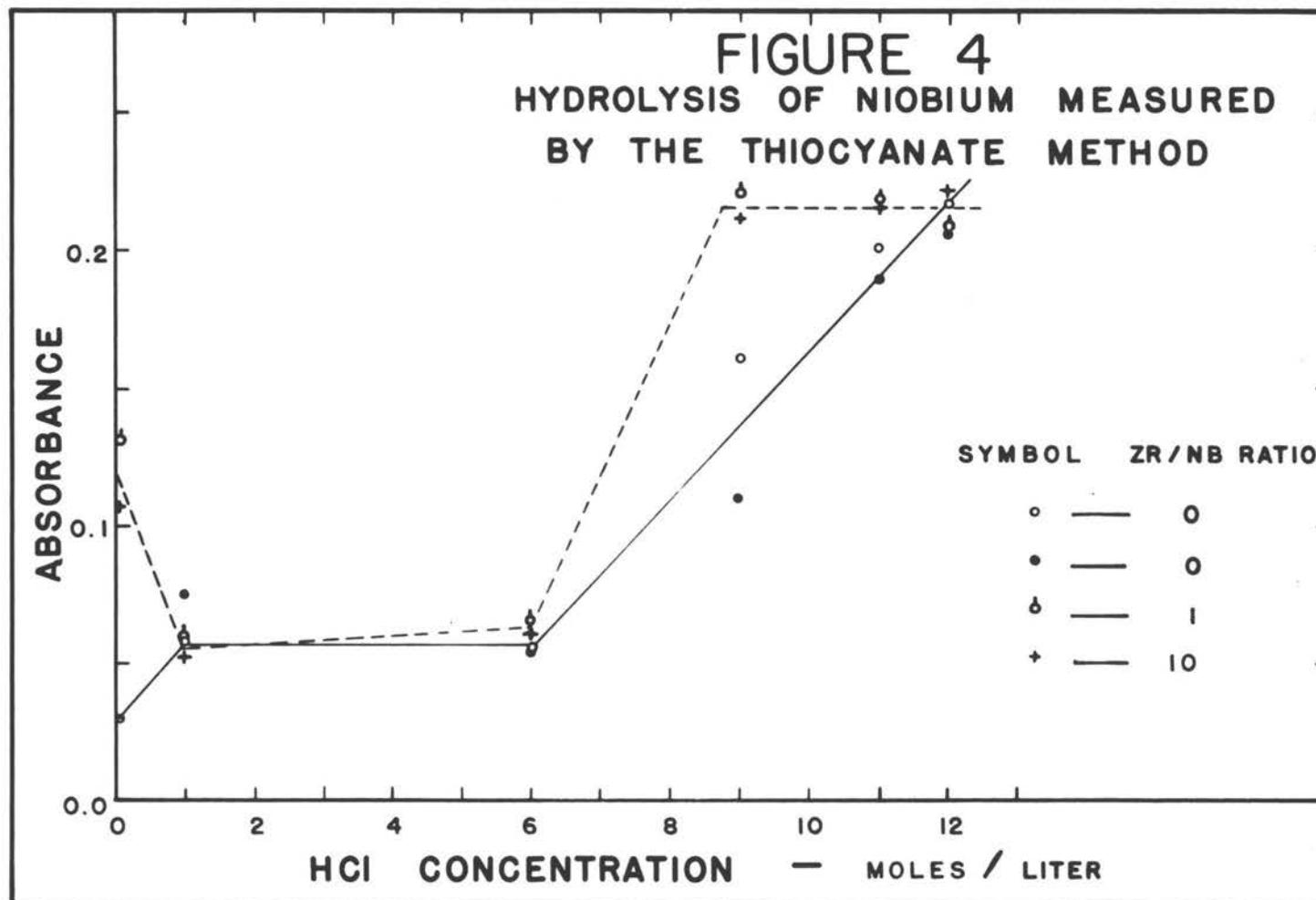
The anomalous behavior of niobium in dilute HCl solutions in the presence and absence of zirconium required further investigation. A point of attack on this problem was suggested by the variability of the absorbance of the niobium-thiocyanate complex prepared from niobium solutions 6 $\underline{N}$ or less in HCl. The further observation was made that the color in these samples increased rapidly with time while the samples prepared from more concentrated HCl solutions remained relatively constant.

Thiocyanate Studies of the Stability of Niobium in HCl Solutions - Samples containing 8 µg. Nb/ml. were prepared in solutions of varying HCl concentrations and allowed to age five days. The HCl concentrations were determined by density measurements with a Westphal balance (see Appendix C). The thiocyanate complex was formed from portions of these samples and the absorbance measured at 385 mµ at the times, measured from the time of adding the thiocyanate, indicated in Table V. Figure 5 displays this data and Figure 6 is the same with the blank curves subtracted (blank 1BR was carried along with samples 2R and 3R; 4BR with the remainder).

Several features of these curves are surprising. The first of these is the rapid increase of absorbance in those samples prepared from niobium solutions less than 8 $\underline{N}$ in HCl. Stranger yet is the fact that after three

TABLE V

ABSORBANCE VS. TIME FOR Nb-THIOCYANATE COMPLEX
OBTAINED AFTER HCl SOLUTION HAD AGED 5 DAYS

(All absorbances vs. water blank)

Sample No.	HCl moles/l.	Hrs.	A
1BR	--	0.22	0.014
		.30	.012
		.38	.013
		.50	.017
		.62	.016
		3.17	.055
		3.27	.059
		5.82	.130
2R	11.8	0.25	0.390
		.37	.372
		.48	.374
		.60	.371
		3.15	.402
		3.27	.401
		5.80	.458
3R	11.4	0.28	0.362
		.33	.354
		.45	.350
		.57	.350
		3.17	.375
		3.22	.375
		5.77	.414
4BR	--	0.35	0.010
		.42	.010
		.75	.021
		.87	.025
		2.03	.044
		2.20	.052
		4.98	.150

TABLE V (Cont'd.)

Sample No.	HCl moles/l.	Hrs.	A
5R	9.88	0.30	0.375
		.38	.365
		.72	.365
		.82	.368
		1.98	.391
		2.15	.389
		4.93	.458
6R	7.96	0.28	0.365
		.37	.364
		.70	.358
		.80	.362
		1.95	.391
		2.13	.389
		4.92	.456
7R	5.96	0.32	0.182
		.43	.194
		.52	.205
		.78	.251
		1.42	.273
		5.15	.640
8R	.985	0.30	0.086
		.40	.117
		.50	.138
		.75	.195
		1.40	.227
		5.15	.618
9R	0.387	0.30	0.071
		.42	.096
		.50	.118
		.77	.175
		1.42	.219
		5.12	.599

FIGURE 5
STABILITY OF THE NIOBIUM-
THIOCYANATE COMPLEX

SYMBOL		SAMPLE
●	——	I BR
○	——	2 R
◊	——	3 R
+	——	⎰ 5 R
		⎱ 6 R
△	——	7 R
–·–		8 R
▪	——	9 R
▲	——	4 BR

ABSORBANCE

TIME — HOURS
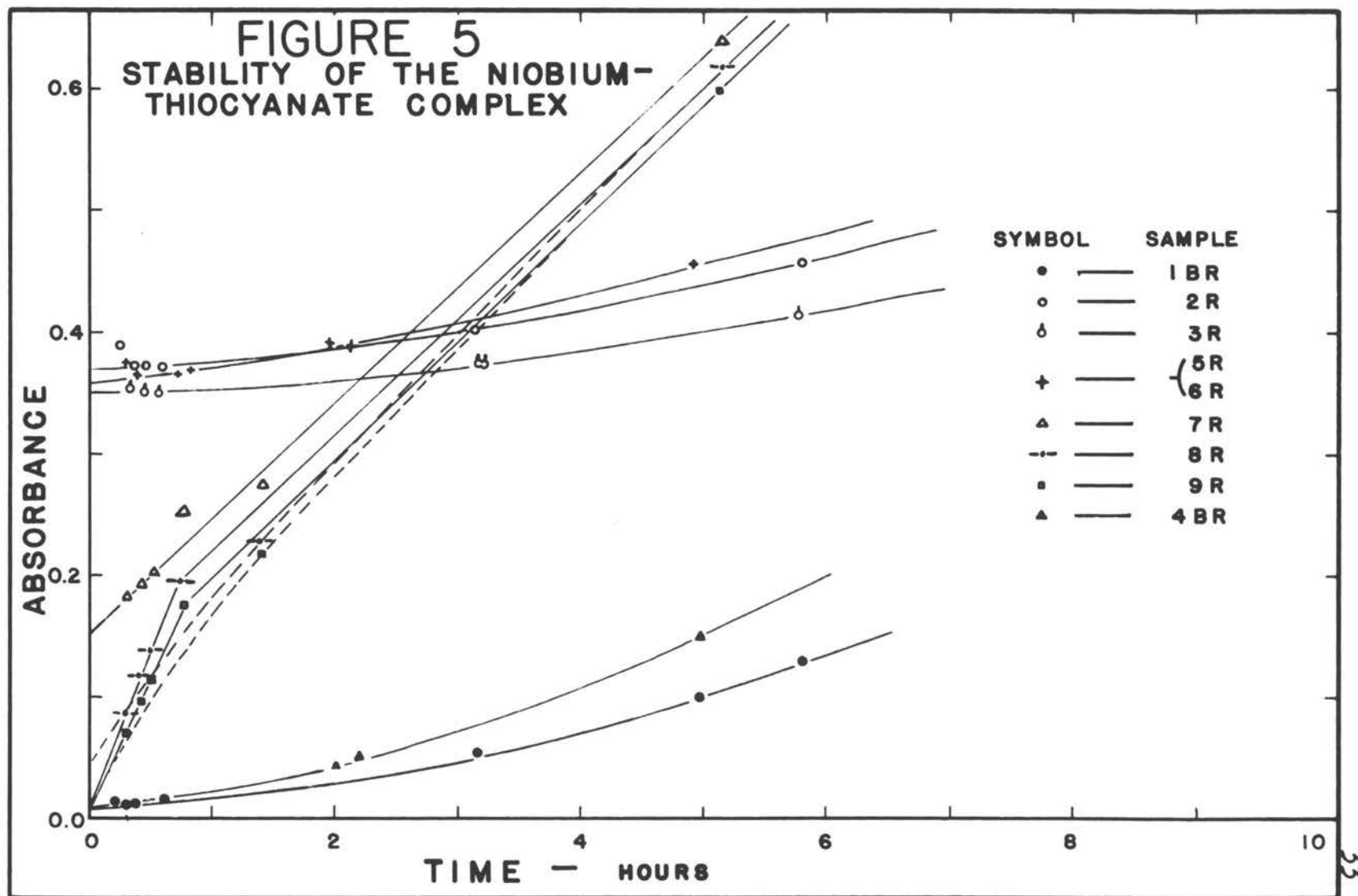
FIGURE 6
STABILITY OF THE NIOBIUM
THIOCYANATE COMPLEX
NET CURVES

SYMBOL	SAMPLE
○	2R
●	3R
⦶	5&6R
+	7R
▪	8R
△	9R

ABSORBANCE

TIME — HOURS
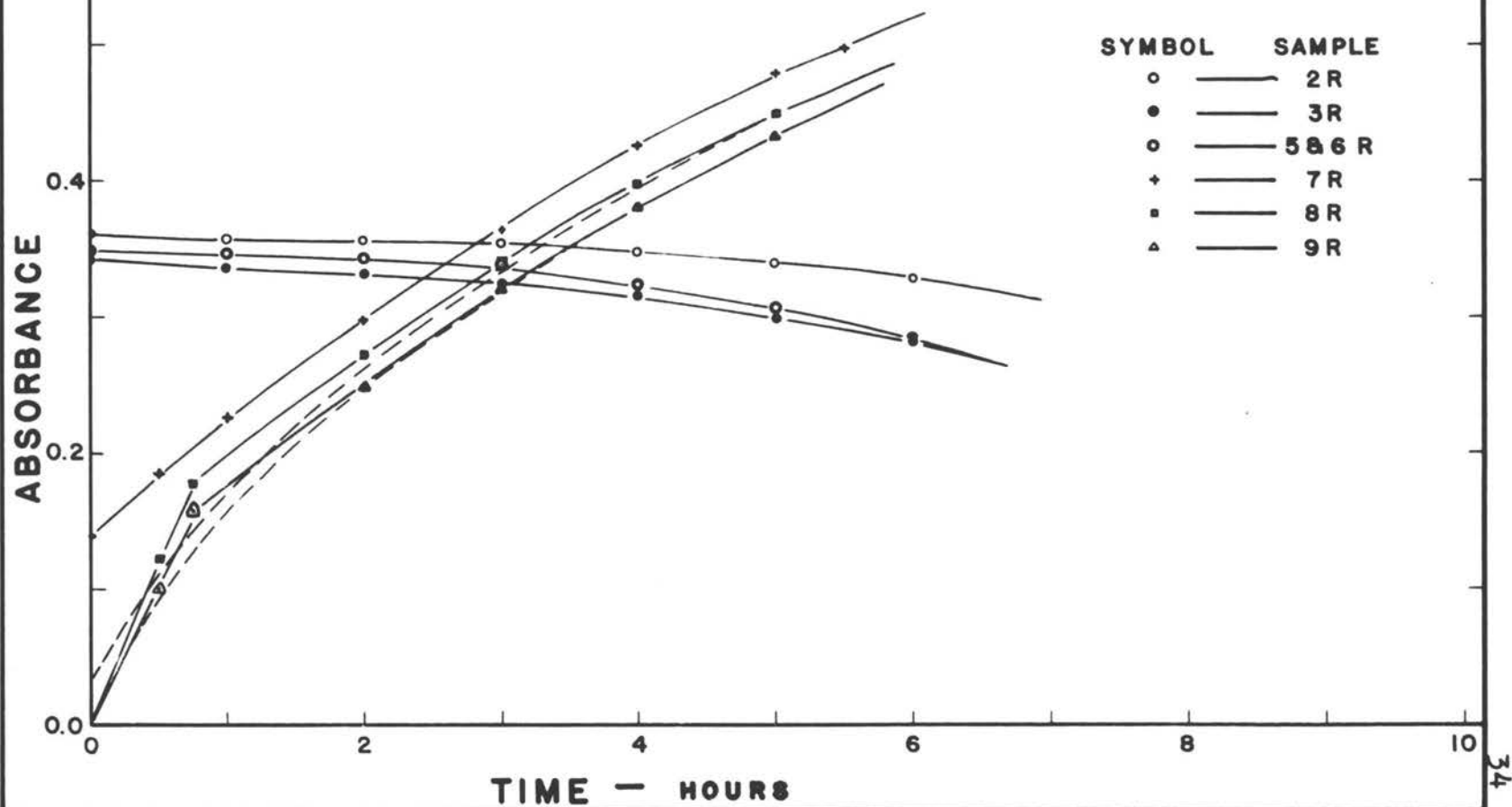
hours, the net absorbance of these solutions became greater than that of the more concentrated solutions.

One possible explanation for this behavior is that the color is formed by two different processes; the first a true complex formation, the second a polymerization of thiocyanate which is catalyzed by the form of niobium present in HCl of less than 8 $\underline{N}$ concentration.

The first few measurements on each sample were made without removing the samples from the spectrophotometer so that these samples were irradiated at 385 mμ several times. The subsequent measurements were made with solution that had not previously been exposed to the high intensity ultraviolet light of the spectrophotometer. The steep initial slope of the curves can be explained as due to a photo-catalyzed polymerization of the thiocyanate.

The experiment was repeated exactly except that in addition to the 8 μg. Nb/ml., the solutions contained 10 μg. Zr/ml. Table VI and Figure 7 display the data of this experiment. Figure 8 shows the variation of absorption with time after the contribution of the blank was subtracted.

A comparison of the curves shown in Figure 6 (without zirconium) with those in Figure 8 (with zirconium) yields some interesting contrasts. The curves for the samples of high HCl concentration are practically

TABLE VI

ABSORBANCE VS. TIME FOR Nb-THIOCYANATE COMPLEX
OBTAINED AFTER Nb-Zr-HCl SOLUTIONS
HAD AGED 13 DAYS

Sample No.	HCl moles/l.	Hrs.	A
10BR	--	0.10	0.007
		.22	.010
		.32	.012
		.67	.025
		.88	.033
		2.13	.040
		3.10	.072
		5.85	.168
		8.68	.233
11R	.397	0.08	0.026
		.22	.045
		.30	.056
		.57	.090
		.78	.114
		1.87	.146
		3.00	.196
		5.77	.311
		8.42	.394
12R	.76	0.10	0.030
		.17	.036
		.22	.042
		.48	.076
		.70	.102
		1.77	.140
		2.92	.194
		5.77	.317
		8.48	.405
13R	5.62	0.08	0.113
		.20	.120
		.33	.126
		.50	.139
		.85	.174
		1.87	.197
		5.07	.350
		7.65	.439

TABLE VI (Cont'd.)

Sample No.	HCl moles/l.	Hrs.	A
14R	7.42	0.05	0.370
		.23	.369
		.40	.367
		.77	.374
		1.77	.390
		4.93	.465
		7.55	.528
15R	9.23	0.08	0.360
		.15	.359
		.67	.367
		1.68	.383
		4.88	.452
		7.45	.511
16BR	--	0.05	0.006
		.30	.013
		.47	.020
		.62	.027
		4.07	.105
		6.38	.177
17R	10.31	0.10	0.359
		.29	.359
		.42	.360
		.58	.360
		4.05	.438
		6.35	.488
18R	11.73	0.10	0.360
		.13	.361
		.30	.362
		.47	.363
		3.92	.448
		6.23	.500

FIGURE 7

STABILITY OF THE NIOBIUM-THIOCYANATE COMPLEX. SAMPLES CONTAINING ZIRCONIUM

FIGURE 8

STABILITY OF THE NIOBIUM-THIOCYANATE COMPLEX. SAMPLES CONTAINING ZIRCONIUM NET CURVES
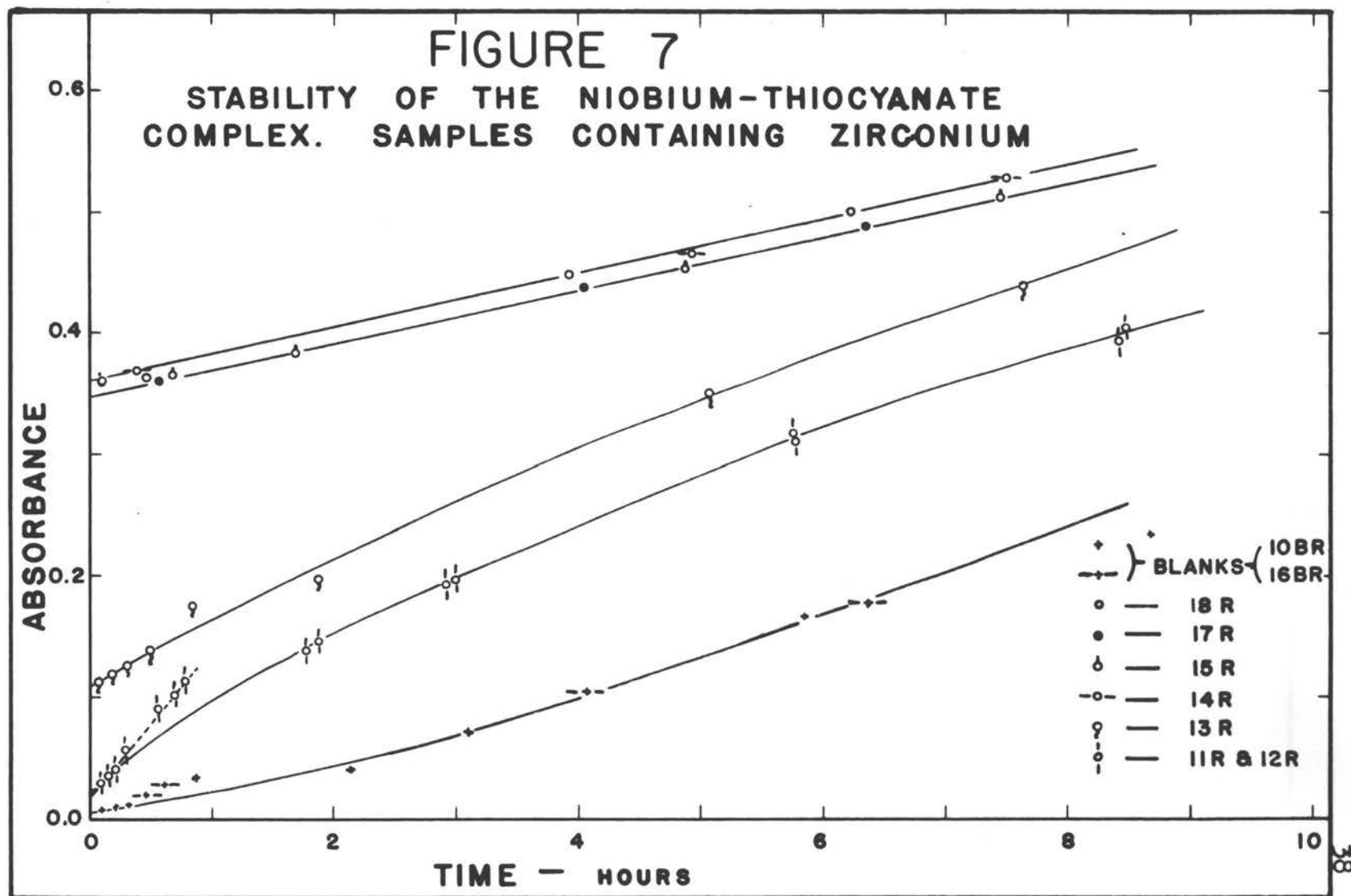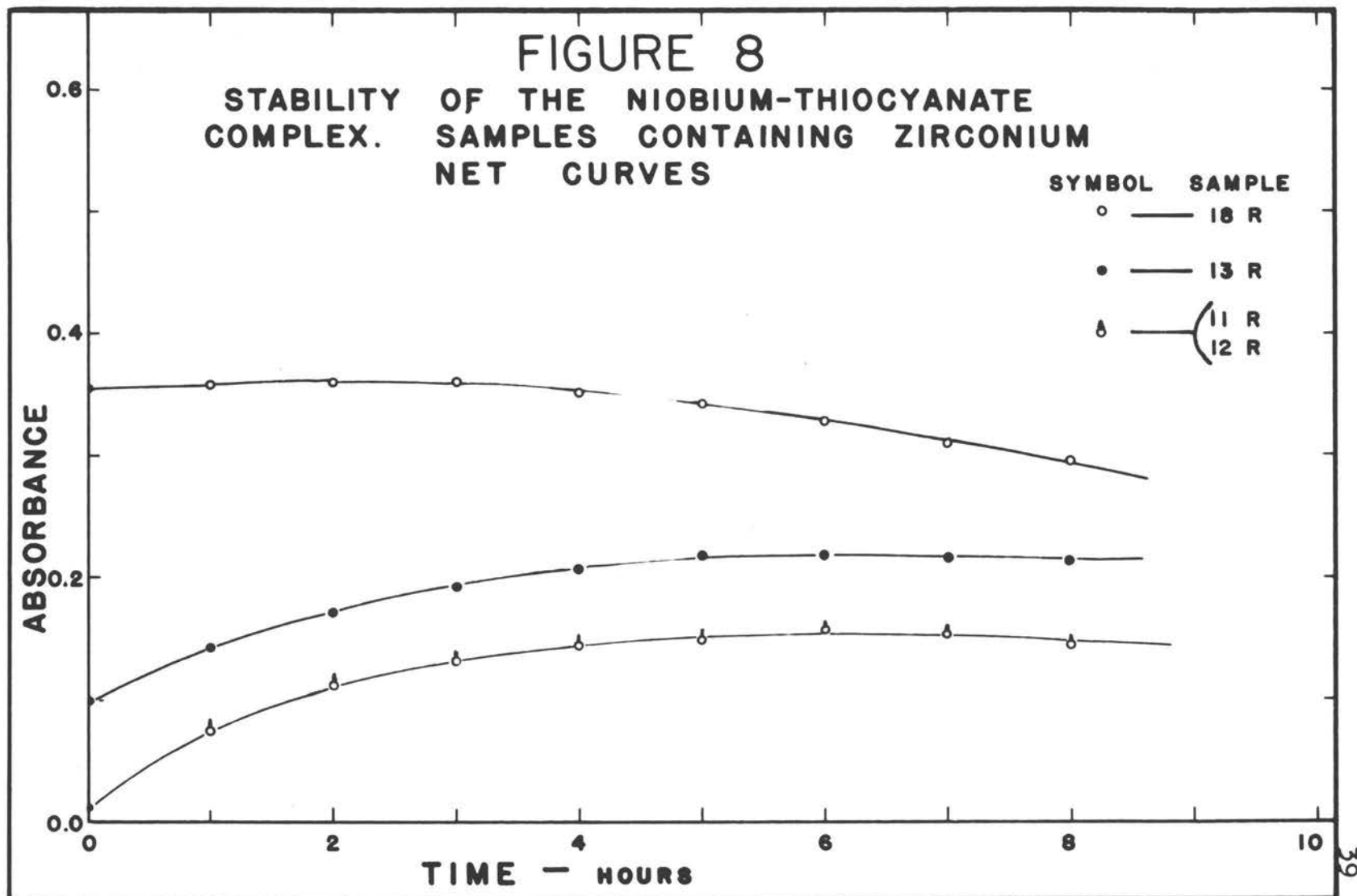
identical. But in low HCl concentrations, the absorbance
of the zirconium containing samples has none of the exal-
tation attributed to thiocyanate polymerization that the
pure niobium solutions exhibit. The lower curves seem to
approach the upper curves as a limit.

The negative slope of the net curves in the concen-
trated HCl solutions may be attributable to the gradual
decomposition of the thiocyanate in acid solution, to the
slow hydrolysis of niobium because the color samples are
only 2.5-3.0 $\underline{N}$ in HCl, or possibly the effect is only an
apparent one caused by negative catalysis of the high acid
niobium solutions on the thiocyanate polymerization.
Likewise the positive slope of the lower HCl samples in
Figure 8 could be caused by a slow conversion of some un-
available form of niobium into a species which will pro-
duce the thiocyanate complex. It is to be expected that
these two tendencies would have some equilibrium value so
that all samples would eventually end up having the same
absorbance, independent of their previous histories and
determined only by the conditions existing in the color
forming solution.

The postulation of the presence of colloidal phases
in the above systems seems to be consistent with most of
the observed facts. This is strongly suggested by the
sharp differences in the behavior of niobium when present

in dilute and in concentrated HCl solutions. The effect
of zirconium on the acid hydrolysis and the colorimetric
determination of niobium could be explained by mixed
crystal formation or by hydrolysis of zirconium and
adsorption of niobium on the colloidal phase of zirconium.

The Ultraviolet Absorption Spectra of Zirconium and
Niobium - An investigation of the ultraviolet absorption
spectra of HCl solutions of zirconium and niobium was con-
ducted in an effort to develop a means of measuring the
niobium present in ionic form without disturbing the
chemical composition of the systems. The fault of the
thiocyanate procedure lay in the introduction of a com-
peting complex system which disturbed the equilibria
actually under investigation.

A concentrated HCl solution containing 125 μg. Nb/
ml. was prepared by wet oxidation with sulfuric and nitric
acids of a tartrate solution of niobium. The sulfate was
eliminated by precipitating the hydrous oxide, centri-
fuging, decanting, and taking up the precipitate in
concentrated HCl. A solution of 2.5 μg./ml. was also
prepared by dilution of the more concentrated solution.
The absorption curves of these solutions are shown in
Figure 9. Another solution was prepared without the use
of tartrate as mentioned in the chapter on apparatus and
solutions. The net absorption curve for this solution (at

FIGURE 9

ABSORPTION OF NIOBIUM IN
CONCENTRATED HCl

125 μG./ML.

10 μG./ML.

2.5 μG./ML.

ABSORBANCE

WAVELENGTH — mμ

42
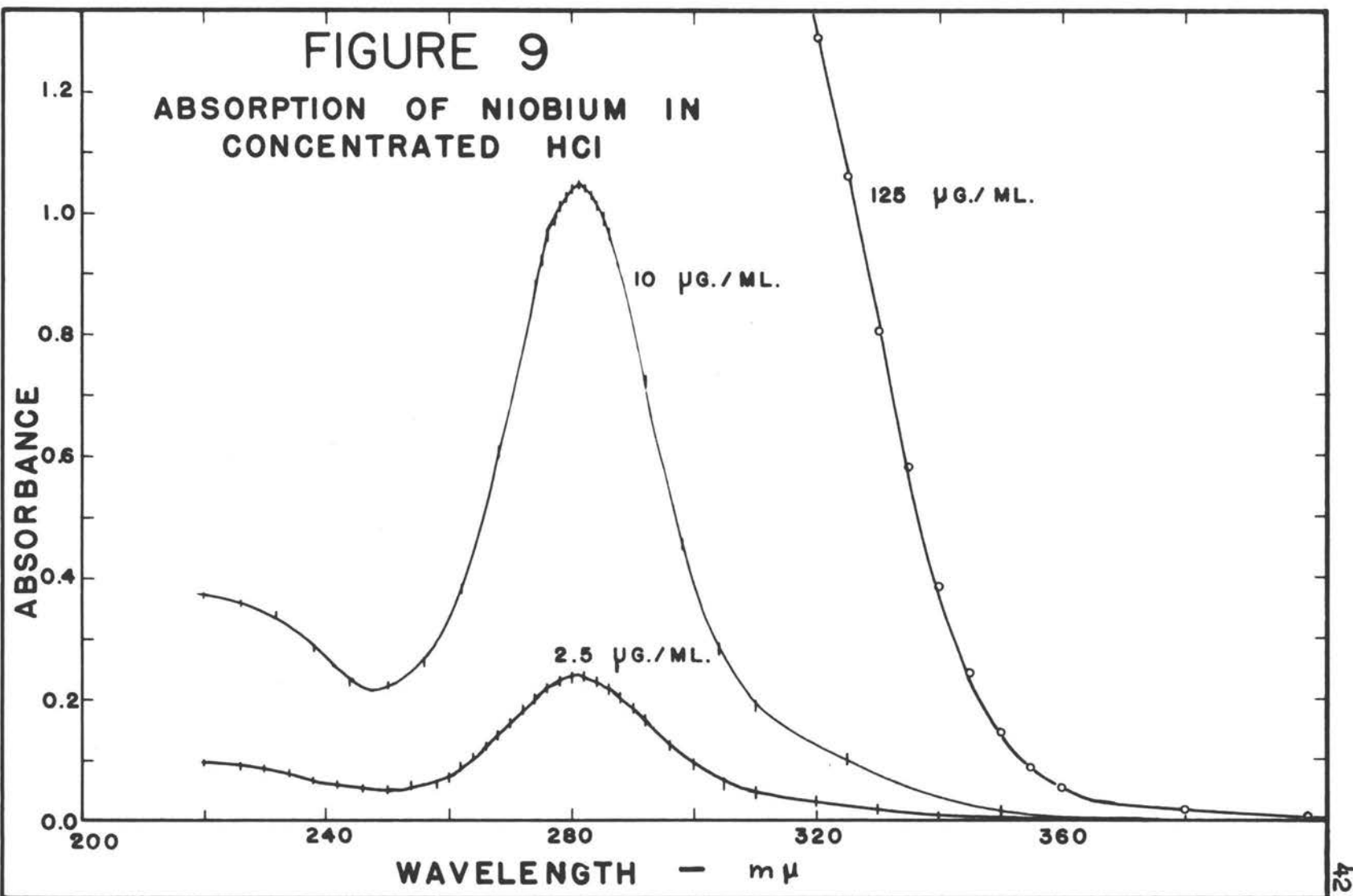
a concentration of 10 μg. Nb/ml.) is also given in Figure 9.

Figure 10 gives the ultraviolet absorption curves for solutions of zirconium in concentrated HCl.

Five mg. of ammonium chloride was dissolved in 25 ml. of concentrated HCl and the absorption of this solution was measured against a concentrated HCl blank. The purpose of this experiment was to determine if the absorption peak observed at 281 mμ could be due to contamination of the niobium solution by ammonium chloride during the sample preparation. The data given in Table VII show that this is not the case.

TABLE VII

ABSORPTION AT 281 mμ OF NH$_4$Cl IN
CONCENTRATED HCl

Slit Width (mm)	Wavelength (mμ)	Absorbance
.60	250	- .009
.56	260	- .007
.53	270	- .005
.52	280	- .005
.50	290	- .005
.47	300	- .006

FIGURE 10
ABSORPTION OF ZIRCONIUM
IN HCl
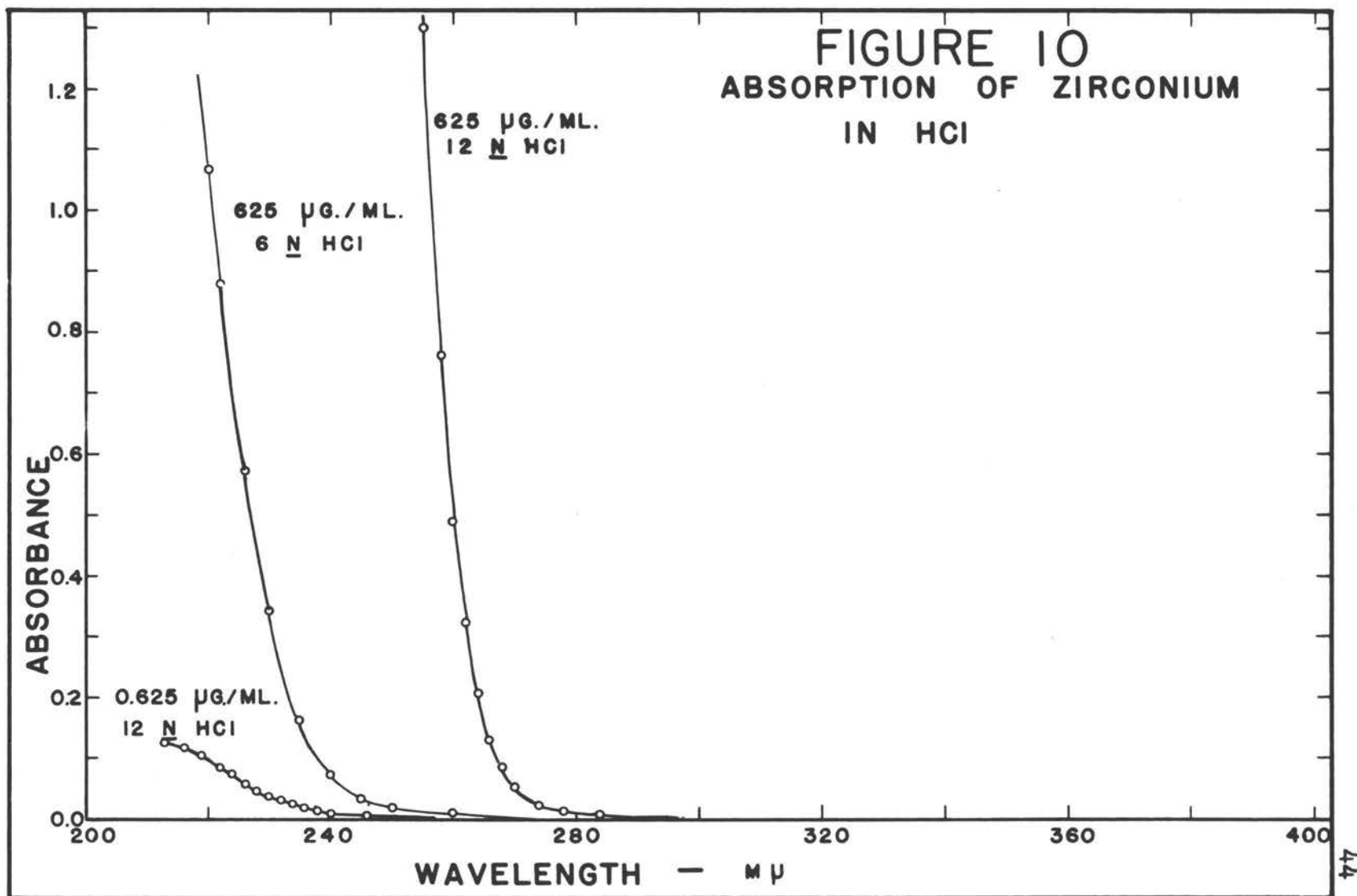
It must be considered to be established, then, that niobium in concentrated HCl solution exhibits an ultraviolet absorption curve having a maximum 281 mμ which appears to be proportional to the concentration of niobium. (During the completion of this investigation, a publication appeared which confirms this fact (9).)

This system may be useful for analytical purposes, and the development of the method is given in a later section of this thesis.

Spectrophotometric Work on Species in HCl Solutions - An experiment was conducted to determine if the profound changes in the behavior of niobium caused by different concentrations of HCl and by the presence of zirconium could be investigated by ultraviolet absorption measurements.

The samples were prepared by introducing, with a pipet, a certain amount of a solution of niobium in concentrated HCl into volumetric flasks. These were diluted with HCl of different concentrations so as to obtain a series of solutions having the same concentration of niobium but different HCl concentrations.

The samples contained 8 μg. Nb/ml. HCl concentrations were measured with the Westphal balance (Appendix C). The absorbance was measured as a function of time at 281 and 220 mμ, as shown in Table VIII. The complete

TABLE VIII

ABSORBANCE VS. TIME FOR Nb SOLUTIONS
IN VARIOUS HCl CONCENTRATIONS

(All absorbances vs. HCl blank)

Sample No.	HCl Concentration	Wave-length, mμ	Hrs.	A
12	11.8	220	0.10	.308
			.97	.315
			4.30	.319
		281	.12	.869
			.95	.868
			4.32	.870
11	11.4	220	0.07	.295
			.85	.291
			4.67	.288
		281	.05	.828
			.88	.828
			4.65	.828
10	9.88	220	0.03	.290
			.85	.287
			4.62	.286
		281	.05	.776
			.83	.772
			4.63	.771
8	7.96	220	0.05	.320
			.80	.316
			4.62	.316
		281	.03	.455
			.83	.450
			4.60	.449
6	5.96	220	0.05	.366
			.80	.399
			4.57	.470
		281	.07	.059
			.78	.066
			4.60	.085

TABLE VIII (Cont'd.)

Sample No.	HCl Concentration	Wavelength, mμ	Hrs.	A
1	0.985	220	0.07	.618
			.73	.640
			4.58	.690
		281	.05	.064
			.75	.074
			4.57	.079
0.1	0.387	220	0.05	.601
			.75	.630
			4.38	.630
		281	.07	.060
			.73	.068
			4.40	.073

ultraviolet curves for these solutions as shown in Figure
11 were measured five days after the solutions were pre-
pared.

The ultraviolet absorption of niobium solutions is
a function of HCl concentration. The general trends are
marked: at 281 mμ the absorbance decreases with decreas-
ing HCl concentration, the maximum there disappearing at
a concentration of about 6 $\underline{N}$. For the shorter wavelengths,
this trend is reversed. At 220 mμ the absorbance in-
creases in a somewhat irregular manner with decrease in
HCl concentration. This type of behavior certainly
suggests the presence of several absorbing species, their
relative concentrations being determined by their stabili-
ties under the conditions pertaining.

Let us assume that curve 1 of Figure 11 represents
the absorption due to one species. If we diminish this
curve in proportion to the decrease of the peak at 281 mμ
(assuming that its height is proportional to the concen-
tration of that species) and subtract the curve so obtained
from one actually measured for the solution, the difference
should represent the absorbance due to all other species
in that solution. The difference curves produced in this
way are shown in Figure 12.

In view of the admittedly rough nature of the
assumptions, these curves show a surprisingly well defined

FIGURE II

ABSORPTION OF NIOBIUM SOLUTIONS
OF VARIOUS HCl CONCENTRATIONS

CURVE	$\underline{N}$ HCl
1	11.8
2	11.4
3	9.88
4	7.96
5	5.96
6	{ .985 .387

ABSORBANCE

WAVELENGTH — Mμ
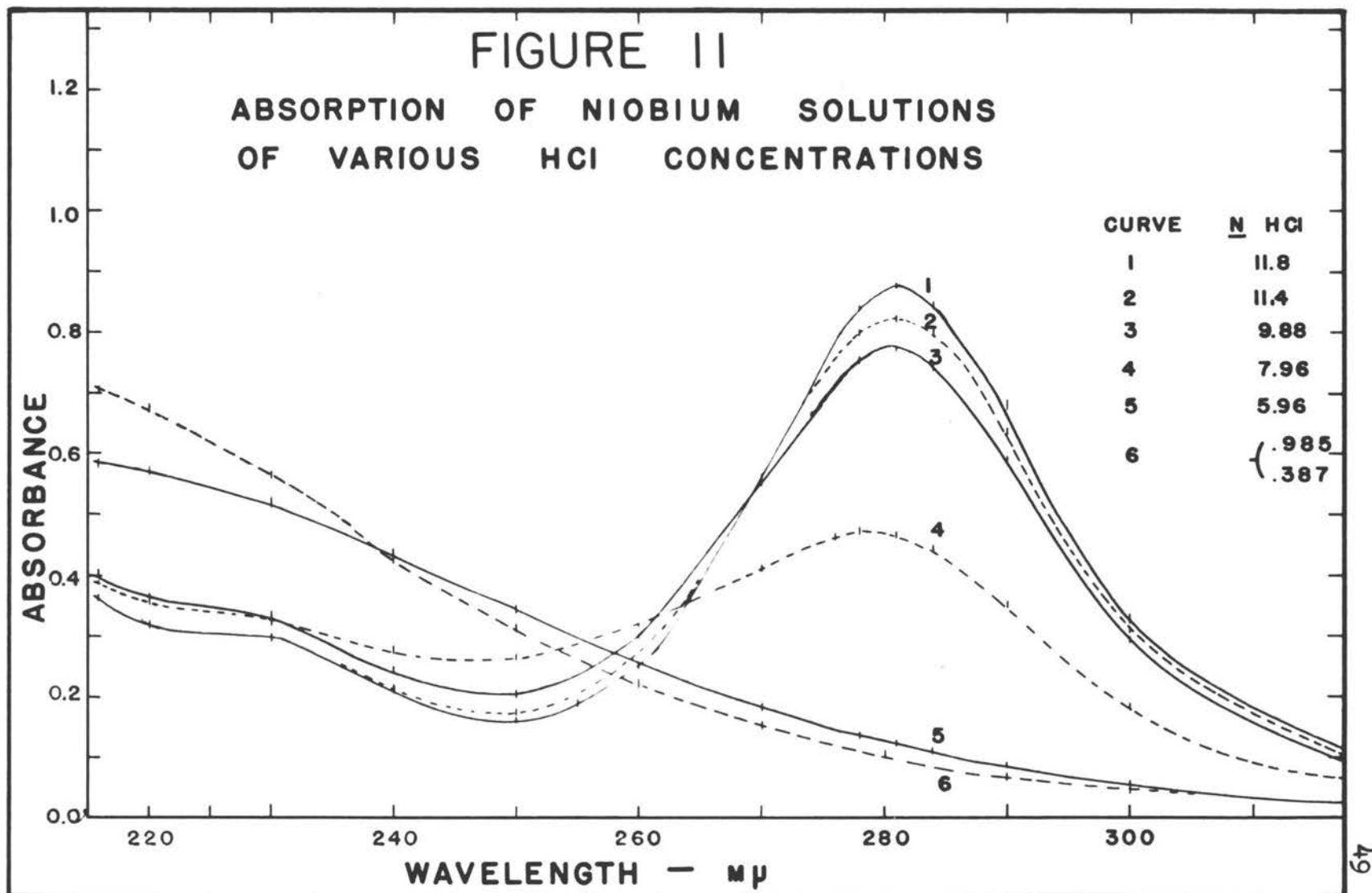
FIGURE 12

ABSORPTION OF NIOBIUM – HCl SOLUTIONS

AFTER SUBTRACTION OF THE 281 mμ PEAK.

SYMBOL	N HCl
1	.985 & .387
2	5.96
3	7.96
4	9.66
5	11.4
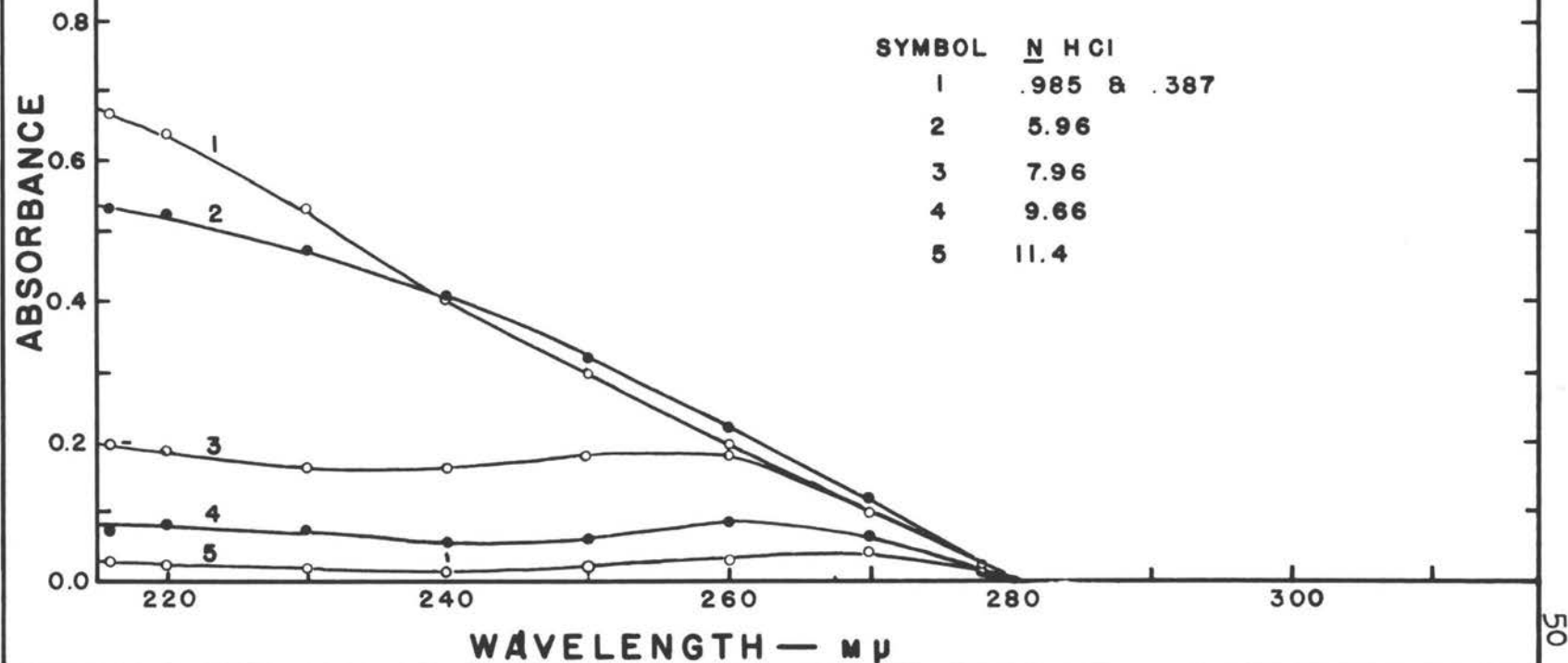
peak at intermediate concentrations in the region of 260 mμ. This is superimposed upon a steadily rising absorption extending beyond the lower limit of the instrument (below 215 mμ). This may be taken as corroboration of the work of Kraus and Moore (33,p.13), who required three species to explain the anion exchange behavior of niobium in HCl-HF mixtures. On the other hand, the absorption in the lowest acid concentrations may be an apparent absorption due to preferential scattering of the short wave-length radiation caused by growth of colloidal-sized particles rather than a real absorption.

While not conclusive, these results indicate that a more careful investigation along these lines may yield sufficiently sharp separation of the peaks to allow the application of certain of the methods available to determine the exact nature of the species.

Using the data of Figures 11 and 12, it is possible to show in another way the necessity for a third species as indicated in Table IX. The table was constructed in the following manner:

Assumptions:

    1.   There are only two ionic species in HCl solutions.

    2.   In 11.8 $\underline{N}$ HCl only one species (A) is present.

3. The absorbance at 281 mμ is a measure of the concentration of (A).

4. In 1 $\underline{N}$ HCl a different species (B) is the only significant ionic species present.

5. The absorption at 220, after the contribution of species (A) at this wavelength has been subtracted (Figure 13), is a measure of the concentration of (B).

In each solution the fractions of the total niobium in form (A) and (B) were calculated and the sum listed in the final column.

If all of the assumptions are correct, then the total niobium fraction should equal 1.00 within experimental error. This is true down to an HCl concentration of 10 $\underline{N}$, but below that it appears that a third species may constitute as high as 20% of the total. Although assumptions 2-5 are admittedly rather rough, the chance of a 20% error arising from their failure is not likely. In fact, it might be expected that colloid formation, a definite possibility, would result in positive deviations from unity rather than negative variations as observed.

TABLE IX

RELATIVE AMOUNTS OF COMPLEX SPECIES
IN HCl SOLUTIONS

Curve from Fig.11	Net Absorbance 281 mμ Fig. 11	Fraction (A)	Curve from Fig.12	Absorbance 220 mμ Fig. 12	Fraction (B)	Sum of Fractions
1	0.875	1.000		0.000	0.000	1.000
2	.819	.935	5	.024	.034	.969
3	.763	.873	4	.083	.130	1.003
4	.438	.501	3	.187	.291	.792
5	.042	.048	2	.528	.826	.874
6	.000	.000	1	.640	1.000	1.000

It seems quite probable that assumption 1 is not valid;
that there are, in fact, more than two ionic species
present.

The Influence of Zirconium on the Ultraviolet

Spectrum of Niobium - A series of hydrochloric acid solu-
tions similar to those in the preceding section were pre-
pared containing 10 μg. Zr/ml. as well as 8 μg. Nb/ml. A
third series containing 10 μg. Zr/ml. alone was also pre-
pared. The absorbances were measured at selected wave-
lengths as a function of time after preparation. The data
obtained are recorded in Tables X and XI.

TABLE X

ABSORBANCE VS. TIME FOR 10 µg./ml. OF Zr
IN VARIOUS HCl SOLUTIONS AT 234 mµ

Sample No.	HCl Concentration	Hrs.	A
12Z	12.42	0.15	0.571
		.83	.576
		2.20	.569
		5.20	.560
		150	.570
11Z	11.40	0.03	0.328
		.70	.346
		2.07	.325
		5.07	.320
		150	.334
10Z	10.37	0.03	0.105
		.68	.105
		2.02	.094
		5.03	.094
		150	.108
8Z	8.29	0.05	0.017
		.70	.009
		2.00	.019
		4.98	.011
		150	.000
6Z	6.21	0.06	0.013
		.63	.012
		1.97	.005
		4.97	.008
		150	.001
1Z	1.04	0.05	0.012
		.58	.011
		1.95	.005
		4.92	.005
		150	.002
0.1Z	0.20	0.03	0.017
		.58	.003
		1.92	.006
		4.90	- .001
		150	- .004

TABLE XI

ABSORBANCE VS. TIME FOR Nb-Zr SOLUTIONS IN VARIOUS HCl CONCENTRATIONS

Sample No.	HCl concentration	Wavelength, $m\mu$	Hrs.	A
12N	11.73	234	0.05	0.825
			.80	.822
			2.45	.820
			7.62	.815
			a	.830
		281	.08	.877
			.78	.874
			2.47	.878
			7.65	.880
			a	.880
11N	10.31	234	0.07	0.470
			.75	.500
			2.45	.474
			7.62	.451
			a	.446
		281	.05	.800
			.77	.816
			2.47	.814
			7.60	.804
			a	.790
10N	9.23	234	0.05	0.332
			.73	.325
			2.42	.329
			7.60	.317
			a	.315
		281	.07	.702
			.72	.700
			2.47	.702
			7.62	.700
			a	.690
8N	7.42	234	0.07	0.307
			.67	.310
			2.47	.310
			7.58	.308
			a	.300

TABLE XI (Cont'd.)

Sample No.	HCl Concentration	Wavelength, mμ	Hrs.	A
8N	7.42	281	0.05	0.293
			.68	.295
			2.43	.292
			7.57	.290
			a	.300
6N	5.62	234	0.03	0.330
			.67	.402
			2.43	.449
			7.53	.474
			a	.516
		281	.07	.056
			.63	.075
			2.47	.092
			7.55	.101
			a	.112
1N	0.76	234	0.07	0.408
			.62	.449
			2.45	.464
			7.53	.469
			a	.490
		281	.05	.053
			.63	.067
			2.43	.075
			7.52	.078
			a	.090
0.1N	0.397	234	0.05	0.397
			.62	.434
			2.40	.444
			7.50	.451
			a	.490
		281	.07	.048
			.60	.060
			2.43	.063
			7.52	.067
			a	.078

a After 5 days - obtained from Figure 13.

No significant change with time is noted in the absorbance of the zirconium solutions at 234 mμ. The measurements at 150 hours are plotted as curve 2 of Figure 13. Here is an indication of the presence of at least two species of zirconium. One of these is stable at low HCl concentrations and does not absorb in the region 215-350 mμ, while the other, stable above 8 $\underline{M}$ HCl concentration, has an absorption peak just below 215 mμ. The previously mentioned anion exchange study (33,p.13) also postulates two species for zirconium in HCl-HF mixtures. It is instructive to note that the minimum in the solubility curve for $ZrOCl_2$ (21,p.205) occurs at about 8.5 $\underline{N}$ HCl. The zirconium species postulated provides an explanation for the increased solubility of zirconium at HCl concentrations above that value.

Curves 1 and 3 of Figure 13 represent measurements of absorbance at 281 mμ on aged niobium-hydrochloric acid samples with and without zirconium. The differences represented here could hardly be considered significant, especially in the region (1-6 $\underline{N}$ HCl) where the greatest effects on the niobium-thiocyanate complex were noted.

Figure 14 gives the ultraviolet absorption curves for niobium-zirconium hydrochloric acid solutions. The peak at 281 mμ behaves very nearly as it did in the absence of zirconium (see Figure 13). The very dilute

FIGURE 13

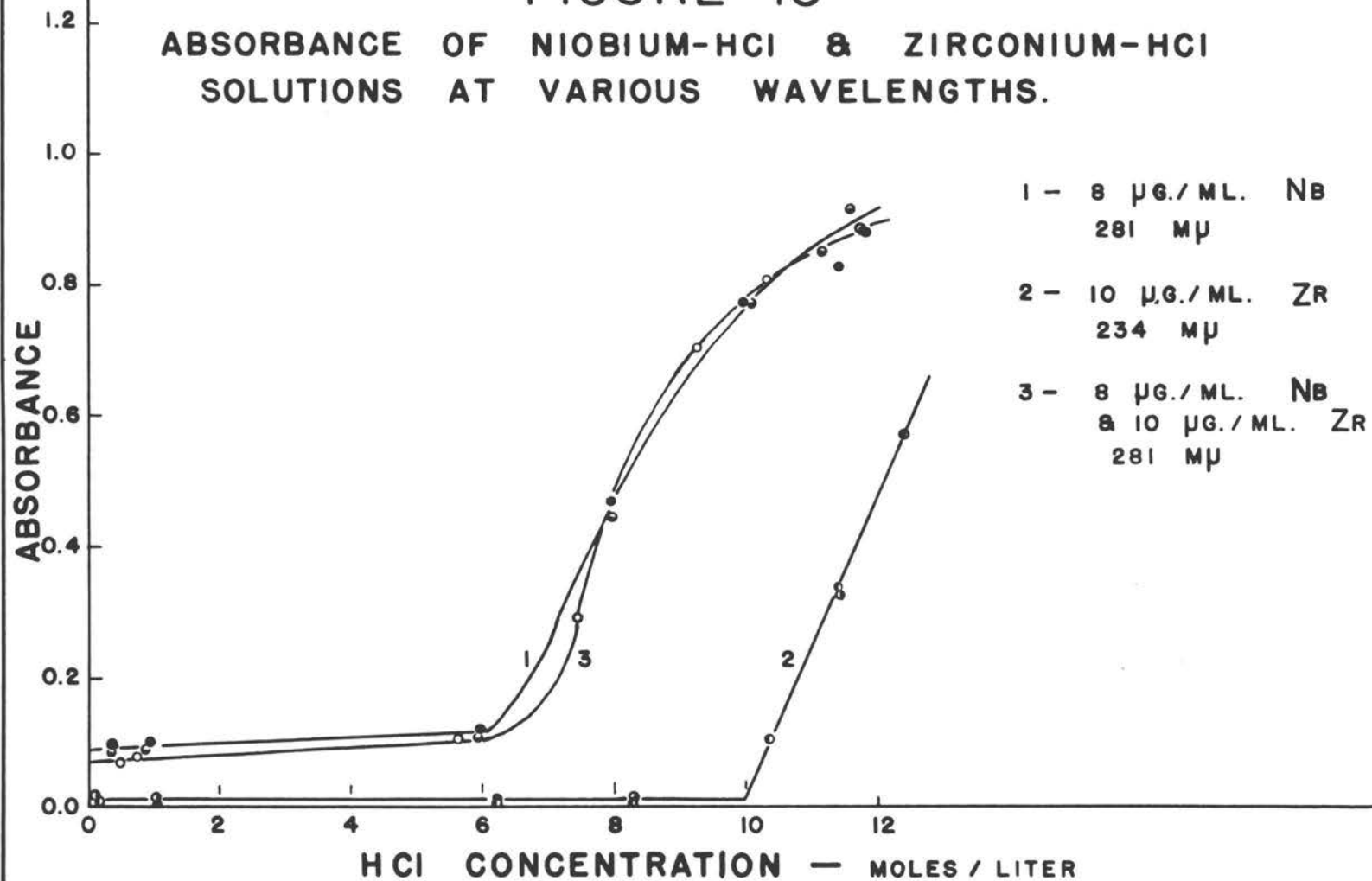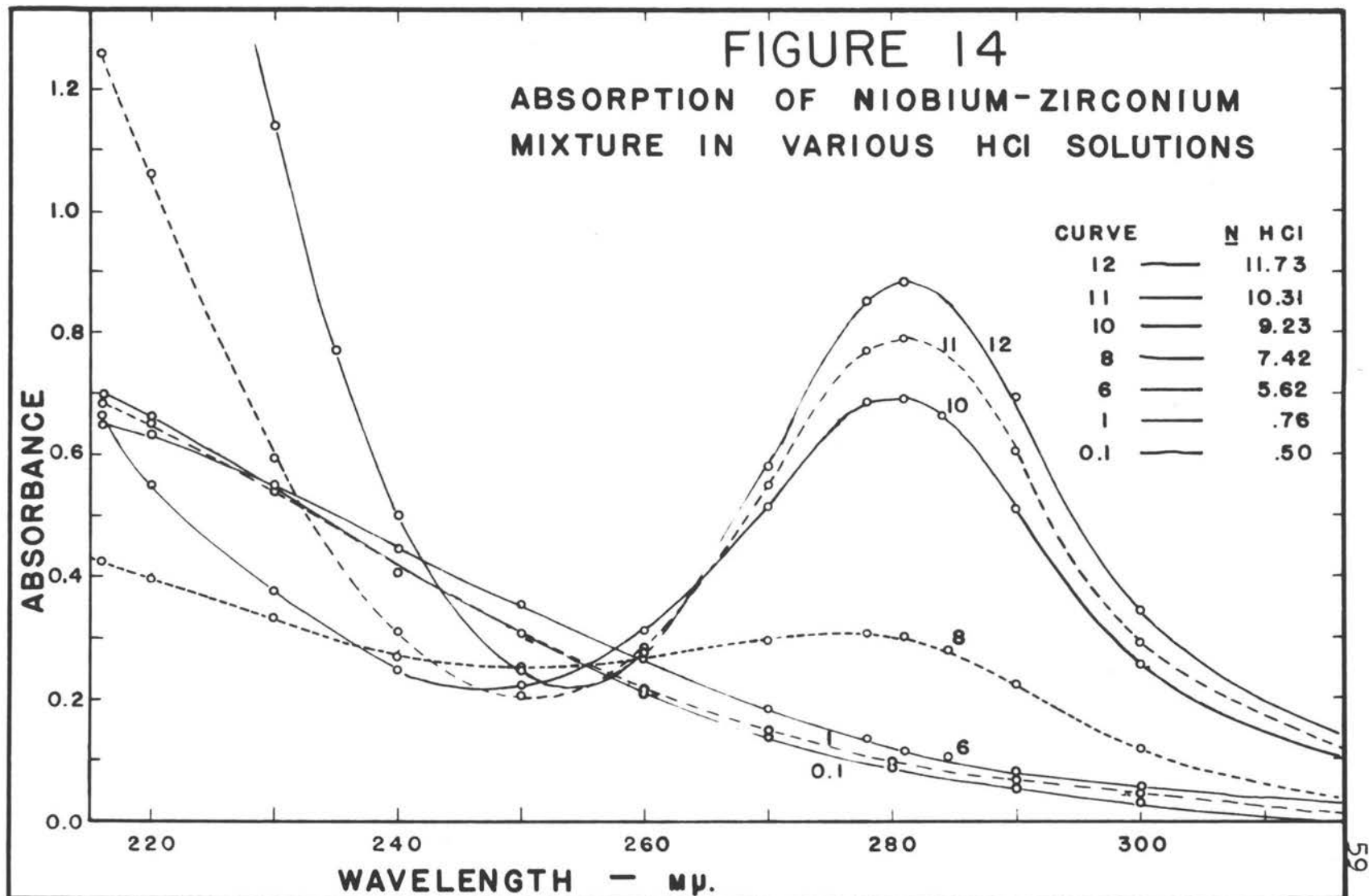ABSORBANCE OF NIOBIUM-HCl & ZIRCONIUM-HCl SOLUTIONS AT VARIOUS WAVELENGTHS.

1 — 8 μG./ML. NB
281 MΜ

2 — 10 μG./ML. ZR
234 MΜ

3 — 8 μG./ML. NB
& 10 μG./ML. ZR
281 MΜ

ABSORBANCE

HCl CONCENTRATION — MOLES / LITER

FIGURE 14
ABSORPTION OF NIOBIUM-ZIRCONIUM
MIXTURE IN VARIOUS HCl SOLUTIONS

CURVE		N HCl
12	——	11.73
11	——	10.31
10	——	9.23
8	——	7.42
6	——	5.62
1	——	.76
0.1	——	.50

solutions are identical, and in the intermediate concentrations there is good reason to believe that the curves represent the sum of the niobium and zirconium absorbances at each wavelength.

These results seem to rule out any ionic species as being the cause of the anomalous results in the thiocyanate complex investigation.

THE ULTRAVIOLET SPECTROPHOTOMETRIC
DETERMINATION OF NIOBIUM IN HYDROCHLORIC ACID

The need for a method for determining niobium that is rapid, accurate and suitable for routine application has already been discussed. The basis for such a method utilizing the spectrophotometric measurement of hydrochloric acid solutions was established in a previous section of this thesis. The necessary details of the effect of variables, the reproducibility of the method and a survey of interferences will complete the investigation to establish the method.

Figure 11 gives the variation in absorbance with change in HCl concentration. It is clear that the HCl concentration must be above 6 $\underline{M}$ before the analytically important peak at 281 mμ becomes useful. Since the absorbance increases while the rate of change decreases with increasing HCl concentration, the best conditions for the determination include using the highest possible concentration of this reagent that is conveniently obtainable. This will give maximum sensitivity and reliability to the method.

The niobium-chloride complex depends in a complicated manner upon both the hydrogen ion concentration and the chloride ion concentration. These effects and an attempt to explain them in terms of species present will

be given later. It is sufficient to point out that decreasing the chloride or hydrogen ion concentration independently causes a general decrease in the absorption peak at 281 mμ.

The analytical curve shown in Figure 15 was prepared by proper dilution of a 10 μg./ml. niobium solution with concentrated HCl. The data are given in Table XII. Beer's law is followed up to 10 μg. Nb/ml. The absorbance of the latter solution was 1.05. No attempt was made to verify this relationship at higher concentrations.
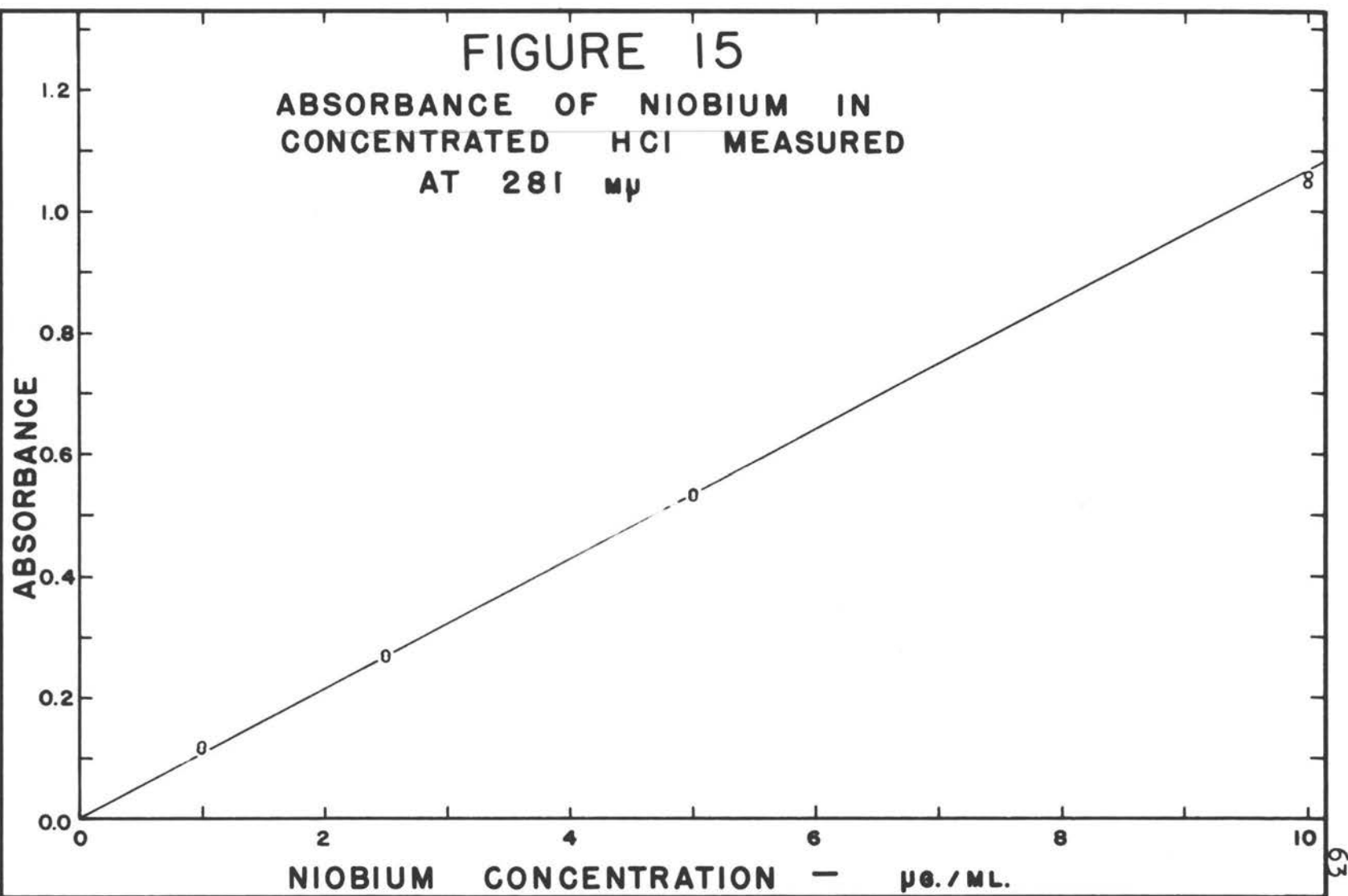
TABLE XII

ABSORBANCE AT 281 mu OF NIOBIUM
SOLUTIONS IN CONCENTRATED HCl

Sample No.	Concentration of Niobium (μg./ml.)	Absorbance
1	10.0	1.045
2	5.0	.530
3	2.5	.270
4	1.0	.116
5	10.0	1.06
6	5.0	.536
7	2.5	.264
8	1.0	.120

FIGURE 15

ABSORBANCE OF NIOBIUM IN
CONCENTRATED HCl MEASURED
AT 281 mμ

ABSORBANCE

NIOBIUM CONCENTRATION — μg./ML.

The reproducibility of the method was determined by measuring the absorbance at 281 mμ of six runs of five samples each, prepared and measured over a period of one week. Five supposedly identical volumetric flasks were used for all six runs. For each run, an aliquot of niobium solution was introduced such that the final concentration would be 5 μg. Nb/ml. when the flask was filled to the mark with concentrated HCl. Table XIII shows the absorbance values obtained.

TABLE XIII

REPRODUCIBILITY DATA

Run	Flask No.				
No.	1	2	3	4	5
1	0.530	0.525	0.525	0.523	0.525
2	0.533	0.524	0.523	0.521	0.522
3	0.528	0.524	0.521	0.518	0.517
4	0.523	0.523	0.516	0.519	0.519
5	0.523	0.518	0.514	0.514	0.515
6	0.538	0.518	0.515	0.515	0.516

These data were treated by the analysis of variance as a two-way classification with single replication. In this way, the variance due to differences among the flasks could be separated from the differences among runs, the latter being of interest as an estimate of reproducibility

of the method. The mean absorbance was 0.522, and the estimated standard error of the runs was equal to 0.003 (see Appendix D). The obvious downward trend in the results is attributable to the fact that the hydrochloric acid used was kept in a ground-glass bottle from which hydrogen chloride could escape. Unless standards are to be carried along with the samples, the hydrochloric acid used as a reagent for this method should be protected from loss of strength by storage in a pressure tight bottle.

Interferences were studied by measuring the absorption curves of a large number of cations in hydrochloric acid solution. The weights of the elements which caused an absorbance equal to 5% of the absorbance of 5 μg. Nb/ml. were calculated from measurement of several different concentrations of each ion at 281 mμ. These calculated weight ratios, given in Table XIV, are presented as guides to the relative errors caused by the presence of the various ions and are not necessarily highly accurate. Furthermore, it is important to note that not all of the elements follow Beer's law at this wavelength. Many were observed to deviate widely from this relationship.

Simple gravimetric procedures are known which will separate niobium from most of the elements listed to the extent that their interference will be less than 5%.

TABLE XIV

WEIGHT RATIOS OF ELEMENTS CAUSING 5% ERROR

Element	Ratio (M/Nb)	Element	Ratio (M/Nb)
Sn(II)	10	Pb(II)	0.2
Sn(IV)	7	Fe(III)	0.06
Co(II)	50	Cu(II)	0.04
Ni(II)	35	Bi(III)	7
Mn(II)	35	Ta(V)	2
Cd(II)	80	Th(IV)	500
Hg(II)	40	Mo(IV)	0.2
V(V)	0.6	W(VI)	3
V(IV?)	2	Si(IV)	50
Cr(III)	0.1	Ti(IV)	0.15
		Zr(IV)	> 500

Those elements which may cause trouble include vanadium, chromium, lead, iron, copper, molybdenum and titanium.

The interference due to the presence of copper can be reduced by the addition of a small measured excess of stannous chloride dissolved in concentrated HCl to both the sample and the blank. The reduced form of copper shows little absorption at 281 mμ. The interference of iron can be reduced temporarily by the addition of a five- to tenfold excess of stannous chloride, but measurements must be made immediately since iron is rapidly reoxidized by air under these conditions. Titanium may be determined independently by the peroxide method and its contribution to the absorbance at 281 mμ subtracted from the total absorbance. Titanium solutions do follow Beer's law at

this wavelength.

The most serious interference is that of tantalum. The solutions should be centrifuged prior to the absorption measurement since tantalum hydrous oxide is peptized by concentrated HCl. Addition of hydrofluoric acid to make the solution 0.01 $\underline{M}$ in fluoride ion increases the weight ratio of tantalum for 5% error to 10.

Sulfate does not interfere up to 0.1 $\underline{M}$ concentration added as potassium bisulfate. Sulfuric acid tends to decrease the solubility of hydrogen chloride and is thus to be avoided.

STRUCTURAL STUDIES

On the basis of the preliminary work in this thesis and the structures suggested in the literature for niobium in hydrochloric acid solutions, it was proposed to attempt three projects, which, if successful should result in a clear-cut picture of the species.

Several of the reports cited conflict in their assignment of charge to the several species postulated, some even differing as to the sign of the charge. The first approach contemplated was the determination of the sign, if not the magnitude, of the charge on the complexes by electromigration experiments.

Some investigators have employed the concept of oxygen-containing vs. non-oxygen-containing species in attempts to explain clear-cut differences in behavior at high and low acid concentrations. Optical measurements in anhydrous media should show if such species exist and yield limiting curves for the series of complexes which are found in aqueous media.

The final approach was anticipated in the preliminary experiments. Careful measurements of absorption curves under varying conditions of hydrogen ion and chloride ion concentration will yield a family of curves which may possibly be analyzed by one of several available

techniques to determine the actual number of ligand atoms
present in each, or at least some, of the absorbing
species.

The Charge on the Ions - At first an attempt was
made to use a three-compartment transference type cell
fitted with sintered glass discs to impede mixing and dif-
fusion. Due to the high electrolyte concentration of the
solution and the relatively low concentration of complex
present, it was found that mixing contributed a greater
amount of transfer than did the electromigration, and that
this was not reproducible.

A more successful technique was developed by using
electrophoresis on paper strips. The apparatus employed
consisted of two carbon electrodes, supported on tantalum
leads, connected by short "bridges" of HCl soaked paper
strip to two porcelain reservoirs containing concentrated
HCl. A piece of filter paper approximately 15 cm. long
and 1.5 cm. wide was held on a glass support in an in-
verted V, each end dipping into a solvent reservoir. The
whole set-up was placed on a glass plate and enclosed by
an inverted 1000 ml. beaker sealed with Apiezon Q wax. A
30 ml. beaker filled with concentrated HCl was also placed
in the enclosure to help maintain a high vapor pressure of
water and HCl.

Potential was supplied by a regulated 300 V. electronic power supply through a voltage divider. The potential across the cell and the current through the cell were measured by meters.

The filter paper strip was folded across the middle, notched there and at a point about half the distance between the middle and each end. These points, equidistant from the middle, marked the original positions of the spots of niobium solution.

The usual technique used involved assembling the apparatus with the filter paper in place and allowing the solution to soak the strip thoroughly, coming to equilibrium. The cover was removed briefly to spot the concentrated niobium solution. An attempt was made to produce as uniform spots as possible, using a tube drawn out to a capillary to measure out the same amount of solution each time and innoculate it reproducibly.

When the voltage was applied across the ends of the paper strip, sufficient i^2r heating occurred in the strip to cause appreciable evaporation along its length. If the current was kept low and non-hardened filter paper (Whatman #1) was used, the strip remained moist enough to continue to conduct the current, the reservoirs supplying enough solvent by capillary action to replace that lost by evaporation. This movement of solvent from the ends of the

strip toward the center tended to wash the niobium spots up; that is, toward the middle of the strip. The effect was presumed to be the same for both spots. However, any electromigration would appear as movement of both spots toward one end of the strip. Therefore, the algebraic difference of the distance the spots moved toward the middle of the strip was taken as a measure of the migration.

The reproducibility of the method was not good, as shown in Table XV, presumably because of the changes in HCl concentration brought about by heating and evaporation. In all of the runs, the net movement of the niobium spot was in the direction of the positive electrode. This is adequate indication that the charge on the complexes in this system is negative, in agreement with most of the previous reports.

Spectra in Anhydrous Solvents - Niobium in aqueous solution is generally believed to be more or less hydrated, hydroxylated, or oxygenated under nearly all circumstances. It is impossible to obtain the absorption spectrum of the completely hydrated niobium ion, for the element apparently hydrolyzes before this stage is reached, passing over into the polymeric or even solid state. It is thus obviously impossible to use the completely hydrated ion as reference point in the attempt to identify the structure

TABLE XV

ELECTROMIGRATION OF NIOBIUM IN
CONCENTRATED HYDROCHLORIC ACID

| Sample No. | Time (hrs) | Current (ma.) | Distance Moved toward Middle | | Net Distance toward Anode (mm) |
			+ side (mm)	- side (mm)	
P9	1-1/4	--	5	9	4
P10	2-1/4	15	14	17	3
P11	1-1/4	28	9	11	2
P12	4	15	5	9	4
P13	5-1/2	5	- 3	- 1	2
P14	5	5	7	12	5
P15	5	5	2	3	1
P16	4-1/2	15	25	29	4
P17	5	15	8	17	9
P18	2	5	5	6	1
P19	2	5	- 3	- 1	2
P20	1-1/2	15	- 2	1	3
P21	1-3/4	12	7	11	4

of the series of ions in which the oxygen or hydroxyl groups are replaced each in its turn by ligand atoms. This approach has been used with some success with the ferric chloride and the cobaltous chloride complexes (29, pp.5464-71) because the aquo ions are relatively stable in solution.

It has been found more satisfactory to determine the structure of the highest complex formed, since the conditions necessary to obtain this generally preclude the presence of other species. Gamlen and Jordan (13,pp.1435-36) review the evidence for the highest chloro complex of iron having the form $FeCl_4^-$. Much of the aqueous spectrophotometric work indicated that this was correct structure for the species, but the work of Friedman (11,pp.5-10) leaves little doubt of it. Of greatest significance was the similarity between the absorption curves of $FeCl_3$ in concentrated aqueous HCl solution and $KFeCl_4$ in anhydrous media and in the solid state. This pointed to the existence of the same ion in each case and precluded solvation of the species responsible for the absorption.

A serious attempt was made to obtain the ultraviolet spectrum of niobium pentachloride. The fact that niobium pentachloride dissolves in various anhydrous solvents has long been known (47,pp.100-18; 17,p.277). It is said to form a stable yellow solution in alcohol, ether,

and carbon tetrachloride.

Niobium pentachloride added to commercial anhydrous ether did form a yellow solution, but in the air this color persisted for only about a minute. It is presumed that traces of moisture from the air caused the rapid hydrolysis and precipitation of the chloride as the oxychloride and oxide.

A small amount of anhydrous ether prepared by Mr. Jerzy Bialy for Grignard reactions was obtained. In this solvent $NbCl_5$ exhibited approximately the same behavior when handled in the air. This ether was placed in a volumetric flask that had been dried at 110°C. overnight and was protected from the atmosphere by a dried vial seal. A small amount of $NbCl_5$ was placed into a similarly dried volumetric flask, sealed with a vial seal and ether added with a hypodermic syringe. After the solution was thoroughly mixed by shaking, it was removed by hypodermic, placed in a dried silica cell and its absorbance measured quickly. Curve 1 of Figure 16 represents this data. HCl gas dried by passing through $CaCl_2$ was bubbled into the solution remaining in the flask. The solution then had the optical absorption shown in curve 2 of Figure 16. Curve 3 represents the difference between curves 1 and 2 and represents the ratio of absorbance.

FIGURE 16
ABSORPTION CURVES FOR NbCl₅
IN ETHYL ETHER
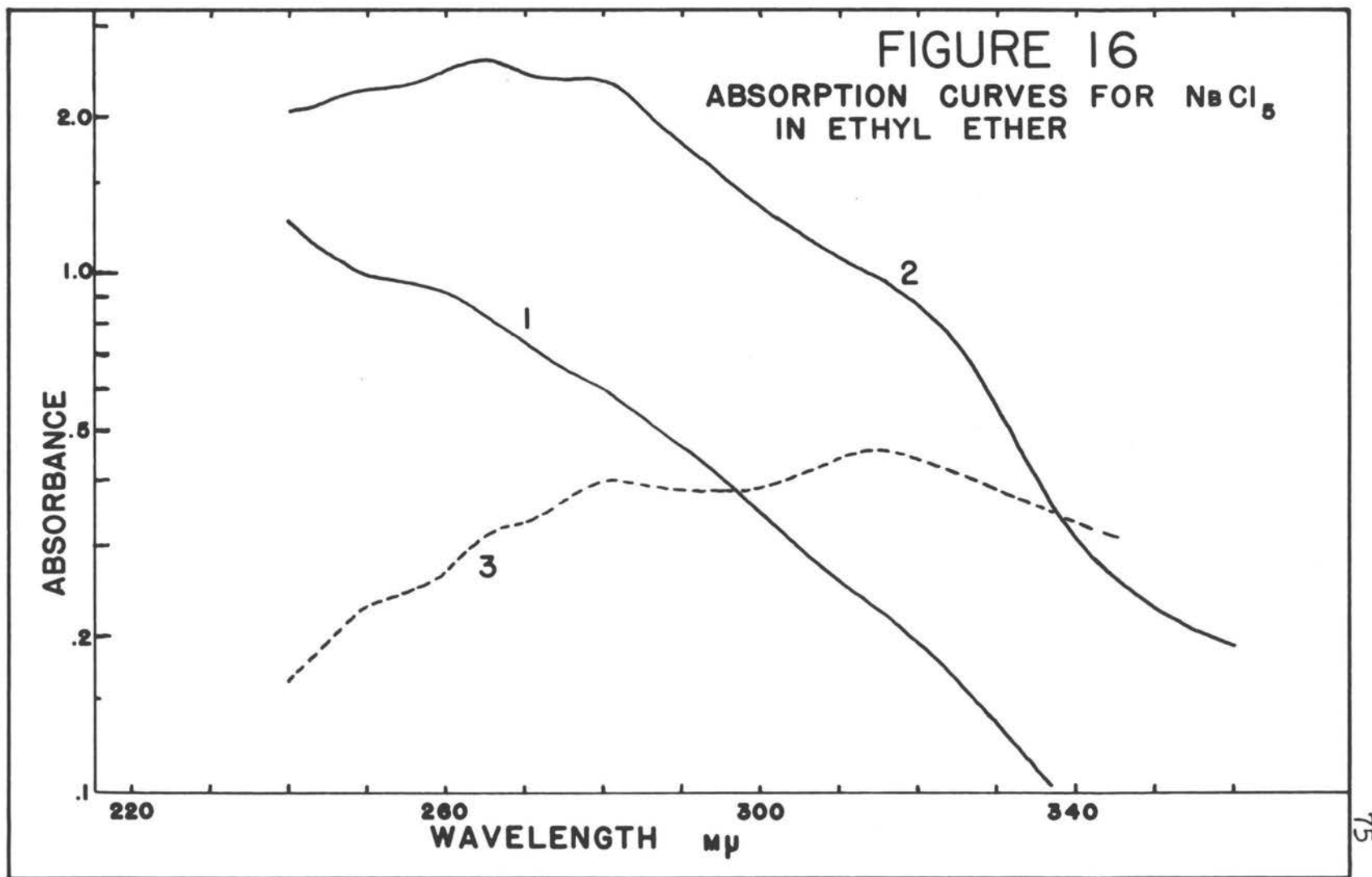
Anhydrous n-butyl ether over sodium was obtained
from Mr. Norman Odell. Employing the same techniques to
protect the material from moisture, curve 1, Figure 17,
was obtained from a solution produced by adding a small
amount of $NbCl_5$ to this solvent. Curve 2 resulted from
the addition of 1.0 ml. of n-butyl ether that had been in
an unprotected bottle for many months and was presumed to
contain some water. Gaseous HCl bubbled into the sample
and blank yielded curve 3.

Again using the same techniques but with redistilled
n-butyl ether curve 1 of Figure 18 was obtained. After
addition of dry HCl gas for one minute to the sample and
blank, the absorption appeared as in curve 2. Further
prolonged addition of HCl produced curve 3.

Anhydrous carbon tetrachloride was obtained by
distillation at atmospheric pressure into a receiver con-
taining phosphorous pentoxide. This receiver was quickly
transferred to a vacuum manifold where the CCl_4 was dis-
tilled at room temperature at reduced pressure into a
special receiver fitted with a vial seal. While the CCl_4
vapor was being condensed at dry ice-acetone temperature,
a small quantity of $NbCl_5$ was sublimed into the vapor
stream with a small flame in such a manner as to be
carried into the receiver. A yellow solution was obtained
in this way, but in spite of all precautions taken, the

FIGURE 17
ABSORPTION CURVES FOR $NbCl_5$
IN n-BUTYL ETHER

FIGURE 18
ABSORPTION CURVE FOR $NbCl_5$
IN DRIED N-BUTYL ETHER
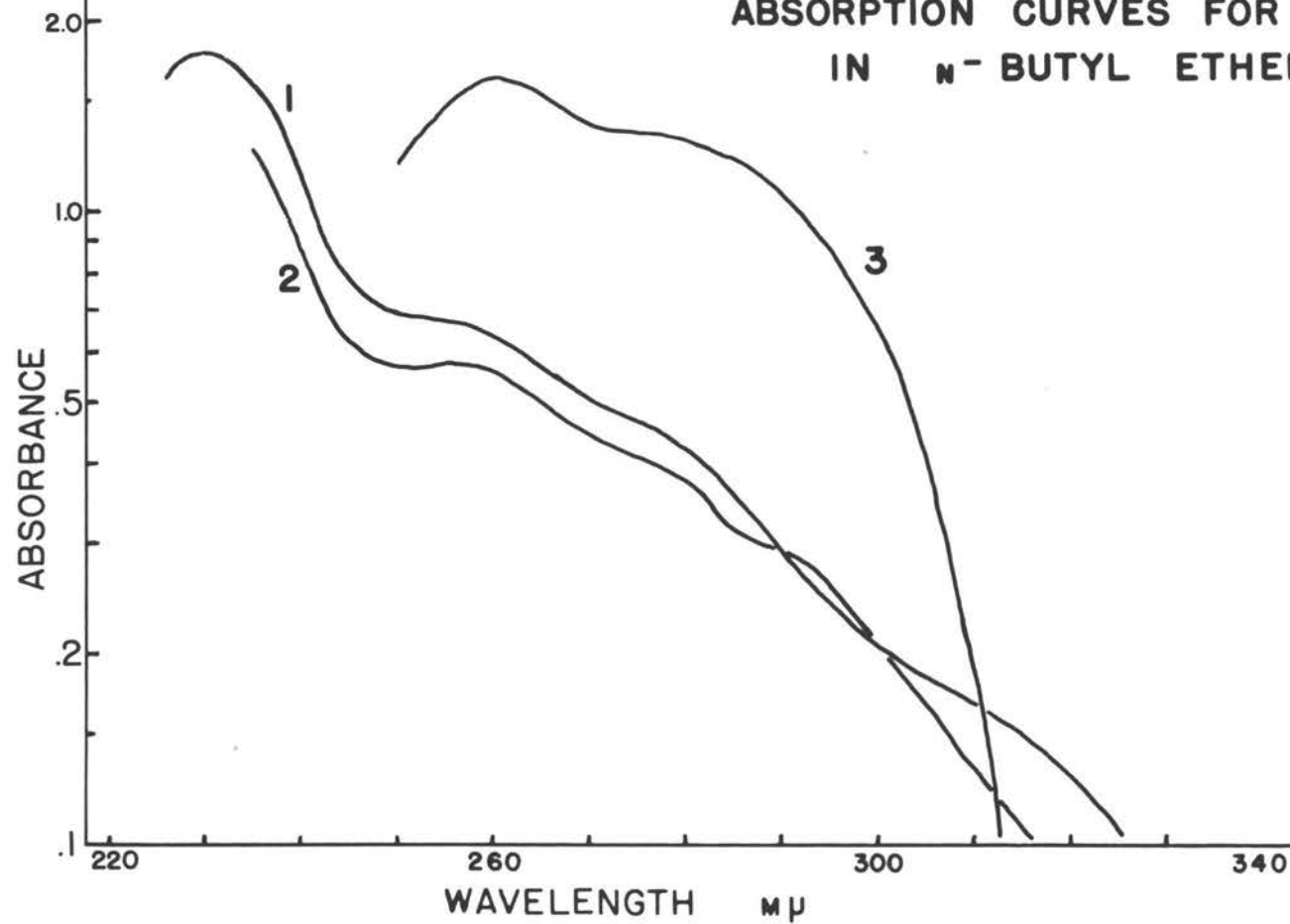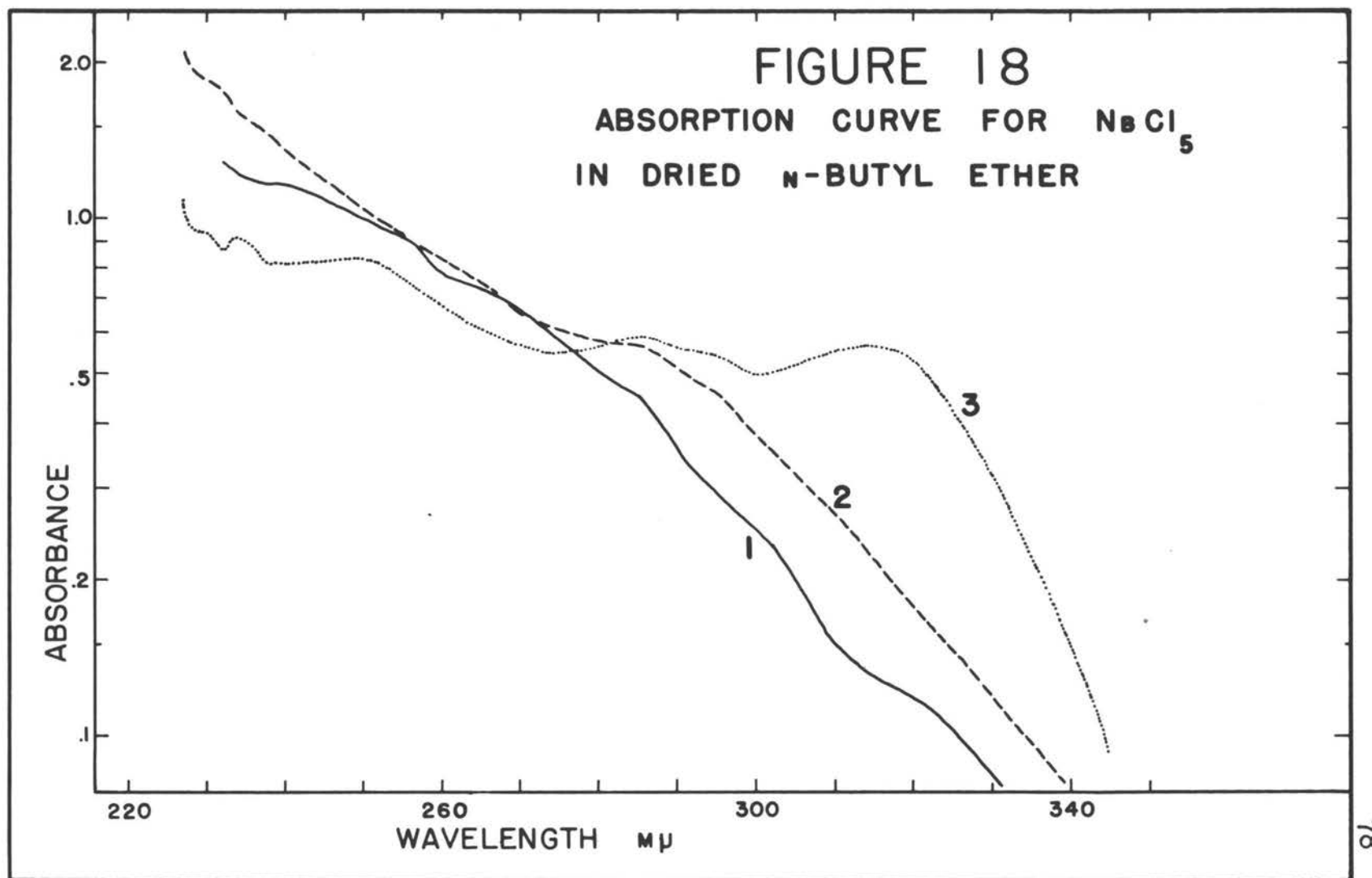
stability of these solutions was limited to a few hours. Dried argon was bled into the system following the distillation. The solutions were transferred to silica absorption cells by hypodermic syringe, but almost immediately upon entering the cells the solutions became colorless and produced a white precipitate.

The absorption curves obtained from these solutions showed a gradually increasing absorption toward the ultraviolet. It was impossible to measure absorption below 260 mμ due to the opacity of the solvent below that wavelength. While the solubility of $NbCl_5$ in CCl_4 is satisfactory, it would appear to be a poor solvent for this work. Many different methods were tried to protect the solutions in the cells long enough for spectra to be measured. Nevertheless, nearly all curves obtained were similar to curve 1 of Figure 19. Curve 2 was measured 24 hours later. The difference here is probably due to sedimentation of the colloidal particles of hydrolyzed material.

In the same apparatus employed for the CCl_4 distillation several solutions were prepared using ethyl ether distilled at reduced pressure from sodium. By rapid work a solution was obtained whose absorbance is shown as curve 3, Figure 19. A repeat measurement made on the same solution as rapidly as possible (about 15 minutes later) is

FIGURE 19
ABSORPTION CURVES FOR $N_B Cl_5$
IN ETHYL ETHER & CCl_4
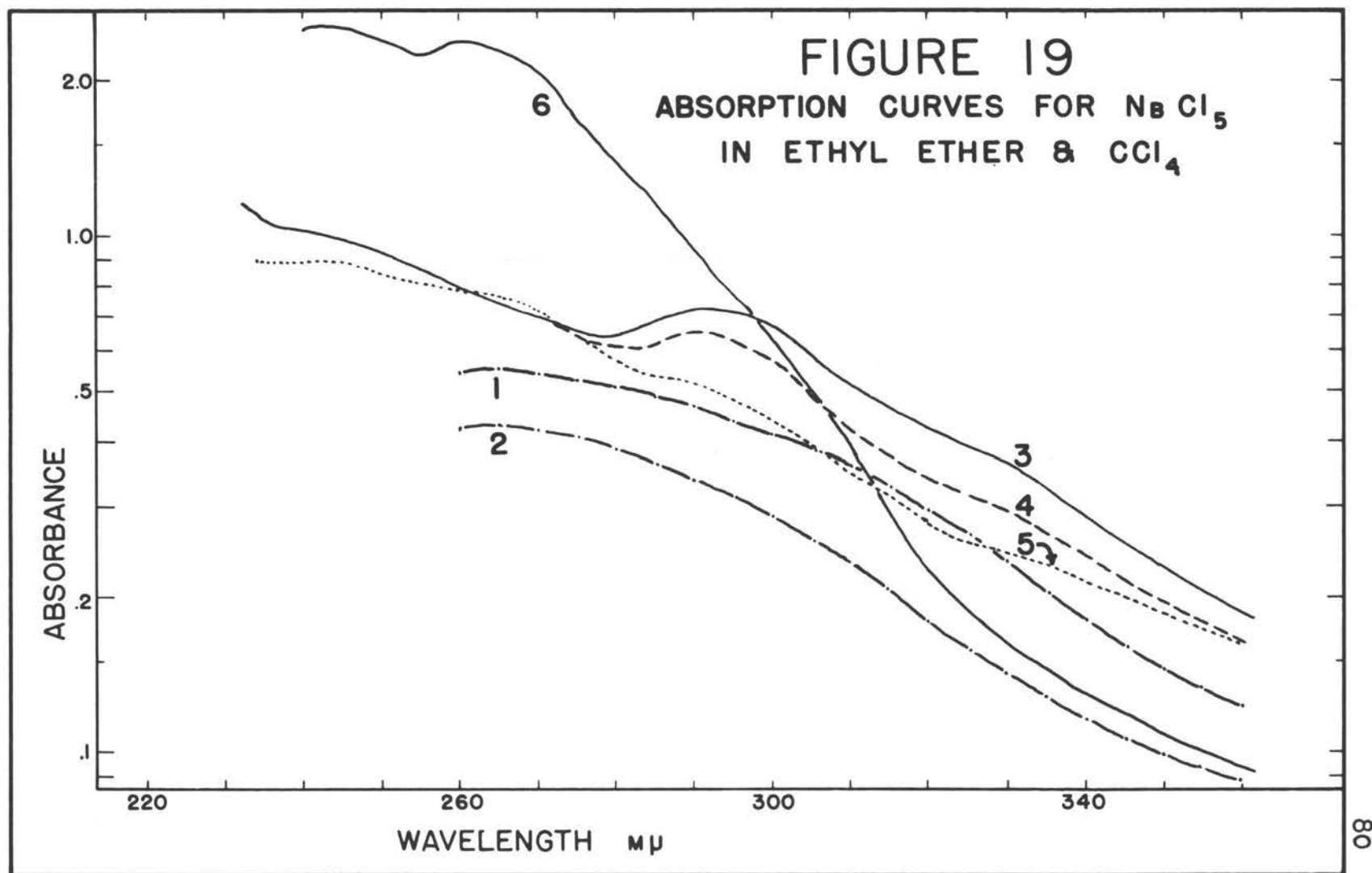
shown as curve 4. Curve 5 was taken after 2-1/2 hours had elapsed. The solution had the absorption shown in curve 6 when measured the next day.

Several test-tube type cells were made from pure silica tubing. An attempt was made to obtain the spectrum of solid $NbCl_5$. The samples were prepared by placing some of the material in the bottom of the tube after it had been evacuated and flamed, evacuating again and warming the tube very gently with a flame to sublime a small deposit on the walls. Curve 1 of Figure 20 was a thin sublimed film. Following this measurement a thick film was produced in the same tube by reheating. When this proved to be too dense for measurement, the film was thinned by gently flaming the surface. Curve 2 gives the spectrum of this thinned film. The film and tube were not disturbed for 12 hours and gave the spectrum shown in curve 3 at that time. The seal was then broken and access to air and moisture provided. After another 12 hours, the film yielded curve 4. Curve 5 is the difference between curves 2 and 4, representing the ratio of absorbance of these two films.

Due to the tremendous difficulty in excluding moisture from the systems employed, little positive information can be obtained from the work in this section of the thesis. Some speculation may be helpful at this

FIGURE 20
ABSORPTION CURVES OF
NbCl$_5$ FILMS
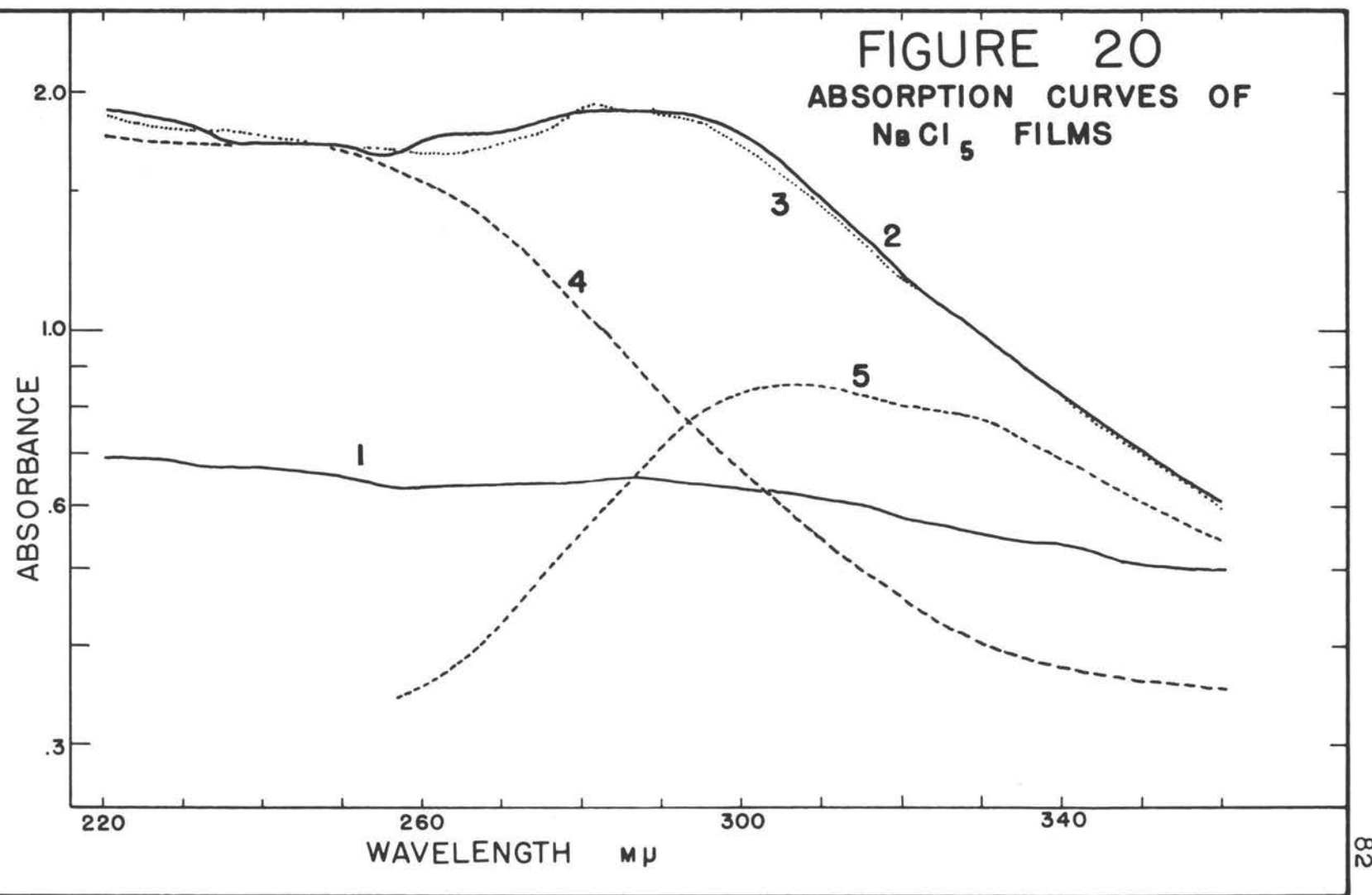
point, and subsequent work may render an explanation of these curves more meaningful.

It is important to remember two points in attempting to analyze spectrophotometric curves. First, in a complex spectrum the apparent maximum of a particular species may be radically shifted from its true position by contributions of neighboring absorbing species. Second, a change in the relative amounts of absorbing species that have overlapping spectra may not be apparent by inspection of the total curve. This is particularly true when the exact number of species present is not known.

To return to the discussion of the curves, it is of interest to see if any species seem to recur as evidenced by the appearance of the same absorption peak in a number of spectra. Most prominent in this system are peaks at about 230 mµ, 260 mµ, 280 mµ and 320 mµ. Figures 17 and 18 give the best contrast for these. The only difference is the presumed presence of water in the ether used in Figure 17. While it is admitted that adequate controls were not present in this experiment, it can serve as a basis for speculation. It is significant that the peak at 320 mµ made an appearance only upon the addition of hydrogen chloride to the supposedly anhydrous solvent. When water was presumed to be present,

peaks developed at 260 and 280 mμ, but absolutely nothing appeared at 320 mμ. This could be interpreted to mean that the 320 mμ absorption was caused by a species containing HCl but no water, OH⁻ or O⁼, such as $HNbCl_6$ or H_2NbCl_7. The other peaks would then be ascribed to oxygenated forms, either of the form $HNbOCl_4$ and $HNbO_2Cl_2$ or, in analogy with Neumann's work with antimony, $HNb(OH)Cl_5$ and $HNb(OH)_2Cl_4$.

The other curves are subject to a large number of interpretations. For example, the ethyl ether curves, Figures 16 and 19, have little similarity. Suffice it to say that this may be due to the greater contribution of solvolysis in the case of the ethyl ether resulting in a greater effect of changes in water and HCl content.

Perchloric Acid Solution of Niobium - A solution of niobium in concentrated perchloric acid was obtained in the following manner:

About 1 g. Nb_2O_5 was dissolved in 20 ml. of H_2SO_4 by fuming until the solution was clear. The volume of acid was reduced to about 15 ml. and the solution poured, while hot, into a 100 ml. volumetric flask which contained concentrated perchloric acid. The voluminous precipitate which formed was allowed to settle and the clear solution, when cool was shown by colorimetric comparison to contain
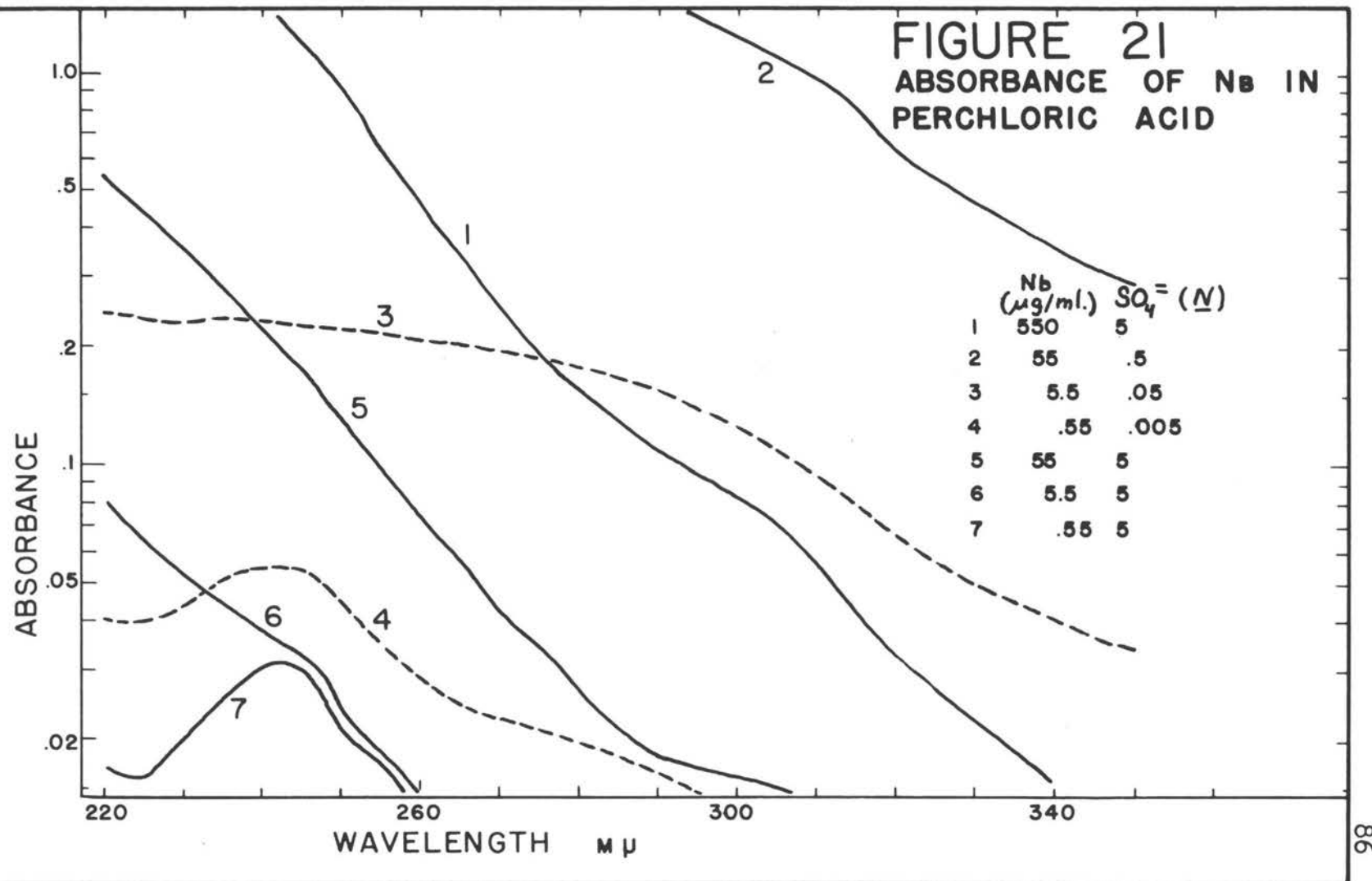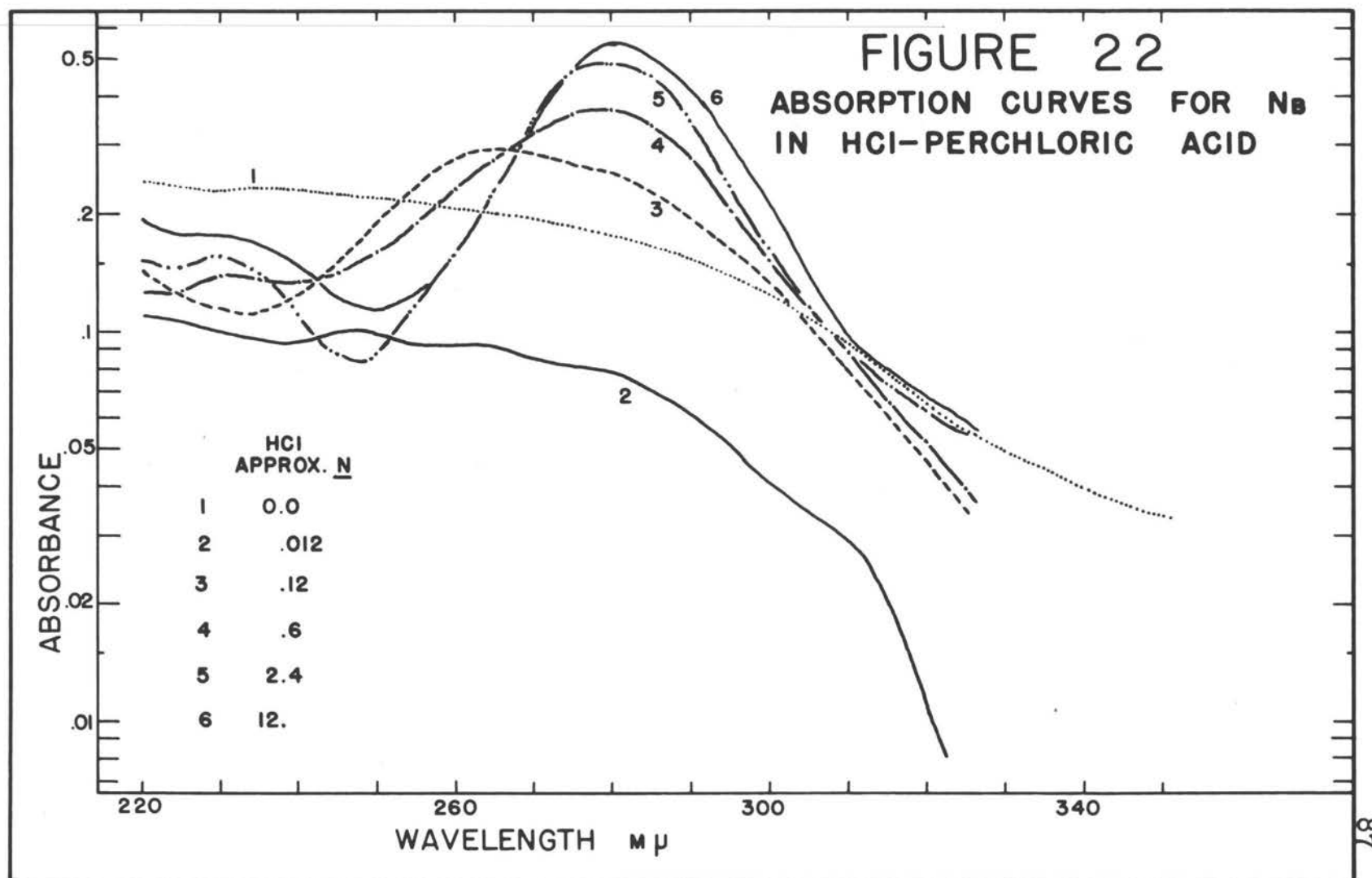
approximately 0.550 mg. Nb/ml.

The absorption curve of this solution is shown in Figure 21 as curve 1. Unfortunately the measurements on the original solution were not carried below 245 mμ. Curve 2 represents the absorption of the solution when diluted to one-tenth concentration with concentrated $HClO_4$. It was noticeably cloudy. Curves 3 and 4 represent further dilutions by a factor of ten times each. For curve 5, the original solution was diluted one to 10 with a solution of 15% H_2SO_4 in concentrated $HClO_4$ and curves 6 and 7 represent ten-fold and hundred-fold dilutions of that solution with the same solvent.

A series of samples was prepared from the perchloric acid solution of niobium. To 0.1 ml. of the stock solution were added the following volumes of concentrated HCl: (1), 0.00 ml.; (2), 0.01 ml.; (3), 0.1 ml.; (4), 0.5 ml.; (5) 2.0 ml.; (6) 9.9 ml. The solutions were then diluted to 10.00 ml. and the absorption curves obtained. The numbers given in parentheses correspond to the curve numbers in Figure 22. All samples contain approximately 5.5 μg. Nb/ml.

Figure 21 demonstrates the colloidal nature of perchloric acid solutions. Dilution of the solution caused a precipitate which slowly dissolved to yield, in solution, either a sulfate complex or a hydrated ion of

FIGURE 21
ABSORBANCE OF Nb IN
PERCHLORIC ACID

	Nb (μg/ml.)	$SO_4^=$ (N)
1	550	5
2	55	.5
3	5.5	.05
4	.55	.005
5	55	5
6	5.5	5
7	.55	5

FIGURE 22
ABSORPTION CURVES FOR Nb
IN HCl-PERCHLORIC ACID

HCl
APPROX. N

|	
1	0.0
2	.012
3	.12
4	.6
5	2.4
6	12.

ABSORBANCE

WAVELENGTH Mμ

perhaps polymeric structure. The peak at 242 mμ is likely due to a sulfate complex. The presence of sulfate in the diluent eliminated the visible precipitation, but the solutions definitely did not follow Beer's law, a fact that indicates a profound change in the nature of the absorbing species.

The interesting point to note in Figure 22 is the presence of those four peaks previously found in the anhydrous work - 230 mμ, 260 mμ, 280 mμ, and a suggestion of a peak at 320 mμ.

Extraction by Ethyl Ether - A single experiment was conducted to determine the extractability of niobium into ether from concentrated HCl solutions. One part of concentrated HCl was added to approximately 3 parts of ethyl ether and the mixture was cooled in an ice bath while HCl gas was bubbled into the lower phase. The addition was continued with occasional vigorous shaking until each phase occupied approximately half the volume. The aqueous phase was 5.46 $\underline{N}$ in HCl. One ml. of a solution of 0.25 mg. Nb/ml. in concentrated HCl was diluted to 50.00 ml. with the above ether-saturated aqueous HCl solution. The absorption curve of this 5 μg./ml. solution of niobium measured against a blank of the solvent is given as curve 2 of Figure 23.

FIGURE 23
NIOBIUM SPECTRA IN
HCl-WATER-ETHER
SYSTEMS
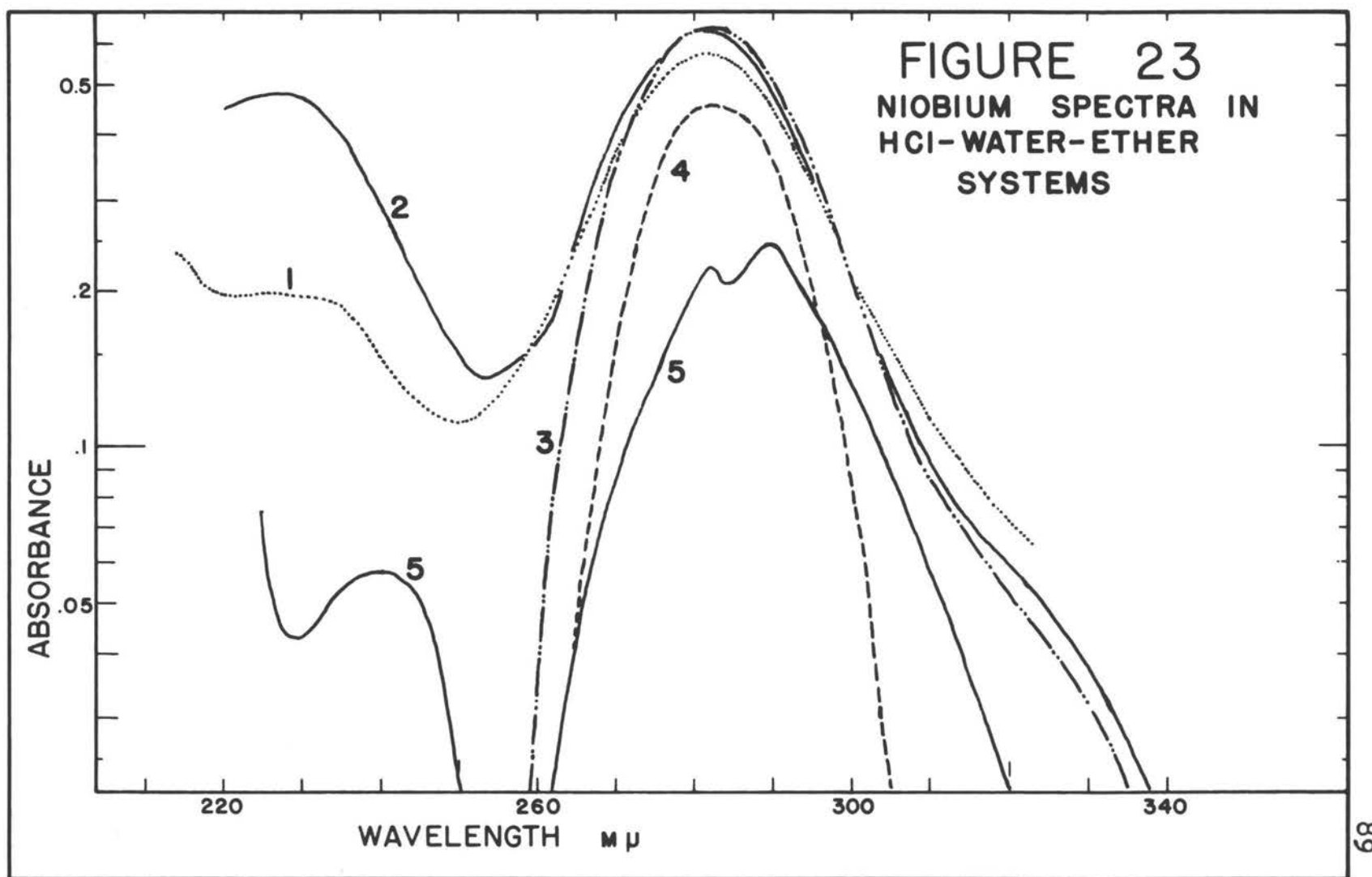
Further addition of hydrogen chloride to the previously prepared two phase system caused the disappearance of the upper layer. The HCl concentration then measured 5.59 $\underline{M}$. A niobium solution, prepared from this solution as above gave curve 3 of Figure 23.

A small amount of ether added to the ether-HCl solution produced two phases. The aqueous layer contained 4.9 $\underline{M}$ HCl. A 5 μg./ml. niobium solution, prepared as above but with this latter aqueous phase, resulted in two phases. Curve 4 of Figure 23 gives the absorption of the aqueous or lower layer, curve 5 that of the organic phase measured against a blank of the dilution solution.

Curve 1 in Figure 23 is the spectrum of the same concentration of niobium in concentrated HCl for comparison. The effect of the addition of ether to the solutions seems to be the strengthening of the absorption at 230 mμ at higher HCl concentrations, but at a higher concentration of ether and a lower HCl concentration this peak was practically eliminated. In the extraction process, 28% of the niobium went into the organic phase under the conditions employed. The absorption curve of the aqueous phase was of the usual shape, but in the ether layer, a peculiar double peak at 282 and 290 mμ was found, and the absorption at 230 mμ had shifted to 240 mμ. The meaning of these changes is not clear. They may be associated

with solvation or compound formation of ether with the niobium complexes extracted (see Figure 19).

The Chloride and Hydrogen Ion Dependence of the Absorption Spectra - Optical absorption spectra serve as a powerful tool for the elucidation of structure (19,pp. 4488-93). The many methods developed for analyzing such data are special cases of a general approach. Discussions of the applicability and bases for the methods emphasize the assumptions inherent in each particular procedure (58,pp.6091-6; 27,pp.3397-3405).

An assumption basic to all the procedures developed up to this time is that the activity coefficients of all species involved in the various equilibria do not change significantly. The experimental conditions have been adjusted to achieve this. Some systems have been dilute enough that the assumption that $\gamma_{\pm} = 1$ holds. For more concentrated systems, the total ionic strength has been maintained at a level high enough to insure the constancy of the activity coefficients when the concentrations of the participating ions were varied.

The systems under consideration here are not amenable to either means of avoiding the use of activities, rather than ordinary concentrations units, in quantitative expressions describing the relationships among the ions. The tendency of the metal ion to

polymerize and hydrolyze limits the usable range of metal ion concentration to extremely dilute solutions. Furthermore, the stability of the complex is such that high effective concentrations of HCl are required for its existence. In these high concentrations the constancy of ionic strength is not sufficient to insure the constancy of the activity coefficients. The reacting particles make up too large a fraction of the solution to follow ideal behavior predicated upon their relative isolation.

It was felt that the only approach lay in describing the system thoroughly in terms of activities of the ions which would be present in high concentration, in this case the hydrogen and chloride ions. Although it may injure the sense of propriety of the more exacting, the assumption was made that measurement of the actual concentrations, rather than activities, of total niobium present (as obtained by analysis) and the complexes produced (as determined by optical measurements) would suffice in view of their low concentrations (2×10^{-5} $\underline{M}$ or less).

The systems chosen are time honored in that they have been employed in many investigations of structure in which activity factors were considered.

Lithium chloride was used to maintain a constant concentration of chloride. The data of Hawkins suggests

that activity coefficients in LiCl and HCl of the same concentration should be similar (20,pp.4480-7). This would be only approximately true at high ionic strengths because of the fact that HCl is associated to a higher degree than is LiCl.

Perchloric acid was chosen to maintain the concentration of hydrogen ion. Its high degree of ionization (46,pp.13-17; 3,p.21) and lack of complexing action make it the best choice possible for this purpose. The only data available on the variation of activity coefficients in $HClO_4$-HCl solutions were taken at an ionic strength of one (40,pp.4074-9). Under these conditions a change from approximately 0.1 $\underline{M}$ to 0.5 $\underline{M}$ in the HCl concentration caused a negligible effect in its activity coefficient. This is admittedly small evidence for extrapolation to 10.5 $\underline{M}$ solution, but it is an indication, at least, that the substances have similar properties.

The measurement of activity of solutions containing varying concentrations of H^+ and Cl^- but at a total ionic strength of 10.5 ± 0.1 was carried out in a manner similar to that which had been employed for aqueous HCl solutions (1,p.1855). Details of the method of measurement and calculations are given in Appendix E. Results of these measurements are given in Tables XVI and XVII and in Figures 24 and 25.

TABLE XVI

SUMMARY OF ACTIVITY MEASUREMENTS
HCl-LiCl SOLUTIONS

Samp. No.	Cl⁻ moles/l.	H⁺ moles/l.	EMF Cell	EMF Corr.	Apparent a_{H^+}
L1	10.5	9.61	-0.0803	- .0796	1103
	10.5	9.75	.0804	.0797	1107
L2	10.5	1.75	- .0462	- .0459	291.4
	10.5	1.72	.0446	.0443	273.7
L3	10.5	.540	- .0210	- .0210	109.0
	10.5	.514	.0185(?)	.0185	98.83
L4	10.59	.261	- .0040	- .0042	56.13
	10.59	.258(?)	.0018	.0020	51.15
L5	10.64	.0888	+ .0205	+ .0202	21.57
	10.64	.0882	.0222	.0219	20.18
L6	10.72	.0443	+ .0365	+ .0360	11.55
	10.72	.0479	.0366	.0361	11.51
L7	10.71	.0127	+ .0607	+ .0601	4.492
	10.71	.0087	.0768	.0763	2.401

TABLE XVI

APPARENT ACTIVITY COEFFICIENTS FOR H^+ IN LiCl-HCl SOLUTIONS

Ionic strength = 10.5

log H^+	log a_{H^+}	log γ
- 1.430	1.000	2.430
- 1.203	1.200	2.403
- 0.977	1.400	2.377
- 0.750	1.600	2.350
- 0.523	1.800	2.323
- 0.299	2.000	2.299
- 0.060	2.200	2.260
+ 0.181	2.400	2.219
0.426	2.600	2.174
0.682	2.800	2.118
+ 0.940	3	2.060

TABLE XVII

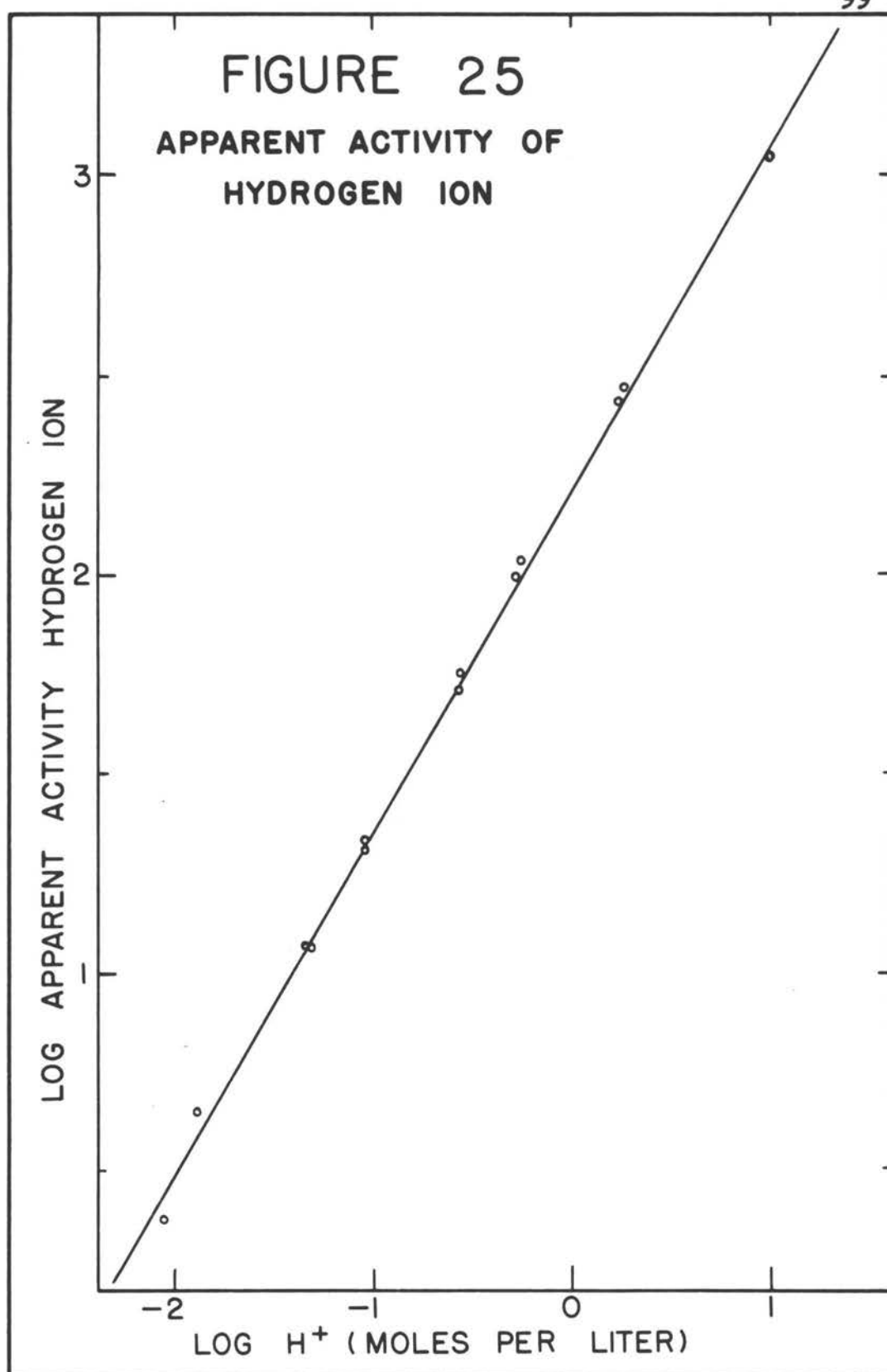### SUMMARY OF ACTIVITY MEASUREMENTS
HCl-HClO4 SOLUTIONS

Samp. No.	Cl− moles/l.	H+ moles/l.	EMF Cell	EMF Corr.	Apparent a_{Cl-}
PA1	8.56	10.25	−0.0888	− .0894	1572
	8.50	10.19	.0863	.0866	1410
	8.54	10.23	.0871	.0874	1454
PA2	5.52	10.08	− .1160	− .1180	4801
	5.57	10.04	.1178	.1196	5111
	5.55	10.07	.1170	.1190	4992
PA3	1.50	9.95	−.1509	− .1591	23880
	1.28	9.81	.1504	.1582	23050
	1.35	9.84	.1435	.1514	17680
PA4	.131	10.3	− .1193	− .1227	5768
	.107	10.2	.1187	.1219	5591
PA5	.0767	10.4	− .1137	− .1157	4385
	.0627	10.4	.1128	.1148	4237
	.0792	10.4	.1115	.1135	4028
PA6	.0199	--	− .0859	− .0870	1432
	.0208	--	.0884	.0895	1579
	.0209	--	.0868	.0879	1484
PA7	.002(?)	10.2	− .0408	− .0408	236.0
	.0017	10.1	.0420	.0417	244.4
	.00211	10.0	.0413	.0407	235.1
PA8	.000404	10.4	+ .0077	+ .0074	65.36
	.000321	10.5	.0052	.0047	57.68
	.000270	10.5	.0076	.0071	63.34
PA9	.00002(?)	10.4	+ .0443	+ .0443	8.52
	.00002(?)	10.2	.0425	.0430	9.07
	.00002(?)	10.4	.0484	.0484	7.26

TABLE XVII

APPARENT ACTIVITY COEFFICIENTS FOR Cl^-
IN $HClO_4$-HCl SOLUTIONS

Ionic strength = 10.5

log Cl^-	log a_{Cl^-}	log γ
- 4.57	1.00	5.57
- 3.91	1.50	5.41
- 3.26	2.00	5.26
- 2.60	2.50	5.10
- 1.96	3.00	4.96
- 1.29	3.50	4.79
- 0.64	4.00	4.64
- 0.38	4.20	4.58
+ 0.07	4.38	4.31
+ 0.58	4.00	3.42
+ 0.83	3.50	2.67

FIGURE 24
APPARENT ACTIVITY OF
CHLORIDE ION

FIGURE 25
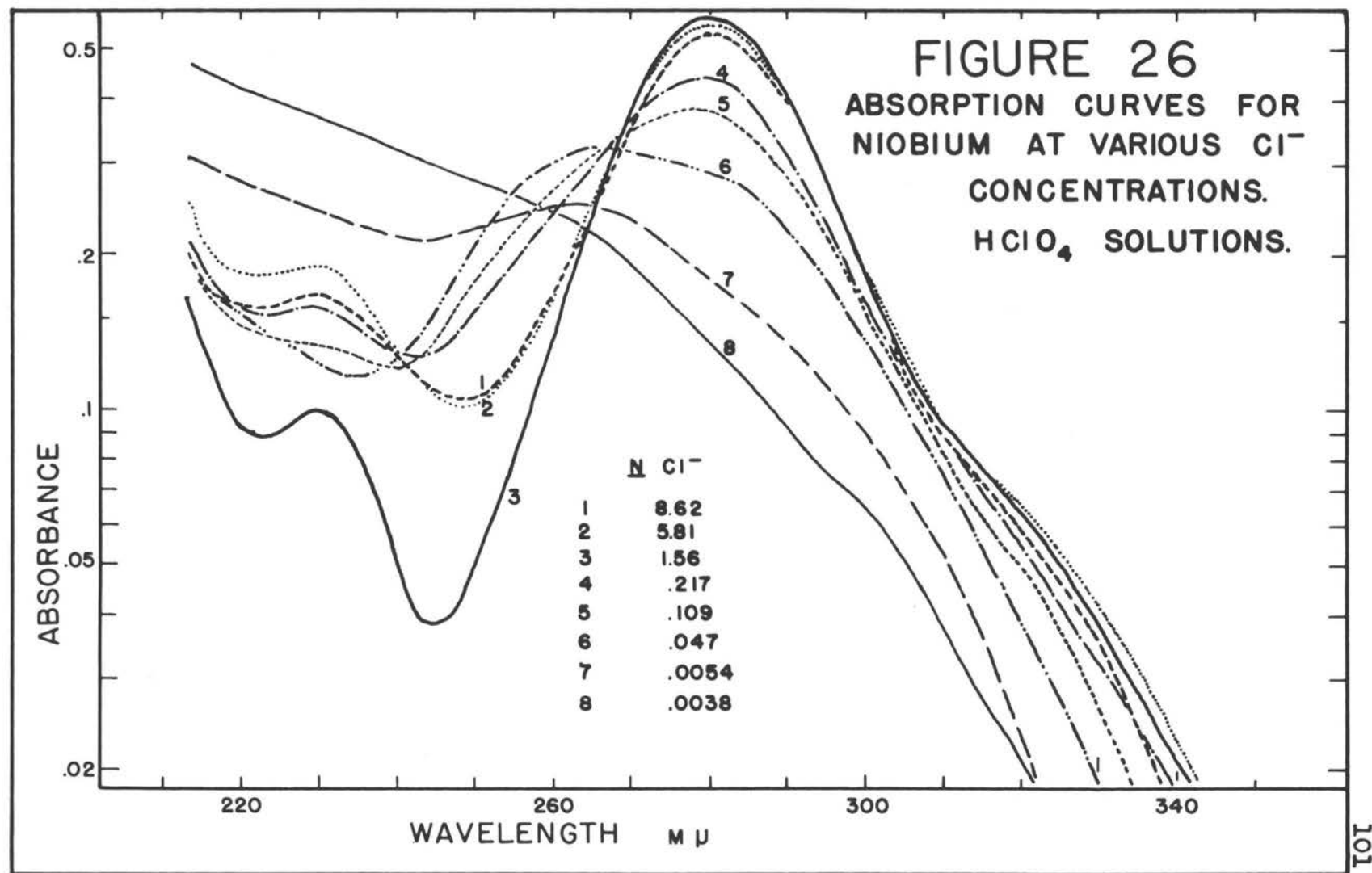APPARENT ACTIVITY OF
HYDROGEN ION
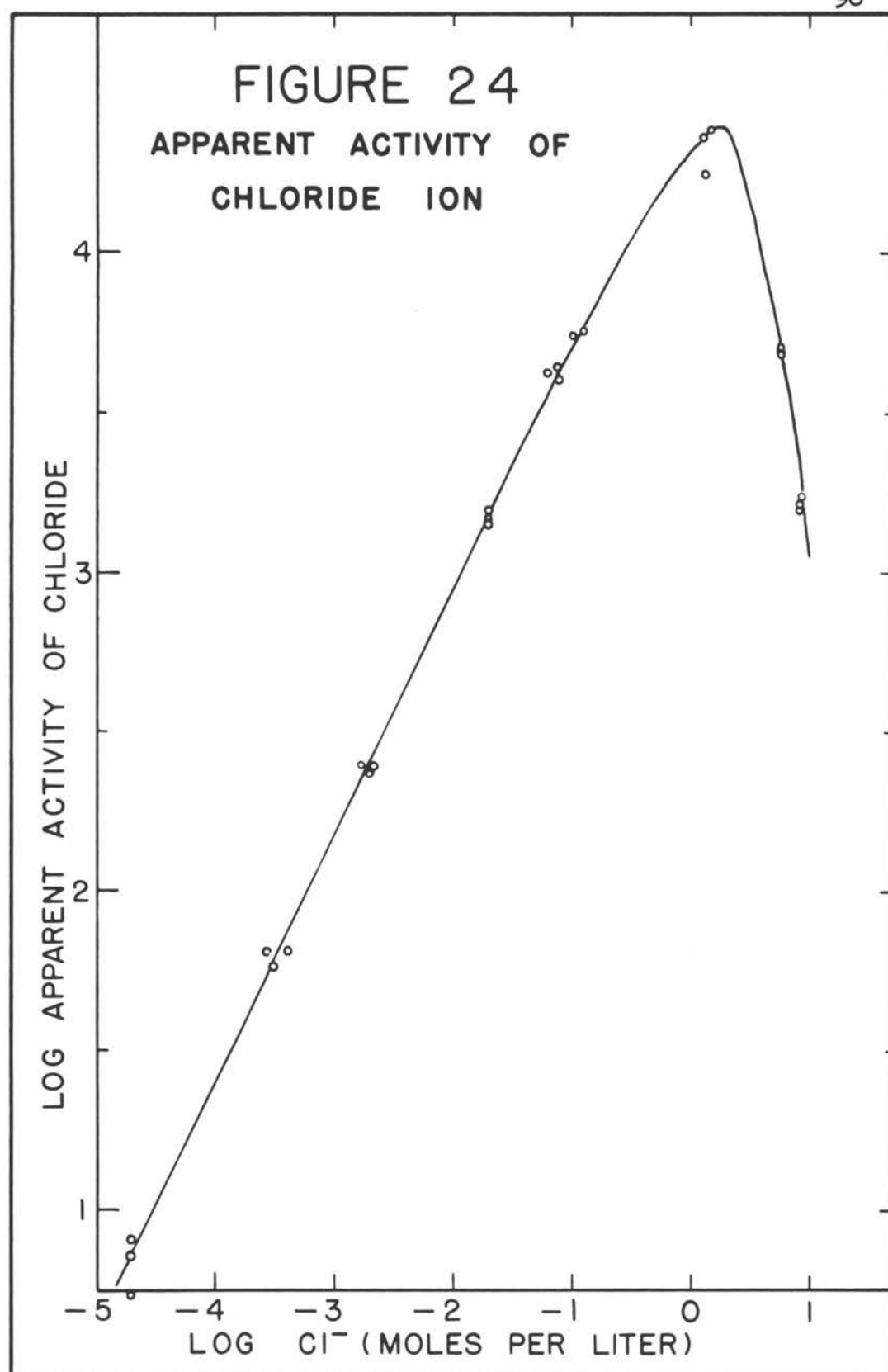
The same solutions used for activity measurements were employed as solvents for the spectrophotometric work. A standard solution of niobium was prepared which analyzed 6.59 mg. Nb/ml. (94.1 and 94.6 mg. ignited oxide from 10.0 ml. aliquots as precipitated by the tannin procedure). An aliquot of 0.04 ml. of this solution was introduced into 50.00 ml. volumetric flasks in a standardized manner from a 0.1 ml. pipet and diluted to the mark with the previously mentioned LiCl-HCl and HClO4-HCl solutions. Spectral absorption measurements were made at 5 mμ intervals from 215 mμ to 300 mμ and at 310, 320, 340 and 360 mμ. Small corrections were applied to the absorbance readings below 260 mμ to compensate for slight differences in transmission of the quartz cells. A portion of each sample was conserved for subsequent analysis of the ion whose concentration was varied. Chloride was determined argentometrically, using a potentiometric end-point. Acid concentrations were determined by titration with dilute standardized sodium hydroxide to the phenolphthalein end-point.

The absorption curves are shown in Figures 26 and 27; the analytical data are summarized in Tables XVIII and XIX.

Figures 26 and 27 are plotted using the logarithm of the absorbance in order to emphasize changes in the
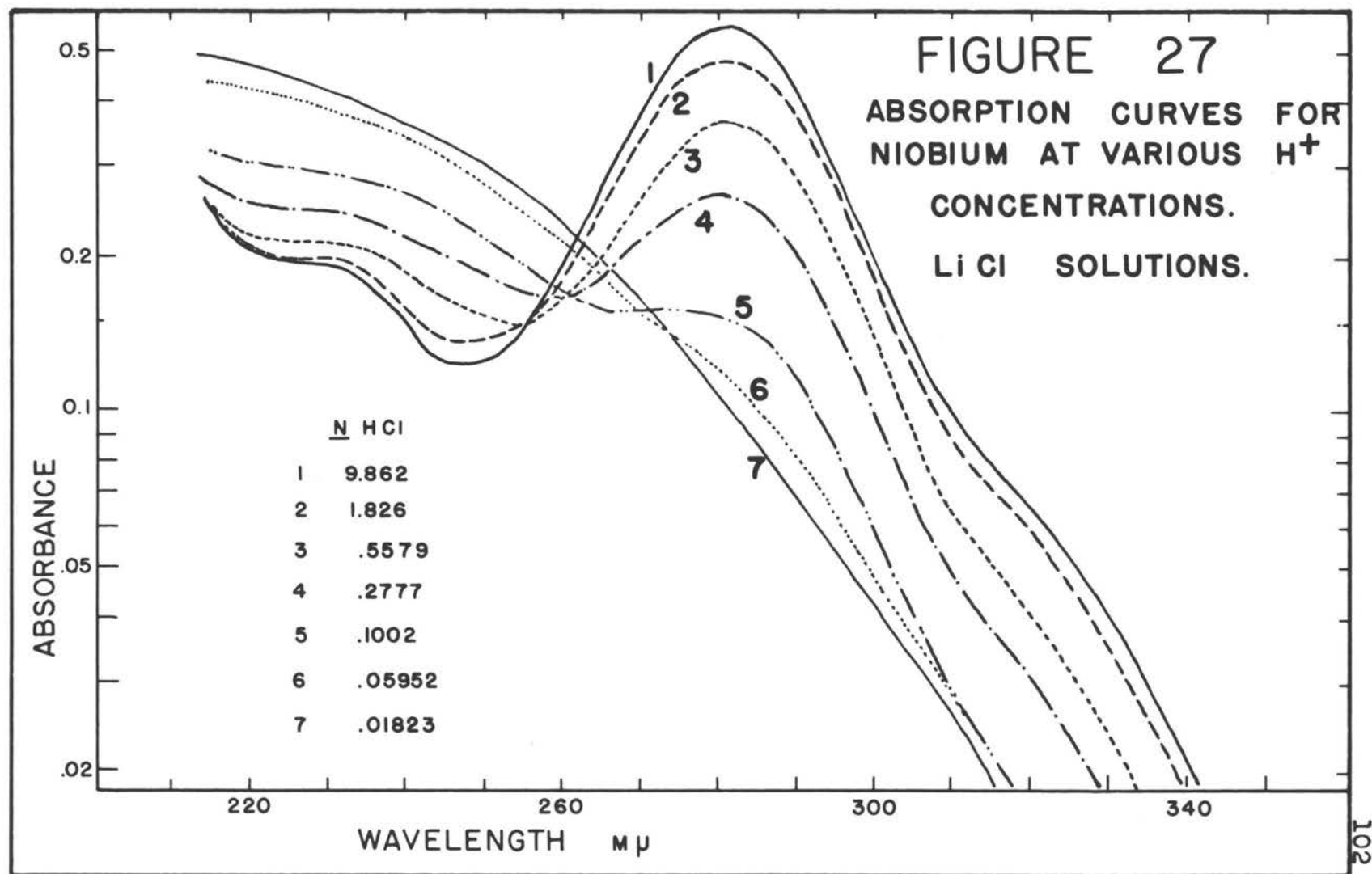
FIGURE 26
ABSORPTION CURVES FOR
NIOBIUM AT VARIOUS Cl⁻
CONCENTRATIONS.
HClO₄ SOLUTIONS.

N	Cl⁻
1	8.62
2	5.81
3	1.56
4	.217
5	.109
6	.047
7	.0054
8	.0038

FIGURE 27

ABSORPTION CURVES FOR NIOBIUM AT VARIOUS H⁺ CONCENTRATIONS.

LiCl SOLUTIONS.

	N HCl
1	9.862
2	1.826
3	.5579
4	.2777
5	.1002
6	.05952
7	.01823

TABLE XVIII

ANALYSIS OF $HClO_4$-HCl SAMPLES FROM FIGURE 25

Sample No.	Volume Sample (ml)	Volume $AgNO_3$ 0.1003$\underline{N}$ (ml)	Dilution Factor	Average Chloride Normality	log Cl^-	Apparent a_{Cl^-}
PB1	5.00	8.625	50	8.62	0.94	1850
	5.00	8.623	50			
PB2	5.00	5.820	50	5.81	0.76	4500
	5.00	5.814	50			
PB3	5.00	8.230	10	1.65	0.22	22000
	5.00	8.240	10			
PB4	4.615	10.00	--	.217	-0.66	9800
	4.642	10.00	--			
PB5	9.250	10.00	--	.109	-0.96	5800
PB5R	5.362	5.00	--	.094	-1.03	5100
	5.342	5.00	--			
PB6	2.140	1.00	--	.047	-1.33	2980
	8.286	4.00	--			
PB7	9.91	1.00	--	ca. .009	-2.05	840
ca. 11.		1.00	--			
PB7R	.940	1.00[a]	--	.0112	-1.95	1000
	4.396	5.00[a]	--			
	8.978	10.00[a]	--			
PB8	7.50	4.00[a]	--	.0054	-2.27	570
PB10	2.636	1.00[a]	--	.0038	-2.43	360
	2.678	1.00[a]	--			

[a] $AgNO_3$ normality 0.0100.

TABLE XIX

ANALYSIS OF LiCl-HCl SAMPLES FROM FIGURE 26

Sample No.	Volume Sample (ml)	Volume NaOH 0.0894$\underline{N}$ (ml)	Dilution Factor	Average Acid Normality	log H$^+$	Apparent a_{H^+}
L1	4.00 4.00	8.820 8.832	50 50	9.862	0.994	1110
L2	10.00 10.00	8.132 8.148	25 25	1.820	0.260	292
L3	10.00 10.00	6.240 6.240	10 10	.5579	-0.253	109
L4	2.00 2.00	6.210 6.220	-- --	.2777	-0.556	59.5
L5	5.00 5.00	5.600 5.608	-- --	.1002	-0.999	24.0
L6	10.00 10.00	6.654 6.660	-- --	.05952	-1.225	15.1
L7	10.00 10.00	2.042 2.063	-- --	.01823	-1.739	5.4

shape of the curves. This type of plot has the character-
istic that a solution undergoing dilution without changes
in species will exhibit absorption curves before and after
dilution having exactly the same shape. The curves will
be displaced vertically due to the change in concentra-
tion. Therefore, a change in the shape of these curves is
evidence for a change in the relative concentrations of
the species present.

Inspection of these curves reveals the same major
peaks that were observed in the anhydrous work, i.e.,
those at 230, 260, 280 and 320 mμ. The changes in the
spectra involving variation in H^+ concentration seem to be
much simpler than in the spectra involving variation in
Cl^- concentration. The major differences are lack of
appearance of the 260 mμ peak in the high chloride solu-
tions and, in the same solution, the gradual shift in the
maximum at 230 mμ to longer wavelengths. The points of
obvious similarity are the gradual decrease in the absorp-
tion peak at 281 mμ with decreasing ligand concentration
and the shape of the curves at the lowest concentrations.
The latter is so striking as to suggest that the final
species produced by decreasing either the chloride or
hydrogen ion concentration are the same.

In spite of the qualitative data that have been
obtained thus far, it seems impossible to assign even

tentative structures to the species absorbing at each
wavelength. The application of the most rigorous methods
for determining the stability constants of complexes in
any but the simplest systems requires prior knowledge of
the general behavior of the system. The lack of any such
knowledge for the niobium-HCl system makes it necessary to
employ a simpler approach.

Neumann (41,pp.2611-5) has determined the species
of antimony (V) in hydrochloric acid solution. He ob-
tained from the measured absorption curves net curves for
each species present using a graphical method similar to
that previously employed in this thesis (Figure 12).
Starting with the absorption curve in ether of a solid
antimony compound, $H_3OSbCl_6 \cdot H_2O$, he was able to recon-
struct net spectra of other species with peaks at 272, 252
and 220 mu from spectra in solutions of varying HCl con-
centration. He calculated equilibrium "constants" based
upon the several possible forms for a particular species,
such as $SbOCl_4^-$, $Sb(OH)_2Cl_4^-$, and $Sb(OH)Cl_5^-$, using the
data obtained at the wavelength postulated for that
species. The set of calculations giving the most constant
value of the "constants" indicated which of the assumed
formulas actually represented the species present. The
series of hydrolytic species found in this investigation
were $SbCl_6^-$, $Sb(OH)Cl_5^-$, $Sb(OH)_2Cl_4^-$, etc.

The similarity of the main features of the spectra for the antimony and niobium chloride is somewhat surprising; although they are in the same periodic group, their electronic configurations are quite different. The niobium spectrum is considerably more complex than that of antimony, but it may be profitable to attempt to analyze the data by the same procedure.

Figure 27 should provide the simplest test of the method. Curves 1, 2 and 3 have an isosbestic point at 255 mμ, an indication that only two species exist over this concentration range. Let us assume that at the extremely high chloride activity of curve 3, Figure 26, only the single species, designated as species (I), having a maximum absorption at 281 mμ is present and that this curve therefore represents the absorption of pure (I). Let us further assume that the other species present (II) does not contribute to the absorption at 330 mμ. The subtraction of the absorbance due to species (I) as measured by the absorbance at 330 mμ yields net curves for the spectra of the species other than (I).

Figure 28 is the result of this process. Unfortunately, there is little hope of obtaining the net curves of the other species represented here. Indeed, the general behavior of the curves indicates that none of the species that absorb in that region are present in high enough

FIGURE 28

NET ABSORPTION CURVES OBTAINED
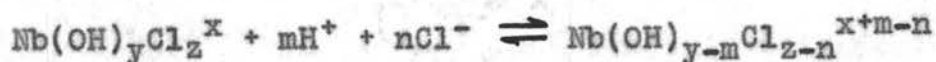FROM FIGURE 27 BY SUBTRACTION
OF THE 281 mμ PEAK.
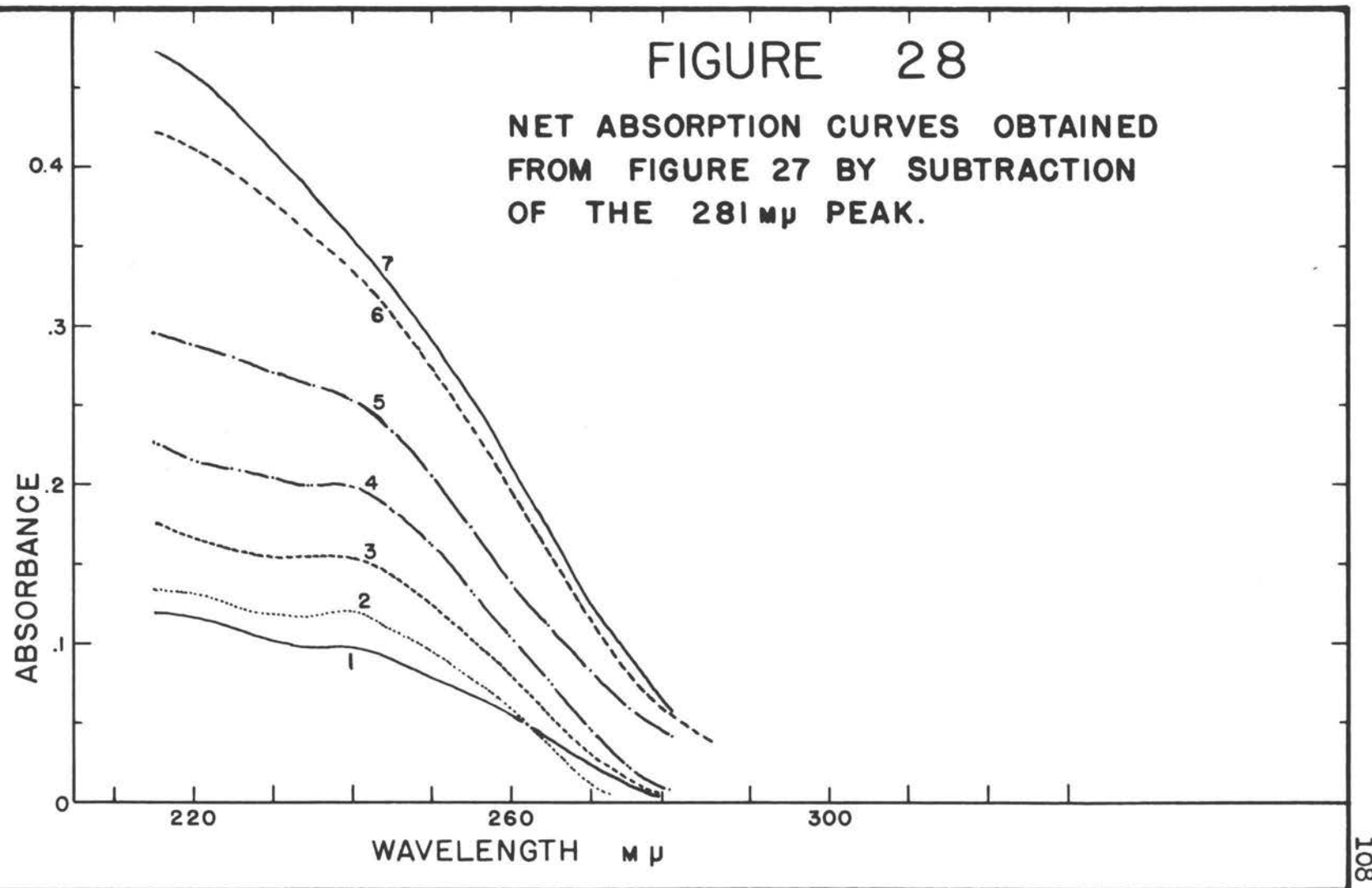
concentration to be separated from the others by this
method.

The same assumptions were applied to an analysis of
the curves of Figure 26. The shape of the net curves ob-
tained indicated that the assumption that no species other
than (I) absorbed at 330 mμ was not valid. An estimate of
the correction was obtained from this plot and the sub-
traction process repeated. The adjusted net curves are
shown in Figure 29. A species designated as (III) is
prominent in this set of curves, with an absorption peak
at about 260 mμ.

In both Figures 28 and 29, decreasing HCl activity
is accompanied by a sharp increase in absorption at the
lower wavelengths, perhaps resulting from an absorbing
species with a high extinction coefficient at a wavelength
below the usable range of the D.U. spectrophotometer. The
unfortunate circumstance that this absorption peak spills
over into the regions where species (II) and (III) absorb
makes any further analysis of the curves in Figures 28 and
29 highly subjective and useless for obtaining structural
information. However the data on the variation of the
absorption of the peak at 281 mμ obtained from the prepara-
tion of the net curves may yield some information con-
cerning species (I).

FIGURE 29

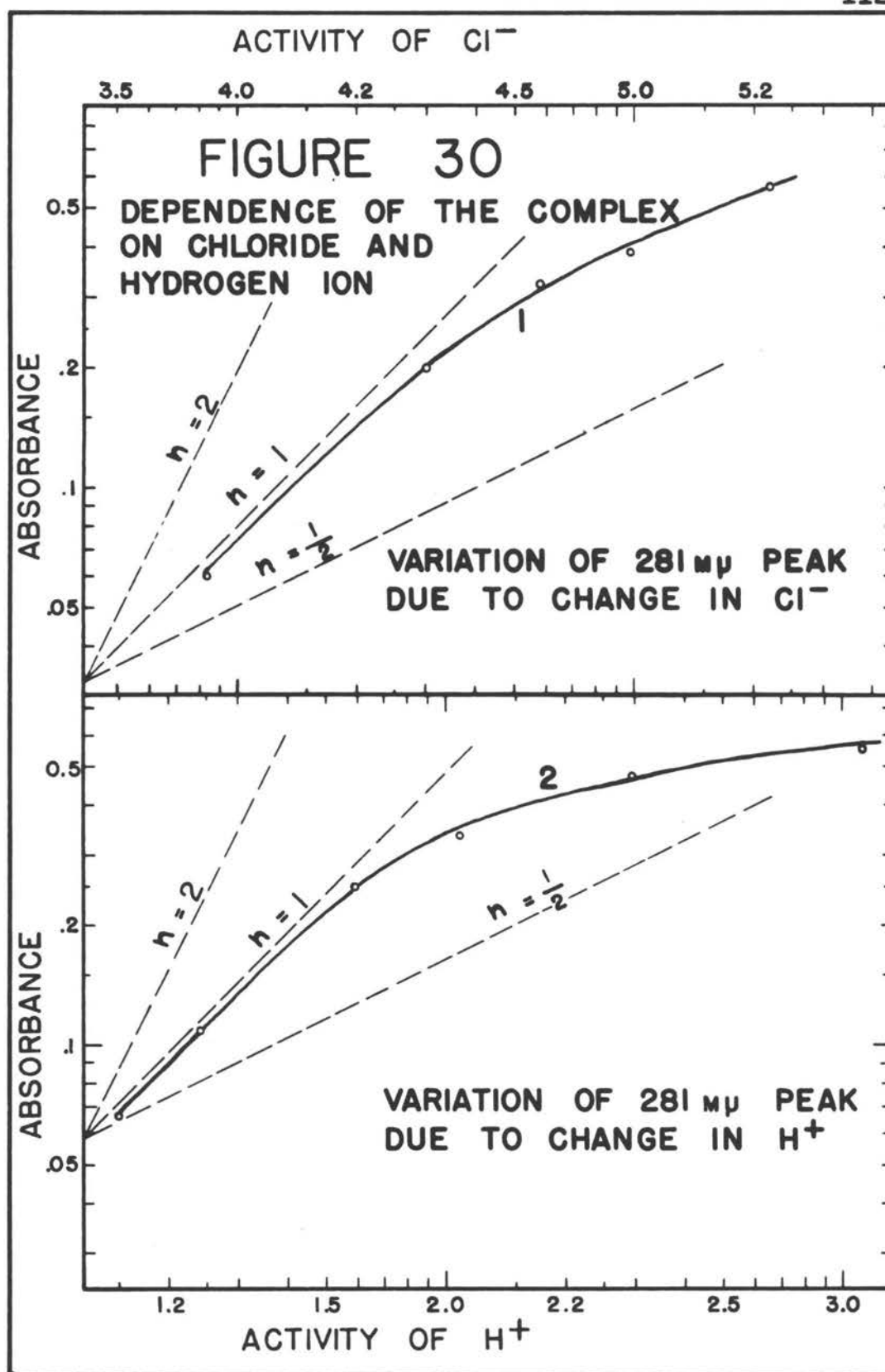NET ABSORPTION CURVES OBTAINED
FROM FIGURE 26 BY SUBTRACTION
OF THE 281 mμ PEAK.
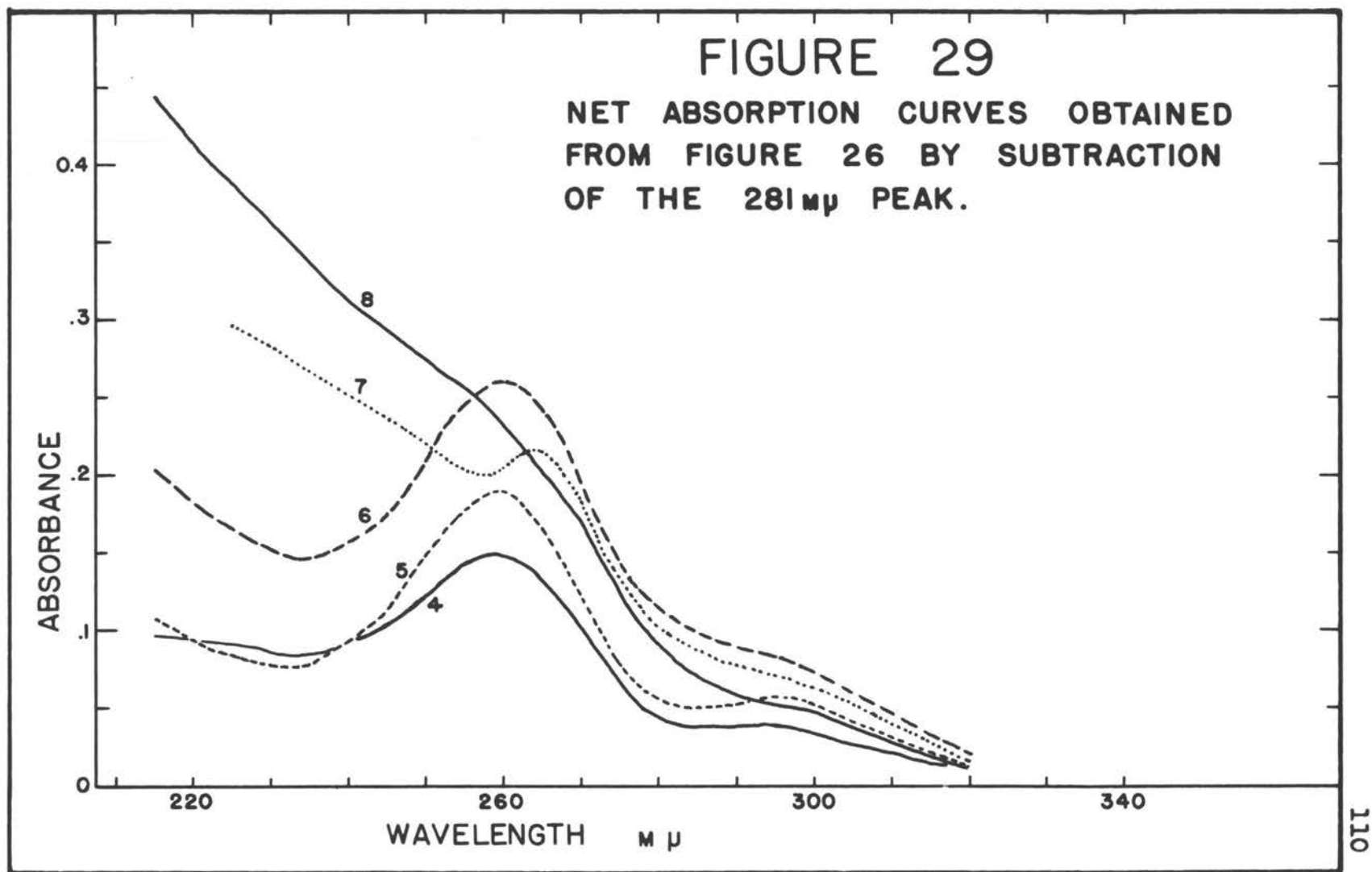
If we consider the reaction

$$Nb(OH)_yCl_z{}^x + mH^+ + nCl^- \rightleftharpoons Nb(OH)_{y-m}Cl_{z-n}{}^{x+m-n}$$

as taking place in the formation of (I), the equilibrium constant would be represented by:

$$\log K_c = \log \left[Nb(OH)_{y-m}Cl_{z-n}{}^{x+m-n} \right] - \log \left[Nb(OH)_yCl_z{}^x \right]$$
$$- m \log \left[H^+ \right] - n \log \left[Cl^- \right] .$$

If the total amount of niobium and the hydrogen ion concentration are kept constant, then a relationship containing n as a factor should exist between the concentration of the complex, as measured by its absorbance, and the concentration of chloride ion. As the chloride concentration becomes low, a plot of log absorbance vs. $\log \left[Cl^- \right]$ will approach a slope of n. The value of m may be evaluated from the limiting slope of the plot of log absorbance vs. $\log \left[H^+ \right]$ at constant chloride ion concentration.

By substituting activities for concentrations in the preceding expressions, the method may be extended to all systems. As previously stated, it is assumed that the activity coefficients of the niobium species do not change appreciably in the LiCl-HCl solutions or below 1 $\underline{N}$ HCl concentrations in HClO4-HCl solutions. Figure 30 gives the plots of log A vs. log chloride ion activity (curve 1)

FIGURE 30
DEPENDENCE OF THE COMPLEX
ON CHLORIDE AND
HYDROGEN ION

VARIATION OF 281 mµ PEAK
DUE TO CHANGE IN Cl⁻

VARIATION OF 281 mµ PEAK
DUE TO CHANGE IN H⁺

and log A vs. log hydrogen ion activity (curve 2).

Both curves appear to have a limiting slope of one, signifying the involvement of one chloride and one hydrogen in the formation of species (I) from its precursors. Since the latter are unknown, no structure may be assigned to (I) with certainty, but no information has been presented in this thesis to conflict with the frequently postulated $HNbOCl_4$ or H_2NbOCl_5. If (I) was given the formulation H_2NbOCl_5, a moderately strong acid whose ion $(HNbOCl_5)^-$ was responsible for the characteristic absorption at 281 mμ, then at lower hydronium ion or chloride ion concentrations loss of an HCl could produce $HNbOCl_4$, again a moderately strong acid. In highly acid solutions, the unionized form could exist with a spectrum characteristic of species (III), but in low hydronium ion concentrations, the acid would ionize to the $(NbOCl_4)^-$ ion, which could be without optical absorption in this region.

An alternative explanation involves the postulation of polymeric species. By analogy with the chromate-dichromate system, (I) and (III) could be monomeric and dimeric forms, respectively. (I) is definitely monomeric because of the linear relationship between the absorbance at 281 mμ and the concentration of niobium (see Figure 15). An increased tendency to form polymeric species is to be expected in niobium solutions as the activity of the

complexing agent decreases. A dimeric form having a different optical absorption spectrum could exist over a limited concentration range. This supposition should be checked by studies in which the concentration of niobium is varied.

SUMMARY

An investigation of the behavior of niobium in
hydrochloric acid solutions has been justified by a lack
of specific information concerning the aqueous chemistry
of this element. A continuing need exists for the
development of analytical procedures for niobium that com-
bine freedom from interference, sensitivity, and accuracy
with simplicity and speed in handling. The peculiar
properties of niobium and the elements which accompany it
require that the element be separated or determined while
in an ionic form. For these elements, this requirement
means that complexation must be employed for the analysis.

The chloro complexes of niobium formed in highly
concentrated hydrochloric acid provide a usable system for
analysis. Niobium hydrous oxide is quite soluble in
highly concentrated hydrochloric acid.

Preliminary experiments to determine the effect of
large concentrations of zirconium in solutions containing
niobium showed that increasing the amount of zirconium
above a ten to one ratio resulted in the incomplete pre-
cipitation of niobium. The zirconium did not keep the
niobium in ionic form, however, but apparently acted to
form highly stable colloidal solutions, not detectable by
ordinary optical means, but capable of adsorbing or

including niobium and preventing it from exhibiting its
characteristic properties. Indications are that the
niobium is included in relatively low molecular weight
polymers that are quite stable toward coagulation, but
allow the niobium to remain in slow equilibrium with ionic
species.

Dilute hydrochloric acid solutions containing
niobium appear to exert a marked catalytic effect on the
polymerization of acetone-potassium thiocyanate solutions.

Hydrochloric acid solutions of niobium were found
to have an absorption spectrum in the region 215-360 mμ
which exhibited a change in shape with changes in concen-
tration of the acid. The most prominent feature of this
spectrum was an absorption maximum at 281 mμ. Zirconium
also absorbed in the spectral region investigated, with a
maximum apparently just below 215 mμ, the lower limit of
the spectrophotometer.

Mixed solutions of zirconium and niobium in hydro-
chloric acid solutions gave spectra that very nearly
coincided with the sum of the individual absorption spec-
tra. There is then, little ionic interaction and apparent-
ly little adsorption of ionic species in these solutions.

A spectrophotometric method for niobium was
developed using concentrated hydrochloric acid as the
reagent. The absorbance at 281 mμ was found to be directly

proportional to the concentration of niobium from zero to 10 μg./ml. The molar absorbance index, a, equals 1 x 10^4 (a = $\frac{A}{b \cdot c}$; A = absorbance; b = cell thickness; c = molar concentration). Reproducibility and the effect of variables were determined. The interference of selected ions was shown.

The charge on the complexes in concentrated HCl solution was shown to be negative. Attempts to obtain the spectrum of NbCl$_5$ in anhydrous medium were inconclusive due to shortcomings in the equipment at hand. There were indications of absorptions corresponding to those obtained in concentrated aqueous hydrochloric acid, but the absence of water could not be assured. Solvent effects with ethyl ether were noted.

It was shown that niobium can be extracted into ethyl ether from highly concentrated hydrochloric acid solution. The spectrum of the extracted species was obtained.

Absorption spectra for three different species were definitely observed, the 281 mμ peak, one at about 260 mμ, and one having a strong absorption below 215 mμ. Indications were obtained for species absorbing at 230 mμ and 320 mμ.

The relative activity of chloride ion in perchloric acid solutions and hydrogen ion in lithium chloride

solutions was obtained at ionic strengths of 10.5. These
were used in determining the chloride and hydrogen ion
dependence of the species absorbing at 281 mμ. The data
indicate that one hydrogen and one chloride ion partici-
pated in the formation of this species.

All of the observations were consistent with the
assumption that the 281 mμ peak is associated with a
species of the form H_2NbOCl_5.

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APPENDICES

APPENDIX A

SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS
OF NIOBIUM PENTOXIDE

The sample was representative of the "Columbium Pentoxide" obtained from MacKay. The analysis was performed by the Northwest Regional Laboratory of the Bureau of Mines, Albany, Oregon.

Element	Estimated Range (%)
Al	0.001 - 0.01
Ca	0.01 - 0.1
Cu	0.001 - 0.01
Mg	0.001 - 0.01
Ni	0.001 - 0.01
Fe	0.01 - 0.1
Mn	0.01 - 0.1 (+)
Si	0.01 - 0.1
Ti	0.01 - 0.1
Nb	Over 10%
Zr	0.001 - 0.01
B	0.001 - 0.01
Ta	Less than 0.10

APPENDIX B

PREPARATION AND ANALYSIS OF
ZIRCONYL CHLORIDE HYDRATE

Impure $ZrCl_4$ was dissolved in a minimum of water
(about 100 g. crude tetrachloride to 500 ml. water) and
the insoluble residue was filtered off. The clear solu-
tion was heated on the hot plate to about 70-80°C. and an
amount of concentrated HCl was added to bring the final
concentration to 8.5 $\underline{N}$ HCl (about 975 ml. 12 $\underline{N}$ HCl). The
calculations took into consideration the HCl produced by
the hydrolysis in water of the tetrachloride. The solu-
tion was allowed to cool to room temperature and finally
was cooled in an ice bath.

The precipitate formed was filtered into two 12 cm.
Buchner funnels using Angel #202 paper. Sintered glass
would be more suitable. The precipitate was dissolved in
a minimum amount of hot 2 $\underline{N}$ HCl and precipitated in the
hot with that amount of concentrated HCl calculated to
give a final concentration of 8.5 $\underline{N}$. The precipitate was
removed by filtration as before from cold solution and air
was pulled through the filter cake overnight. It would be
best to have the precipitate in as thin a layer as pos-
sible on the filter.

The precipitate was spread out on large watch glasses and broken up as much as possible using a glass spatula. The watch glasses were placed in a vacuum desiccator and the precipitate dried over solid NaOH flakes until the odor of HCl had disappeared.

The solutions from the various precipitations were reduced in volume by evaporation and in the process the HCl concentration was reduced to 6 $\underline{N}$. Concentrated HCl was added in an amount calculated to raise the HCl concentration to 8.5 $\underline{N}$ and further hydrate was thus obtained. The corresponding solutions from several runs were combined and it was possible in this way to recover most of the zirconium in a pure form.

The combined product from several runs was powdered as much as possible by hand grinding with a glass spatula and was tumbled in a bottle for 24 hours to attain uniformity.

The zirconium content was determined by weighing out in weighed platinum dishes duplicate samples of the chloride hydrate, dissolving in several ml. of water, adding 3-5 drops of 28% ammonium hydroxide, and evaporating the solution to dryness and allowing them to remain for 3-4 hours. The residue was ignited in the furnace overnight at 800-900°C. and weighed as ZrO_4. The data for the zirconyl chloride hydrate prepared for this paper

are as follow:

No.	Sample Weight (grams)	Oxide Weight (grams)	Zirconium Weight (grams)	% Zirconium
1	0.4205	0.1770	0.1310	31.13
2	0.3011	0.1273	0.0943	31.28

Average 31.20%

Calculated: $ZrOCl_2 \cdot 5H_2O = 29.49\%$

$ZrOCl_2 \cdot 6H_2O = 31.46\%$

APPENDIX C

The following is an illustration of the method employed in determining the HCl concentration of the stability samples. The specific gravity (column 2) is determined by careful measurement with a Westphal balance. The literature (23,p.1501) gives the corresponding % HCl (column 3) from which the actual weight per liter and moles per liter (corresponding to normality) may be calculated.

Sample No.	Specific Gravity	% HCl	Weight HCl g./l.	True $\underline{N}$
12N	1.1788	35.76	421.5	11.56
11N	1.1731	34.62	406.1	11.14
10N	1.1586	31.72	367.5	10.08
8N	1.1288	25.76	290.8	7.97
6N	1.0988	19.76	217.1	5.95
1N	1.0153	3.12	31.7	.87
.1N	1.0062	1.38	13.9	.38

APPENDIX D

REPRODUCIBILITY DATA

Run No.	Flask No. 1	2	3	4	5	T_R	$\bar{X}_R$
1	30	25	25	23	25	128	25.6
2	33	24	23	21	22	123	24.6
3	28	24	21	18	17	108	21.6
4	23	23	16	19	19	100	20.0
5	23	18	14	14	15	84	16.8
6	38	18	15	15	16	102	20.4
						GT	645
T_F	175	132	114	110	114		
$\bar{X}_F$	29.17	22.00	19.00	18.33	19.00		

ANALYSIS OF VARIANCE CALCULATIONS
Preliminary Calculations

(1) Source of Variation	(2) Total of Squares	(3) No. of Items Squared	(4) Observations per Squared Item	(5) Total of Squares per Observation (2) ÷ (4)	(6) Sum of Squares (5) - correction
Correction	416,025	1	30	13,867.5	0
Flask	86,141	5	6	14,356.8	489.3
Run	70,637	6	5	14,127.4	259.9
Ind. Obs.	14,817	30	1	14,817.0	949.5

Analysis of Variance

Variation Due to:	Sum of Squares	Degrees of Freedom	Mean Square	F
Flask	489.3	4	122.325	12.21
Run	259.9	5	51.98	5.19
Error	200.3	20	10.015	
Total	949.5	29		

For 0.5% Significance Level, $F_{flask} = 5.17$; $F_{run} = 4.76$.

$$\sigma^2_{error} = 10.0 \qquad \sigma_{error} = 3.2$$

$$s^2_{run} = \frac{52-10}{5} = 8.4 \qquad \sigma^2_{run} = 8.4 \qquad \sigma_{run} = 2.9$$

APPENDIX E

THE DETERMINATION OF ACTIVITIES

Activities of the $HClO_4$-HCl and LiCl-HCl solutions were measured by means of the EMF developed by the cell

$$Pt, H_2(1 \text{ atm}) \mid H^+ \, Cl^- \mid AgCl, Ag \quad .$$
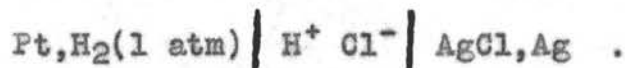
The observed potential E was assumed to follow the relationship

$$E = E^O - \frac{RT}{F} \ln \, a_{H^+} \, a_{Cl^-} \qquad E^O_{250} = 0.2221$$

regardless of the nature of the solvent.

The systems measured were kept at nearly constant ionic strength (10.5) by the addition of $HClO_4$ and LiCl. Under these conditions, it was assumed that in the first case hydrogen ion and in the second case chloride ion activities remained constant. This assumption is obviously not true, but would become essentially true as the actual concentration of HCl becomes small. This means that the absolute values of activities may be in gross error, but their relative values should be meaningful below concentrations of approximately 1 M.

From the data of Åkerlöf and Teare (1, pp.1855-68), the mean ionic activity of HCl at 25°C. and 10.5 M was calculated to be 121. The two equations used to calculate

the activities then become:

$$\log a_{H^+} = 0.0992 - E$$

$$\log a_{Cl^-} = 0.0992 - E$$

A correction was applied to the observed potential for deviations from ionic strength of 10.5 in some of the more volatile solutions and also for the partial pressure of the solutions. The former was never more than 1.7 mv. while the latter amounted to approximately 10 mv. in one case. The corrections were calculated from the following formulae:

$$\Delta E = -0.0295 \log \frac{760}{p} \quad \text{where } p = \text{partial pressure } H_2$$

$$\Delta E = 0.059 \log \frac{10.5}{c} \quad \text{where } c = \text{molar concentration of } H^+ \text{ or } Cl^-.$$

The vapor pressures were determined to a sufficiently high degree of accuracy by means of an isotensiscope. The data for $HClO_4$-HCl solutions are given in Figure 31. The $LiCl$-HCl solutions exhibited low vapor pressures. The solution 10.5 $\underline{M}$ in chloride and 9.7 $\underline{M}$ in hydrogen ion had a vapor pressure of 41 mm Hg. All others were 20 mm Hg or lower.

The actual EMF measurements were carried out in a cell divided by a sintered glass disc into two compartments, one for the H electrode and the other for the Ag-AgCl electrode. The cell was rinsed three times with

the solution to be measured and filled with approximately 10 ml. of solution. Tank hydrogen was bubbled through 50 ml. of the same solution, using a sintered glass wand, in order to saturate with the vapor of the test solution and was bubbled into the hydrogen electrode compartment from half to three-quarters of an hour prior to introduction of the electrodes. The platinized platinum hydrogen electrode was introduced and hydrogen was bubbled in at the rate of approximately two bubbles per second for five minutes. The Ag-AgCl electrode was inserted and allowed to equilibrate for two minutes. Four to six readings of the potential were taken at one minute intervals, the potentiometer being standardized against a reference cell before each reading. The average reading was taken unless a tendency to drift was noted. In these cases readings were continued until four readings were obtained having a maximum spread of approximately .2 - .3 mv.

FIGURE 31

VAPOR PRESSURE VS. HCl CONCENTRATION
PERCHLORIC ACID SOLUTION
IONIC STRENGTH 10.5