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WITH TETRAPHENYLARSONIUM CHLORIDE.

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THE EXTRACTION OF TITANIUM- AND NIOBIUM-THIOCYANATE
COMPLEXES WITH TETRAPHENYLARSONIUM CHLORIDE

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Norman, Oklahoma

1966

THE EXTRACTION OF TITANIUM- AND NIOBIUM-THIOCYANATE
COMPLEXES WITH TETRAPHENYLARSONIUM CHLORIDE

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Dedication

Dedicated to the belief and hope that there will evolve a better world, and for many there will be the gift of immortality.

This work is also dedicated to my parents and teachers, all of whom have instilled in me the idea that perseverance is the catalyst for a fruitful endeavor.

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THE EXTRACTION OF NIOBIUM- AND TITANIUM-THIOCYANATE
COMPLEXES WITH TETRAPHENYLARSONIUM CHLORIDE

CHAPTER I

INTRODUCTION

Arylarsonium salts have been the subject of extensive investigation because of their wide applicability as analytical reagents. These salts have been found to be useful in volumetric, gravimetric, electrochemical, and spectrophotometric methods and are of interest in particular as cations of ion-pairs which may be extracted from aqueous solutions into non-aqueous solvents. Bock and Beilstein¹ have studied the distribution of ion-pairs of tetraphenylarsonium ion, TPA, with a number of inorganic anions between water and chloroform. Analytical procedures based on the extraction of complex anions of tantalum², gold³, palladium⁴, cobalt⁵, tungsten⁶, and iridium⁷ into chloroform as TPA ion-pairs have been described. Arylarsonium salts have been shown to be excellent for the analysis of certain complex metal ions, and when the precipitation reaction for forming the arsonium ion-pair is combined with a solvent extraction separation scheme, a high

selectivity of analysis is frequently possible. The extractability of an anionic metal complex, as an arsonium ion-pair, is a function of the nature of the arsonium cation, polarity and dielectric of the solvent, the acid strength and ionic strength of the aqueous medium, and the stability of the anionic complex. By varying these parameters it is possible to achieve separation of one metal or a group of metals from another group prior to a final measurement on the extracted species.

Other desirable properties of extraction methods of analysis which utilize arylarsonium salts is their simplicity, and the rapidity of the experimental procedure used. In many cases, metals which are difficult to separate by precipitation, by extraction procedures alone, or even ion-exchange procedures, are easily separated by precipitation and subsequent extraction of an onium salt. The application of ion-pair extraction schemes to the analysis of complex material (steels, alloys, etc.) has been quite successful in shortening the time required for a complete analysis since lengthy separation procedures are no longer required. An advantage of ion-pair extractions over chelate extraction systems is that the equilibrium reaction for the formation of the ion-pair usually proceeds at a much faster rate than for the formation of a chelate. Several chelate systems have been reported in which the extraction varied from several minutes to an hour or more in

order to extract an appreciable quantity of the metal complex⁸.

When the desired constituent is separated from the sample, the final analysis can be achieved by many methods. It appears that absorption spectrophotometry is the simplest technique for those complexes which have absorbance bands in the visible or near-ultraviolet spectral regions. With the recent discovery of atomic absorption spectroscopy, and application of gas chromatography to inorganic analysis, it appears that onium extraction methods of separation will be of even greater use in the analysis of metals.

The behavior of tetraphenylarsonium chloride, TPACl, in aqueous and non aqueous media has recently been reported upon by Fok and Sandell⁷. The solubility of TPACl and TPACl·HCl in chloroform is 0.703 and 0.0391 M, respectively, whereas the solubility of TPACl·2H₂O in water is 0.990 M. The ionization constant of TPACl in water is 7.1×10^{-2} M, and the association constants in chloroform for the formation of dimers and tetramers are 106 M^{-1} and $3.4 \times 10^5 \text{ M}^{-3}$, respectively, at 25°C. The partition coefficient between water and chloroform, $\frac{[\text{TPACl}]_{\text{org}}}{f \times [\text{TPACl}]_{\text{aq}}}$, where $\log f = 0.6$ u for sodium chloride, at infinite dilution is given as 3.2 ± 0.1 . Additional empirical equations are given which describe the chloroform extraction system of TPACl in aqueous solutions $\leq 2 \text{ M NaCl}$ and $\leq 0.1 \text{ M HCl}$ and TPACl up to 0.2 M in chloroform. Polymerization of

TPACl must be considered when the concentration of TPACl in chloroform is greater than 1×10^{-3} M; and in hydrochloric acid solutions, additional reactions which lead to the formation of TPACl·HCl must be considered. It is reported by Fok that further work is necessary to elucidate the TPACl·HCl formation in solutions of high hydrochloric acid concentrations.

Data from vapor pressure lowering measurements with a thermoelectric osmometer made on TPACl solutions in anhydrous chloroform at 25°C are also used to calculate dimer and tetramer constants having values of 72 M^{-1} and $4.0 \times 10^5 \text{ M}^{-3}$, respectively. The difference between vapor pressure and extraction results is attributed to the presence of water in the chloroform in the extraction studies.

The TPA salts of several anions have been studied with respect to their solubility and thermal decomposition characteristics⁹. Cole and Pflaum also measured the molar absorptivity, ϵ , of TPACl in aqueous solutions. Values of 3230 and $3160 \text{ M}^{-1} \text{ cm}^{-1}$ at 264 and 271 m μ are a little lower than the value of $3400 \text{ M}^{-1} \text{ cm}^{-1}$ at 264 m μ which is reported by Fok. In addition to the above studies, Forster and Goodgame recently prepared the TPA isothiocyanato-complexes of Ni(II) and Cu(II), after which the electronic and infrared spectra were investigated¹⁰.

The development of analytical methods for the analysis

of niobium was hindered for many years due to the similarity of the chemistry of niobium and tantalum. The similar behavior of these elements as well as their natural occurrence as mixtures in ores led to much confusion with respect to their discovery, and in their characterization. The development of separation schemes for these "twin" elements was also hampered by the complexity of the ores in which they occurred.

In 1925 Schoeller¹¹ introduced tannin, tannic acid, as a valuable tool in earth-acid analysis. Tannin acts as a colloidal precipitant and permits the separation of niobium and tantalum from titanium in dilute sulfuric acid. More recent advances have resulted in the use of cupferron as a precipitant for the precipitation of niobium, tantalum, titanium, vanadium, iron (III), uranium (VI), tungsten, molybdenum, and a few other elements. When the cupferron precipitation separation is combined with an anion-exchange resin separation, niobium and tantalum can be separated from all other elements as well as from one another¹². The above method is excellent for the separation of niobium, and its only disadvantage is that it is time consuming. The ion-exchange methods were very significant in contributing to recent developments and simplifications in earth-acid analysis. Fundamental studies of the ion-exchange behavior of niobium and tantalum have been of major importance in elucidating the subtle differences in the behavior and solution chemistry of niobium

and tantalum.

The titrimetric determination of niobium, in principle, can be accomplished by reduction of Nb(V) to Nb(III) in a Jones Reductor followed by indirect titration procedures using iron (II) and potassium permanganate.¹³ The interferences in this method are severe, and of course require a prior separation of the niobium.

Solvent extraction methods for the separation and subsequent spectrophotometric determination of the niobium are increasing in popularity. These methods are rapid, require only a minimum number of preliminary separations from associated elements, and are capable of differentiating between the two earth acids. One of the more promising solvent extraction methods for niobium is the 8-quinolinol (oxine) method,¹⁴ which involves the chloroform extraction of the niobium oxinate chelate from an ammoniacal citrate solution. Since the chelate is colored, spectrophotometric measurements can be made on the organic phase. The method has some disadvantages in that many elements form colored oxinates, and consequently a prior separation of niobium must frequently be made before extraction with oxine.

Hydroquinone¹⁵ has been introduced as a chromophoric reagent for the spectrophotometric estimation of niobium; however, the reagent cannot be used as an extracting agent. Consequently the niobium must be separated by other means prior

to forming the chelate. Even though the chelate is unstable, temperature sensitive, and is subject to the usual interferences, the reagent has been of use in determinations of niobium.

Other chelating reagents used for the analysis of niobium are pyrogallol¹⁶, sulfosalicylic acid¹⁷, disodium, 2-dihydroxybenzene-3, 5-disulfonate (tiron)¹⁸, and ascorbic acid¹⁹. These reagents have been found to be limited in applicability and unfortunately are plagued by interferences.

Other chelating reagents recently introduced for the determination of niobium are xylenol orange^{20,21}, 4-(2-pyridylazo)resorcinol²²⁻²⁵ and 1-(2-pyridylazo)-resorcinol²⁶. In the case of xylenol orange, titanium, tantalum, and aluminum are masked with ascorbic acid. It is reported by Elinson that 50 μ g of niobium can be determined in the presence of 5 mg of molybdenum and tungsten. Also, the above mentioned azo derivatives of resorcinol show promise as acceptable reagents for niobium. Alimarin²⁷ has recently reviewed the photometric determination of niobium with azo-dyestuffs and concludes that this class of reagents have considerable promise as specific reagents for niobium.

Chromogenic reagents which form complex ions with niobium are the peroxide and thiocyanate ions. The peroxide method, like all other colorimetric methods for niobium, is

beset with the problem of interferences; however, it is possible to analyze for niobium in the presence of titanium by developing the color of the complex in a mixture of concentrated sulfuric and phosphoric acid.

The reaction between niobium and thiocyanate ion, which was first described in 1896²⁸, was developed into a quantitative colorimetric procedure²⁹ for niobium in 1946, and is probably the most widely used method for the determination of niobium. In one thiocyanate procedure, the yellow color of the niobium thiocyanate complex is developed in a homogeneous water-acetone medium³⁰. The homogeneous method has many interferences from metals which are difficult to reduce or mask under the conditions necessary for the determination, and consequently requires a time consuming prior separation of the niobium. An interference with the determination of niobium has also been reported to occur from the polymerization of thiocyanic acid. Moreover the concentration of the reagents must be closely controlled since the color intensity of the niobium complex is sensitive to any changes in reagent concentration.

Another thiocyanate method for niobium involves the solvent extraction of the niobium thiocyanate complex into organic solvents such as ether^{29,31} or ethyl acetate³². This method has the disadvantage that the niobium sample must be repeatedly evaporated down to the occurrence of sulfuric acid

fumes prior to analysis in order to convert the niobium into a "reactive" ion, which is a nonhydrolyzed species. The method is also subject to interference by hydrolysis of the niobium and tantalum which results in an incomplete extraction of the niobium. Again, the procedure must be modified by using preliminary separation steps in order to analyze for niobium in the presence of more than small quantities of tungsten, rhenium, platinum, vanadium, and molybdenum. The concentration of reagents must also be controlled since the complex is sensitive to any changes, and the usual interference from polymerization of thiocyanic acid is noted. Recently, a thorough study of the variables for development of the color of the complex and its subsequent extraction was reported³³.

Many modifications of the basic thiocyanate methods for niobium have appeared in the literature in recent years. Hume and co-workers^{34,35} pointed out that tartaric acid could be used to dissolve fused niobium samples that were insoluble or metastable in hydrochloric acid. Vanossi^{36,37,38} reported that the extraction of the thiocyanate complex of niobium with ethyl acetate, EtOAc, helps avoid the problem of hydroxyl complex formation that previous workers had noted. Tungsten, tantalum, and niobium were extracted with EtOAc; niobium and tantalum were subsequently separated from tungsten by precipitation. Hastings and McClarity³⁹ analyzed for niobium in pure tantalum or Ta_2O_5

by extraction of the thiocyanate complex of niobium using ethyl ether. It was necessary to construct calibration curves corresponding to several ratios of tantalum to niobium. Moreover, molybdenum interfered seriously. Milner and Smales⁴⁰ separated niobium from ores by means of a cinchonine precipitation prior to using the aqueous acetone procedure. Marzys⁴¹ used both the ether extraction and aqueous acetone method to analyze for niobium in ores. The careful control of experimental conditions was emphasized.

Crouthorn and co-workers⁴² investigated the color development step of titanium, vanadium, and niobium in aqueous acetone. Niobium was separated from interferences by extraction of a niobium fluoride complex with methyl ethyl ketone prior to developing the thiocyanate complex. The effects of hydrolysis and hydration in hindering the reaction of thiocyanate with niobium were found to be real, and were dependent on the nature and concentration of the acid in which the niobium sample was dissolved. Furthermore, the yellow complex which is formed in the aqueous acetone medium was shown to be anionic in nature. Crouthorn concluded that Nb(V) complexes and NbO^{+3} or $\text{Nb}(\text{OH})_x^{+(5-x)}$ were the "reactive" forms of niobium and that "nonreactive forms" were probably niobates and polymeric forms of niobium, which require a very long time to reach an equilibrium with thiocyanate.

Bacon and Milner⁴³ have made a thorough study of the conditions for formation of niobium thiocyanate complexes and of the decomposition of thiocyanate ion in acidic aqueous acetone media.

Ziegler⁴⁴ has shown that niobium and tantalum may be separated by precipitation or extraction of thiocyanate complexes with polyethylene glycol esters, or polypropylene glycol esters; also, amines⁴⁵ such as tributyl amine permit the separation of niobium and tantalum. A single stage extraction gives 95% Nb_2O_5 , and the purity may be increased through multistage extraction.

Grimaldi⁴⁶ extracted niobium thiocyanate into EtOAc after separating the niobium from tungsten, vanadium, molybdenum, and rhenium with a sodium hydroxide fusion and leaching step. A detailed study was also made on the interference of various cations and anions.

The use of nitron, (4,5-dihydro-1, 4-diphenyl-3,5-phenylimino-1, 2, 4-triazole), in dioxane as an extracting agent for niobium thiocyanate complexes has been investigated by Babenko.⁴⁷ Yoshimura has recently studied the extraction of niobium with several amines in chloroform.⁴⁸ Mari⁴⁹ made a detailed study of the extraction of niobium, titanium, and tantalum thiocyanate complexes with esters, ethyl ether, alcohols, chloroform, carbon tetrachloride, and benzene. Using radiotracer

techniques he found that 1.0% niobium is extracted from a 1 M sulfuric acid-2 M thiocyanate medium with chloroform.

Talipov⁵⁰ extracted a niobium thiocyanate complex with 1,4-bis(3,4-dihydroxyphenylazo) benzene in chloroform. Tungsten, vanadium, thorium, and manganese do not interfere, nor does a three-fold excess of titanium or a five-fold excess of tantalum.

Other investigations and modifications of the thiocyanate procedures for niobium have been reported by Pilipenko,⁵¹ McCown,⁵² Ward,⁵³ White,⁵⁴ and Shrimal.⁵⁵

C. M. Ni and S. C. Liang reported the extraction of niobium from hydrochloric acid or sulfuric acid into chloroform using N-benzoyl-N-phenylhydroxylamine, BPFA.⁵⁶ Molybdenum, tungsten, vanadium, and zirconium are not serious interferences; however, titanium is. Using the method of continuous variations and the method of Bent and French, Ni found the composition of the extracted species to be: Nb/BPFA/SCN = 1/2/1, which indicates a monothiocyanato complex of niobium.

A novel separation for niobium has been suggested by Marchenko.⁵⁷ Niobium, thiocyanate, and methylene blue form an aqueous insoluble triple complex which is quantitatively separated by flotation from an aqueous solution by toluene. After separation and washing of the precipitate, it is dissolved and niobium is determined by the ether extraction

method. Masking agents are added to eliminate the interferences of titanium and molybdenum. Yoshida⁵⁸ has analyzed for niobium in tantalum and Ta_2O_5 by masking niobium with fluoride, extraction of tantalum with methyl isobutyl ketone, demasking niobium with boric acid, and extracting the thiocyanate complex of niobium with ethyl acetate.

Another extensive investigation of the niobium thiocyanate extraction system has been made by Minczewski⁵⁹⁻⁶². The addition of carbon tetrachloride, benzene, chloroform, and 1,1,1-trichloroethane to ether extracts of the complex caused dissociation of the thiocyanate complex. It was further noted that the addition of carbon tetrachloride to the extract changed the absorbance and shifted the wavelength of maximum absorbance, $\lambda_{max.}$, to longer wavelengths whereas acetone caused $\lambda_{max.}$ to shift to shorter wavelengths. Minczewski also studied the extraction of niobium with tributyl phosphate in chloroform and recommends elimination of the molybdenum and titanium interferences by using hydrogen peroxide to mask niobium while Mo(VI) is extracted with ether. Titanium and niobium are extracted as thiocyanate complexes with tributyl phosphate and titanium is subsequently removed from the extract by backwashing with 1.8 M hydrochloric acid.

The composition of the thiocyanate complexes of niobium has not been investigated as thoroughly as the separation

and analysis of this element; however, the nature of niobium ions in aqueous media, and its halide, oxalate, and oxo complexes have been the subject of several investigations in recent years.

Werner⁶³ studied the distribution of radioactive Nb-95 between aqueous hydrochloric acid and methyl isobutyl ketone as a function of hydrogen, chloride, and thiocyanate ion concentrations at an ionic strength of 7, and assigned to the species extracted, the formula $\text{Nb}(\text{SCN})_6^-$ associated with oxonium ions of the type $(\text{R}_2\text{OH})^+$ where R is an alkyl group. The species NbCl_6^- was also reported to occur. Troitskii⁶⁴ studied the mechanism of the extraction in butyl alcohol, and concluded that the extracted species is $\text{HMbO}(\text{SCN})_4$. Also reported is a compound with the formula $\text{H}[\text{NbO} \{ \text{O}(\text{C}_2\text{H}_5)_2 \} (\text{SCN})_4]$ which occurs in diethyl ether; however, no evidence is presented to affirm its presence. Evidence is presented for both a colorless thiocyanate complex of niobium and a colored complex. The former complex occurs at very low thiocyanate concentrations and can be extracted immediately after mixing niobium and thiocyanate solutions.

Golub and Sych⁶⁵ made a thorough investigation of the thiocyanate complexes in methanol, butanol, and dimethylformamide (DMF) using conductance techniques, spectrophotometry and preparation of the niobium salts by forcing their precipitation

through evaporation of the solvent. Spectrophotometric results, analyzed by plotting $\log \left[\frac{A}{A_{\max} - A} \right]$ versus $\log [KSCN]$, indicated complexes having thiocyanate/niobium ratios of 1/1, 2/1, and 3/1 in methanol; 1/1, 2/1, and 4/1 in butanol; and 1/1 and 7/1 in DMF. Precipitated niobium salts were isolated with a ratio of 4/1 and 7/1 in the methanol and DMF systems, respectively; the reported compositions were $K[Nb(OMe)_2(CNS)_4] \cdot MeOH$ and $K_2[Nb(CNS)_7] \cdot 3DMF$. The same authors report that "Alimarin and Podval'naya studied the mechanism of formation of the yellow complex in acid media, determined the composition of addition products of the thiocyanato-complex of niobium with alkaloids (Quinine, cinchonine, etc.), and concluded that the complex $H[NbO(SCN)_4]$ was present in solution." After reviewing the work of Alimarin and Podval'naya, and Troitskii, Golub and Sych conclude that "all available information on the thiocyanato-complexes of niobium is purely qualitative." Ni has recently reported the extraction of a monothiocyanato complex of niobium with BPFA, in which the Nb/BPFA/SCN ratio is 1/2/1. (see page 12).

The most recent publication on the niobium thiocyanate complexes, by Pilipenko and Savranskii, presents evidence for a complex of niobium with acetylacetone and thiocyanate in which the niobium/acetylacetone/thiocyanate ratio is 2/1/1, indicating a dinuclear complex involving niobium atoms bonded

together by an oxygen bridge. Most of the evidence for the oxygen bridge is based on an infrared band at 800-850 cm^{-1} that is attributed to a Nb-O stretching absorption⁶⁶.

In the case of thiocyanate complexes, the mode of bonding of the thiocyanate ion to the central atom or metal ion may occur through a metal-sulfur bond (M-SCN^-) or through a metal nitrogen bond (M-NCS^-), which is an isothiocyanate complex. Mitchell and Williams⁶⁷, made a study of the infrared spectra of a number of inorganic thiocyanates and isothiocyanates and concluded that the isothiocyanates have a C-N stretching vibration between 2105 cm^{-1} and 2060 cm^{-1} while the corresponding thiocyanate frequency occurs at 2145 cm^{-1} . Hence infrared spectra are valuable in distinguishing between the two structures.

Other investigations concerning the mode of bonding in the thiocyanate complexes of W were made by Funk and Bohland⁶⁸, in which they concluded that all were isothiocyanates. Colthup⁶⁹ reported absorptions for inorganic thiocyanate ions at 2090-2020 cm^{-1} (asymmetric stretch, strong), 950 cm^{-1} (bending overtone, weak), 750 cm^{-1} (symmetric stretch, weak), and 470 cm^{-1} (bending frequency, weak). Pecile⁷⁰ reported that the MNCS configuration is characterized by a band at 860-780 cm^{-1} and MSCN at 720-690 cm^{-1} .

With complexes of the transition metal ions, the question frequently arises concerning the presence of oxo or

hydroxy ligands in the complex. For those cases in which the isolation and purification of the complex is difficult or impossible, infrared spectra are frequently valuable in establishing the presence of oxo ligands.

The M=O stretching vibration in vanadium chelates of acetylacetonate are reported to occur at 995 cm^{-1} ⁷¹, whereas more comprehensive studies list a range of $1050\text{-}950\text{ cm}^{-1}$ for the V=O vibration. The stretching vibrations of other metal oxygen double bonds such as U=O and Mo=O^{71,73}, and Ru=O^{71,74} appear in a similar frequency range.

Keller⁷⁵ recently investigated the cesium and potassium salts of the NbOF_5^{--} ion ($\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$) as solids and solutions by means of Raman and I.R. methods. Absorption bands at 932 and 935 cm^{-1} (I.R. and Raman, respectively) were assigned to a metal-oxygen stretching vibration. Sabatini and Bertini⁷⁶ reported Nb-O bands at 930 cm^{-1} (v.s.), 928 cm^{-1} (v.s.), 927 cm^{-1} (s.), and 977 cm^{-1} (v.s.) for the salts $\text{Rb}_2 [\text{NbOCl}_5]$, $\text{Cs}_2 [\text{NbOCl}_5]$, $\text{Rb}_2 [\text{NbOBr}_5]$, and $\text{Cs}_2 [\text{NbOBr}_5]$, respectively. Analogous tungsten salts showed tungsten-oxygen bands at $957\text{-}968\text{ cm}^{-1}$. The above author does not distinguish between a M-O or M=O stretching vibration. Selbia⁷⁷ has recently reviewed the oxocations of the transition metals, in which he gives the Nb=O frequency for a variety of compounds, all falling within the range $923\text{-}942\text{ cm}^{-1}$. The Ti=O band for two different Ti

saits is given at 1078, and 1020-1035 cm^{-1} , and Ti-O stretching vibration is listed at 836 and 840 cm^{-1} .

Considerable work has been done in developing and modifying methods for the analysis of niobium in complex material. Yet in spite of the large volume of work, a rapid and sensitive universal method for the analysis of niobium has not been reported. It appears that the best method to date for the analysis of niobium involves an anion-exchange separation in hydrochloric-hydrofluoric acid media, followed by colorimetric estimation of niobium as the thiocyanate complex.

The composition of the thiocyanate complex of niobium has been studied, and several complexes have been reported. In spite of several indications in the literature that the complex in non-aqueous media might actually involve equilibria between one or more complexes, no quantitative investigations of the equilibria have been reported. This study reports on a new analytical method for niobium and an investigation of the composition and nature of niobium thiocyanate complexes in aqueous and non-aqueous media.

CHAPTER II

STATEMENT OF THE PROBLEM

The investigation reported upon had three principle goals. The primary aim was to study the extraction of the arsonium salts of titanium- and niobium-thiocyanate complexes, and evaluate their extraction behavior with respect to analytical applications.

The second objective was to perfect an analytical procedure for niobium, utilizing the chloroform extraction of the niobium-thiocyanate complex ion as an ion-pair with the tetraphenylarsonium ion.

The final objective was to elucidate the stoichiometry of the extraction process, determine the composition of the extracted species, and investigate the nature of niobium thiocyanate complexes in nonaqueous media.

CHAPTER III

EXPERIMENTAL PROCEDURE

1. Apparatus and Materials

Beckman Model DU, DB, DK-1, and IR-8 spectrophotometers were used for absorption spectra measurements. The DU was operated at a mechanical slit width of 0.06 mm; 1 cm ground glass stoppered silica cells were used for all measurements in the visible and ultraviolet regions.

A buret funnel and 2.5 cm filter paper were used for filtering the non-aqueous extracts. Ground glass graduates, and separatory funnels, 75 and 300 ml, equipped with Teflon stopcocks were used for extractions.

Tetraphenylarsonium Chloride, obtained from K and K Laboratories, Jamaica, New York, and G. F. Smith, Columbus, Ohio, was recrystallized from ethanol-ether solutions if discolored or if it gave a colored solution. 0.05 M solutions were prepared.

Potassium fluoride solutions, 4M, were prepared from Mallinkrodt Analytical Reagent potassium fluoride dihydrate, filtered, and stored in a polyethylene bottle.

Mercaptoacetic acid, 80% in water (analytical grade),

was obtained from Eastmen Organic Chemicals, Rochester, New York.

A 9/2, by volume, chloroform-acetone solution was prepared by mixing 810 ml of commercial chloroform with 180 ml of acetone.

Niobium pentoxide, purportedly 99.8% pure, was obtained from K and K Laboratories, Jamaica, New York.

All other solutions were prepared from salts of analytical reagent quality.

2. Analysis of Niobium Pentoxide

Duplicate samples of the niobium oxide were analyzed gravimetrically after separating the niobium from other elements by means of an ion-exchange procedure⁷⁸. The niobium was precipitated with cupferron and then ignited to niobium pentoxide. The niobium pentoxide was found to be 99.04% pure, with an analysis precision of 0.19% relative deviation.

3. Preparation of a Stock Solution of Niobium

0.095 g of niobium oxide were dissolved by fusing the sample with 3 g of potassium hydrogen sulfate in a 100 ml pyrex beaker until the melt was clear. The melt was cooled, then redissolved in 12 M HCl and the minimum quantity of water necessary to keep the potassium sulfate salts in solution. The

solution was diluted to a final volume of 250 ml with 12 M HCl. Standard niobium solutions were prepared by diluting aliquots of the stock solution with HCl.

4. Extraction of Niobium into Various Solvents

A two ml aliquot of 2.27×10^{-4} M solution of Nb in 12 M HCl was added to a 60 ml separatory funnel equipped with a Teflon stopcock. Four ml of cold water, 6 ml of cold 6 M HCl, and 2 ml of cold 3 M KSCN solution were added to the separatory funnel. Upon addition of KSCN a yellow color appeared and upon addition of 1 ml of 0.02 M TPACl, a yellow precipitate formed, as well as a white precipitate of TPASCN. The aqueous phase was then extracted with 15 ml of chloroform solution by shaking vigorously for 2 minutes. The two phases separated quickly and well, the organic layer having the bright yellow color of the niobium complex.

The extraction procedure was repeated with a 9/2 chloroform-acetone mixture. Again the yellow complex was easily extracted into the organic solvent.

The extraction process was repeated a third time with 15 ml of ethanol-free chloroform and 1 ml of 0.05 M TPACl. The ethanol had been previously removed from the chloroform by shaking with two portions of 1:4 H_2SO_4 and 4 portions of distilled water. Ethanol-free chloroform appeared to extract

the yellow complex quite well.

5. Absorption Spectra of Niobium in Various Solvents

Niobium extracts of various solvents were prepared as described in Section 4-Experimental and then the absorbance was obtained from 500 to 320 m μ using the DB spectrophotometer. The spectra which were recorded as percent transmittance versus wavelength are shown in Figures 1 and 2, page 50. The spectra were obtained with chloroform as the reference.

6. Variation of Extraction Efficiency With Acid

Concentration in the Aqueous Layer,

Chloroform System.

Two ml of 4.36×10^{-4} M Nb in 12.0 M HCl were added to a 60 ml separatory funnel. An aliquot of cold water, x ml, and (15-x) ml of cold HCl of varying concentration were added. After mixing, 3 ml of 1.5 M KSCN were added. Upon addition of KSCN a yellow color appeared in the aqueous solution. One ml of 0.025 M TPACl and 25 ml of chloroform were added and the extraction was performed by shaking for 1-8 minutes. The extract was filtered into a 25 ml volumetric flask and the absorbance of the extract was measured at 390 m μ vs. chloroform on the D.U. The extracts were slightly unstable in that the absorbance decreased by 1-4 % over a period of 15-25

minutes then remained constant. The absorbance, plotted as a function of the HCl concentration, is shown in Figure 3, page 53. The data show that within the range 3-6 M HCl the extraction has the greatest efficiency.

7. Variation of Extraction Efficiency With Equilibration Time.

Two ml of 4.36×10^{-4} M Nb in 12 M HCl were added to a separatory funnel along with 6.0 ml of 6 M HCl, 3 ml of 1.5 M KSCN, 9 ml cold water, 1 ml of 0.025 M TPACl and 25 ml of chloroform. The organic and aqueous phases were equilibrated for a given period of time by shaking vigorously. The absorbance of a filtered extract was measured at 390 m μ . A graph of absorbance versus equilibration time is shown in Figure 4, page 54, illustrating that an equilibration time of 4 minutes or longer is desirable.

8. Variation of Extraction Efficiency With Potassium Thiocyanate Concentration, Chloroform System

Five ml of 1.14×10^{-4} M Nb in 12 M HCl were added to a 100 ml volumetric flask in addition to 7 ml of 6.5 M HCl, x ml of H₂O, (8 - x) ml of 1.5 M KSCN, 1 ml of 0.025 M TPACl, and 25 ml of chloroform. The flasks were shaken for 4 minutes; the organic phase filtered and the absorbance measured at 390 m μ .

A graph of absorbance versus molar concentration of KSCN was constructed and is shown in Figure 4, page 56.

The experiment was repeated using two ml of 2.27×10^{-4} M Nb solution, 6 ml 6 M HCl, 1 ml of 0.02 M TPACl, x ml of water and (6 - x) ml of 0.3 M, 0.12 M, or 0.03 M KSCN, and 15 ml of chloroform. The equilibration time was 3 minutes. The results are shown in Table II, page 59.

The experiment was repeated a third time using the same quantity of reagents as in the previous experiment. These results are also shown in Table II, page 59.

9. Variation of Extraction Efficiency With
Tetraphenylarsonium Chloride Concentration
Chloroform System.

Two ml of 2.27×10^{-4} M Nb in 12 M HCl, 6 ml of 6 M HCl and two ml of 3 M KSCN were added to a separatory funnel, after which x ml of water and (5 - x) ml of 0.05 M, 0.0025 M, or 0.00025 M TPACl were added. The aqueous solution was extracted with 15 ml of chloroform by shaking vigorously for 3 minutes. The absorbance of the filtered extract was measured at 390 m μ . A graph of absorbance versus millimoles TPACl was constructed, and is shown in Figure 4, page 56.

10. Exhaustive Extraction of Niobium Solutions

Chloroform System

Several experiments were performed in which the aqueous phase was extracted repeatedly with TPACl and chloroform. These experiments indicated that a minimum of four extractions were required to remove the niobium when one ml of 0.025 M TPACl and 7 to 10 ml of chloroform were used. The use of 2 ml of 0.025 M TPACl and 7 to 10 ml of chloroform required three extractions for complete removal of the Nb, estimated by measuring the absorbance of each extract and continuing the repetitive extractions until the absorbance of an extract was equal to the blank absorbance.

11. Calibration Curves for Niobium, 390 m μ

a. Chloroform System

Aliquots of x ml of standard Nb solution in 12 M HCl and (5-x) ml of 12 M HCl were added to a separatory funnel prior to adding 5 ml of cold water and 7 ml of cold 6.5 M HCl. After mixing, 2 ml of 1.5 M KSCN and 1½ ml of 0.025 M TPACl were added. The aqueous phase was extracted with 9 ml of chloroform for 2 to 3 minutes. The organic phase was filtered into a 25 ml volumetric flask and two additional extractions were

made with $1\frac{1}{2}$ ml of TPACl and 9 ml of chloroform. After allowing the combined extracts to stand for $\frac{1}{2}$ to 1 hour the absorbance was measured at 390 m μ versus chloroform in the reference cell of the DU, which was operated at a slit width of 0.06 mm. The calibration curve of absorbance versus concentration of Nb was calculated assuming complete extraction of the niobium. The data are given in Table IV, page 77.

b. 9/2 Chloroform-Acetone System

An aliquot, x ml, of a standard Nb solution in 12 M HCl and (3-x) ml of 12 M HCl were added to a separatory funnel in addition to 4 ml of cold 6 M HCl and 2 ml of 0.05 M TPACl. After mixing the contents 2 ml of 3 M KSCN were added. A 15 ml aliquot of 9/2 chloroform-acetone solution was pipetted in and the mixture was extracted by shaking vigorously for two minutes. The organic phase was filtered into a volumetric flask and the absorbance of a portion of the extract was measured at 390 m μ versus chloroform. The aqueous phase was extracted again with 2 ml of TPACl and 15 ml of 9/2 chloroform-acetone solution. The net absorbance of the second extract was 0.005, which indicated that essentially all the Nb was removed from the aqueous phase after the first extraction. The data shown in Table VIIb, page 75, were used to calculate the absorptivity of Nb in 9/2 chloroform-acetone solution.

12. Preliminary Investigation of Interferences

A. Molybdenum

One-half ml of 10^{-2} M Mo (VI) was added to the standard reagent mixture and the Mo (VI) was extracted according to the procedure outlined in Section 10, except that 1/4 ml of 10% SnCl_2 was added to reduce the Mo. The spectrum of the extract indicated an absorbance band at 450 m μ whereas the absorbance at 390 m μ , A_{390} , was 0.096.

The above experiment was repeated using 1/2 ml of SnCl_2 and 1/2 ml of 80% mercaptoacetic acid, MAA. The orange color that appeared upon mixing the reagents, characteristic of molybdenum thiocyanate complexes, faded after a few minutes. A_{390} was 0.010.

B. Iron

Five ml of 5×10^{-3} M Fe (III) were treated with 3/20 ml of 10% SnCl_2 and extracted as outlined in Section 10. A_{390} was 0.003.

C. Tungsten

Five ml of 10^{-4} M W (VI) in 12 M HCl were treated with 1/4 ml of 10% SnCl_2 and extracted as previously outlined. A_{390} was 0.048, which indicated that SnCl_2 would not be suitable

for reducing Mo and Fe to eliminate their interference if W was present since some of the W would be reduced to an interfering oxidation state.

A two ml aliquot of 10^{-3} M W(VI) in 12 M HCl was added to a separatory funnel containing 6 ml of cold 6 M HCl, 2 ml water, and 3 ml of 1.5 ml of 0.05 M TPACl. The mixture was extracted with 15 ml of CHCl_3 for two minutes. A_{390} was 0.080. A_{390} for a blank was 0.011. Hence both W (V) and W (VI) interfered by absorbing in the same region as Nb.

13. Simultaneous Extraction of Niobium and Tungsten

With Stripping of Extract to Separate

Niobium and Tungsten

Two ml of 1.14×10^{-4} M Nb, 2 ml of 12 M HCl, $\frac{1}{2}$ ml of 10% SnCl_2 , 1 ml of 6 M HCl, 3.5 ml of water and 3 ml of 1.5 M KSCN were added to a separatory funnel. The aqueous phase was extracted three times with 1 ml of 0.025 M TPACl and 9 ml of chloroform. The absorbance of the third extract was 0.013 whereas the absorbance of the combined extracts was 0.232. A fourth extract had an absorbance of 0.005.

The combined extracts of the first three extractions were stripped a number of times by shaking with a solution consisting of $\frac{1}{2}$ ml of 0.1 M KF in 5 ml of 6 M HCl. The absorbance of the organic phase after each stripping extraction

was 0.078, 0.042, 0.012, 0.006, and 0.006. After stripping the organic phase three times, all Nb was removed.

The aqueous fluoride solutions were combined and treated with 2 ml of 0.2 M H_3BO_3 and 3 ml of 1.5 M KSCN. Three extractions with 1 ml of TPACl and 9 ml chloroform, when combined gave an absorbance of 0.195. The expected absorbance was 0.284, as inferred from the calibration curve prepared as described in Section 11.

14. Comparison of Various Elements for Demasking
Niobium Fluoride Complexes

Two ml of 1.14×10^{-4} M Nb in 12 M HCl, 1 ml of 0.1 M KF, 1 ml of 0.1 M solution of appropriate element, 3 ml of 1.5 M KSCN, 7 ml of 6 M HCl and 1 ml of H_2O were all added to a separatory funnel. The aqueous solution was extracted with 1 ml of 0.025 M TPACl and 15 ml of chloroform by shaking for 3 minutes.

The results are shown in Table V, page 65.

15. Analytical Procedure For Separation of Molybdenum
and Tungsten From Niobium, Chloroform System.

Part I

Add two ml of Nb solution (or sample) in 12 M HCl and

2 ml of 10% SnCl_2 to a beaker, and heat on a hot plate for 2 to 3 minutes. Cool and rinse the solution into a separatory funnel using 6 ml of cold 6 M HCl. Add 2 ml of 1 M KF and 2 ml of 3 M KSCN. Extract the aqueous phase with 1 ml of 0.05 M TPACl and 9 ml of chloroform by shaking for 2 minutes. Repeat the extraction once or twice in order to remove all the W (V).

Part II

Saturate the aqueous phase with H_3BO_3 , add 2 ml of 3 M KSCN and 2 ml of 6 M HCl. Perform three extractions on the aqueous solution using $1\frac{1}{2}$ ml of 0.025 M TPACl and 9 ml chloroform per extraction.

16. Extraction Efficiency of Niobium in 9/2 Chloroform Acetone Solutions as Function of Reagent Concentration in the Aqueous Phase.

a. Variation of HCl Concentration

A one ml aliquot of 1.43×10^{-4} M Nb solution in 12 M HCl was added to a separatory funnel in addition to (10-x) ml of cold 6 M HCl, x ml of cold water, and 2 ml of 3 M KSCN. After the addition of 1 ml of 0.05 M TPACl, the aqueous mixture was extracted with 15 ml of chloroform-acetone by shaking for

one minute. A small portion of the extract was filtered into a cell for measurement of the absorbance at 390 m μ . The results are shown in Figure 5, page 57.

b. Variation of KSCN and TPACl Concentration

The procedures used are identical to those outlined in Section 24, page 39. The results are shown in Figure 5, page 57 as well as in Tables IX-XI, pages 84 and 85.

17. Extraction Efficiency of Niobium as a Function of Concentration of Acetone in Chloroform.

Two ml of 1.14×10^{-4} M Nb in 12 M HCl and 6 ml of 6 M HCl were added to a 25 ml graduate along with 4 ml of cold water, 2 ml of 3 M KSCN and 1 ml of 0.05 N TPACl. The mixture was extracted with 15 ml of chloroform-acetone solution for 3 minutes. The absorbance of the filtered extract was measured versus chloroform at 390 m μ on the D.U. and the spectrum was obtained on the DK-1. A graph of absorbance versus ratio of chloroform-acetone, (vol:vol), was constructed, and is shown in Figure 6, page 62.

The experiment was repeated using less than the optimum quantity of TPACl. These results are also shown in Figure 6, page 62.

18. Effect of Diverse Elements in the Extraction of Niobium with 9/2 Chloroform-Acetone Solutions.

A one ml aliquot of the diverse element (in the highest oxidation state) and two ml of 1.14×10^{-4} M Nb in 12 M HCl were added to a separatory funnel. The remainder of the procedure is identical to that described for the analytical procedure in Section 20, page 34; however, SnCl_2 was not added in these studies, as is directed in the analytical procedure for those cases in which Fe (III) is coextracted with the Nb.

The results are summarized in Table VI, page 69.

19. Calibration Curve for Niobium, 9/2 Chloroform, Acetone System.

A series of standard solutions were prepared by dilution of aliquots of the stock solution with concentrated HCl. Aliquots were analyzed by the Analytical Procedure, Section 20. The separation and masking steps were included, but the addition of SnCl_2 after the second extraction of Nb was omitted. The absorbance was measured at 390 m μ versus chloroform in the reference cell. The absorbance was plotted versus concentration of Nb in the extract, and the resulting graph is shown in Figure 7, page 72, (Table VII, page 74).

20. Analytical Procedure for Extraction of Niobium with
9/2 - Acetone Solution.

Samples are dissolved by heating in concentrated HCl, to which one ml portions of concentrated HNO_3 are added occasionally to assure complete solution and oxidation. When dissolution is complete, the solution is boiled for 10 to 20 minutes to remove most of the nitrogen oxides. It is not necessary to remove completely the HNO_3 . After boiling, the solution is transferred and diluted to volume with concentrated HCl. The solution should be tested for the presence of oxides of nitrogen by making an extraction on a portion of the sample with chloroform. If the extract has a yellow-brown color, the aliquot of sample should be repeatedly extracted until the chloroform layer is colorless.

A suitable aliquot of the sample, usually 2 ml, is placed in a 60 ml separatory funnel for analysis. Dilute with 3 ml of cold water, add 1 ml of cold 3 M KSCN, followed by 1 ml of 80% mercaptoacetic acid; swirl and let stand for 1 to 3 minutes, or until the red color of the ferric thiocyanate complex is bleached. Add $\frac{1}{2}$ ml of 4 M KF solution and $\frac{1}{2}$ ml of 0.05 M TPACl. Extract with 9-10 ml of chloroform-acetone by shaking for 1 minute. Discard the extract and rinse the aqueous phase with 4-5 ml of solvent in order to remove remaining

droplets of the first extract. Add 2-3 grams of H_3BO_3 to demask the Nb, 5 ml of cold 6 M HCl and 2 ml of cold 3 M KSCN solution. Swirl frequently and let sit for 2-3 minutes so that the H_3BO_3 may have time to dissolve. Add 1 ml of 0.05 M TPACl and swirl to mix. Extract with 13 ml of chloroform-acetone by shaking for 2 minutes. Filter the extract into a 25 ml volumetric flask. Repeat the extraction by adding both TPACl and chloroform-acetone solution. Two extractions are sufficient to remove all of the Nb. If necessary, add 1-2 drops of 10% $SnCl_2$ to the volumetric flask in order to reduce any iron (III) that is present.

21. Analysis of Bureau of Standards Standard Samples.

A. NBS Steel #123b

1. Dissolution of Sample. The sample, 0.1283 gms. was weighed into a 100 ml beaker, treated with approximately 20 ml of 12 M HCl, and heated on a hot plate. Concentrated HNO_3 was added periodically in 1/4 ml increments in order to oxidize the carbon and other elements. After dissolution, the solution was boiled for 20 minutes to remove most of the oxides of nitrogen. The solution was transferred to a 100 ml volumetric flask and diluted to the mark with 12 M HCl.

2. Analysis of Sample. A portion of the sample was tested for the presence of nitrogen oxides by shaking with 10 ml of chloroform. The chloroform layer was colorless, indicating the absence of oxides of nitrogen in the sample.

A two ml aliquot of the sample was then pipetted into a separatory funnel and analyzed according to the analytical procedure described in Section 20. The absorbance of the chloroform extract was used to calculate the percentage of Nb present. The results are shown in Table VIII, page 79.

B. NBS Steel #101e

1. Dissolution of Sample. The sample, 5.5858 gms, was dissolved in 100 ml of 12 M HCl as described above for NBS Steel #123b.
2. Analysis. Two ml aliquots of the sample were taken for analysis using the procedure described in Section 20. The results are shown in Table VIII, page 79.

C. NBS Steel #345

1. Dissolution of Sample. The sample, 0.8729 gms, was dissolved as described above. After the sample was diluted to volume, a chloroform extraction made on an

aliquot, indicated the presence of nitrogen oxides.

Hence, a 25 ml aliquot of the sample was fumed down to a volume of approximately 10 ml, and then transferred into a 25 ml volumetric flask and diluted to the mark.

2. Analysis. Two ml aliquots of the fumed sample were analyzed as described in Section 20, and the results are shown in Table VIII, page 79.

B. NBS Heat-Resisting Alloy #167

1. Dissolution of Sample. The sample, 0.0457 gms, was heated in a beaker containing 50 ml of 12 M HCl for one hour, after which $\frac{1}{2}$ ml of concentrated HNO_3 was added every 20 to 30 minutes until the sample was dissolved. The sample was diluted to 75 ml and then fumed down to a volume of approximately 35 ml, after which it was transferred and diluted.

Two ml aliquots were taken for analysis as described in Section 20.

E. NBS Heat-Resisting Alloy #168

The sample, 0.0908 gms, was dissolved in 200 ml of 12 M HCl and was subsequently analyzed as described above.

22. Preliminary Evaluation of Tetraphenylstibonium Sulfate for Extraction of Niobium.

A Nb solution was extracted according to the procedure in Section 4 except that 2 ml of 0.01 M tetraphenylstibonium sulfate were added to precipitate the Nb complex. The spectrum of the extract showed that the absorption maximum was at 400 m μ rather than 390 as for TPACl. The absorbance was 0.112, considerably less than obtained when TPACl was used for the extraction procedure under identical conditions.

23. Preliminary Evaluation of Ascorbic Acid and Sodium Thiosulfate as Reductants

The usefulness of ascorbic acid and Na₂S₂O₃ as reductants for Mo (VI), Fe (III), and W (VI) was evaluated by first determining if the reductant was strong enough to reduce W (VI) to W (V).

A blank was prepared by extracting a solution containing 2 ml 12 N HCl, 3 ml H₂O, 0.5 g ascorbic acid, 1 ml 3 M KSCN, 3 ml 6 N HCl, and $\frac{1}{2}$ ml 0.05 M TPACl, with 10 ml of 9/2 chloroform-acetone solution. The absorbance at 390 m μ was 0.017.

In the case of W, a $\frac{1}{2}$ ml aliquot of 10⁻² N W (VI) was extracted by the foregoing procedure. The absorbance was 0.085, which indicated that some of the W was evidently reduced to W (V).

24. Composition of the Extracted Species, Variational Method to Determine TPA/Nb and Nb/SCN Ratios

A. 9/2 Chloroform-Acetone System

In order to determine the TPA/Nb ratio, two ml of 1.14×10^{-4} M Nb in concentrated HCl were transferred to a 25 ml ground glass stoppered graduated cylinder which contained 4 ml of cold 6 M HCl. An aliquot (X ml) varying in volume from 0.5 to 5.0 ml of 0.05 M, 0.0025 M, or 0.00025 M TPACl was added. Two ml of 3.0 M KSCN and (7-x) ml of cold, distilled water were added, and the mixture was swirled to mix. Fifteen ml of chloroform-acetone solution were pipetted in, the mixture was shaken for two minutes, the layers were allowed to settle, and the absorbance of the extract was measured at 390 m μ . The absorbance, A_0 , obtained upon complete extraction of Nb was 0.646. All absorbance measurements were corrected for the absorbance of the blank. The data are tabulated in Table X, page 85.

The experiment was repeated using two ml of 2.27×10^{-4} M Nb, for which the value of A_0 was 1.295. The data are shown in Table IX, page 84.

The determination of the SCN/Nb ratio was carried out as follows: Five ml of 2.27×10^{-5} M Nb in concentrated HCl were pipetted into a graduate. One ml of 0.05 M TPACl, x ml of cold water, and (9-x) ml of standard 3 M or 0.3 M KSCN were added.

(x was 0.5, , 3, 4 for the 3 M solution and 0.5, 0.7, 1, 1.5, 2, and 3 for the 0.3 M solution). Fifteen ml of chloroform-acetone solution were used to extract the complex. A_0 was 0.328 (Table XI, page 86).

The experiment was repeated using two ml of 1.14×10^{-4} M Nb as well as 6 ml of 6 M HCl, (6-x) ml of water and x ml of 0.3 or 0.06 M KSCN. In this experiment A_0 was 0.647.

The TPA/Nb ratio is deduced from the experimental data by plotting $\log (A/A_0 - A)$ versus \log (total millimoles TPACl). See Chapter IV, page 81. The slope of the graph is determined as n, the stoichiometric molar ratio of TPA to Nb in the extracted species. The data in Table IX, page 84, was plotted to yield Figure 8, page 89.

The SCN/Nb ratio is obtained by plotting $\log (A/A_0 - A)$ versus $\log V_{\text{KSCN}}$. The slope of the graph is rounded off to the nearest integer to give the molar ratio of thiocyanate to niobium. The data in Table X was plotted to give Figure 9, page 90.

B. Chloroform System

In order to determine the TPA/Nb ratio of the complex species extracted into commercial chloroform, two ml of 2.27×10^{-4} M Nb in concentrated HCl were added to a graduate containing 6 ml of cold 6 M HCl, after which the contents were mixed and

2 ml of 3 M KSCN were added. An aliquot (x ml) varying in volume from 0.5 to 5.0 ml of 0.05 M, 0.0025 M, or 0.00025 M TPACl was added in addition to $(5-x)$ ml of water. Fifteen ml of chloroform were pipetted in and the mixture was shaken for three minutes. The absorbance of a portion of the filtered extract was measured at 390 m μ versus chloroform. A_0 for this experiment was calculated to be 0.936, i.e., the concentration of Nb in the chloroform is 3.03×10^{-5} M assuming complete extraction, and ϵ is 30900 M $^{-1}$ cm $^{-1}$ (from Section II). The data are tabulated in Table XII, page 87.

The data needed for determining the SCN/Nb ratio were obtained by the procedure described above, except that a constant amount of TPACl was added (1 ml of 0.02M) for each extraction. Aliquots (x ml) of 0.3 M, 0.12 M, 0.03 M KSCN and $(6-x)$ ml of water were added. A_0 was 0.936, and the data are in Table XIII.

The TPA/Nb and SCN/Nb ratios were later obtained by treating the data as described previously, after which the appropriate graphs were constructed, Figure X and XI, respectively.

25. Infrared Spectra of Solid Arsonium Metal Salts

Chloroform extracts of the arsonium salts of Nb(V), Co(II), W(V), and Ti(IV) were prepared using the procedure described in Section I. The extract was filtered and the solvent

was evaporated under a stream of air in order to crystalize the arsonium salt. The crystals were washed with water or butanol, and then dried for at least 24 hours in a vacuum desiccator over $\text{Mg}(\text{ClO}_4)_2$. A KBr disc of the salt was prepared by mixing approximately 0.5 mg of the salt with 100 mg of dry KBr and pressing in a pellet press. The infrared spectra were obtained with a Beckman IR-8 Infrared Spectrophotometer. The spectra of Nb and Ti are shown in Figures 14 and 15. In order to assign the I.R. bands, spectra were obtained of TPACl, TPASCN, and KSCN. Pertinent I.R. bands are listed in Table XIV.

26. Dilution of Chloroform Extracts of the Niobium

Thiocyanate Complex

A chloroform extract of niobium was prepared by adding 2 ml of 2.27×10^{-4} M Nb in 12 M HCl, 4 ml cold water, 6 ml cold 6 M HCl, 2 ml 0.3 M KSCN and 1 ml of 0.05 M TPACl to a separatory funnel. Fifteen ml of commercial chloroform were added and the mixture was extracted for 3 minutes. A 4 ml aliquot of the extract was diluted to 5 ml with chloroform, and the absorbance, 390 μ , was recorded as a function of time. The data shown in Table XVI were treated assuming that the dissociation of the niobium complex obeyed first order kinetics, and the appropriate plot is shown in Figure 17.

27. Preliminary Investigations on Role of Dissolved
Water in Chloroform Extracts of Niobium

A Nb extract was prepared by adding 1 ml of 1.14×10^{-4} M Nb in 12 M HCl, 2 ml of 12 M HCl, 8 ml water, 7 ml of 6 M HCl, 1 ml 3 M KSCN, and 1 ml of 0.05 M TPACl to a separatory funnel, and extracting three times with 9 ml of chloroform. Aliquots of TPACl were added prior to each extraction.

A portion of the extract was dried by equilibrating with Mg (ClO₄)₂ for twelve hours. After measuring the absorbance of the partially dried extract, water was added to the extract by equilibrating with a solution of CaCl₂ of a water activity, A_w , of 0.680 for a period of approximately twelve hours. The results are summarized in Chapter 4, page 112.

28. Equilibration of Niobium Extracts in Chloroform
With Solutions of Constant Water Activity

A 5 ml aliquot of 4.26×10^{-4} M Nb solution in 12 M HCl was added to a 300 ml separatory funnel in addition to 30 ml of 12 M HCl and 61 ml of cold water. After mixing, 9 ml of 1.5 M KSCN and 5 ml of 0.05 M TPACl were added. The mixture was extracted for 3 minutes with 110 ml of chloroform, after which the organic phase was filtered into a volumetric flask.

Ten ml aliquots of the extract were added to 25 ml

volumetric flasks. The volumetric flasks were placed in a water bath which was thermostated at $25 \pm 1^\circ \text{C}$, and were equilibrated for 72 hours. After equilibration the solutions were removed, and the absorbance of each solution was measured at 390 m μ versus chloroform on the Beckman D. U. spectrophotometer (slit width = 0.06 m μ). Spectra were obtained on the Beckman DK-1. The data and spectra are shown in Table XIX, and Figure 19, respectively.

The experiment was repeated three times with different concentrations of Nb. The following quantities of reagents were used for the second repetition: 5 ml of 4.265×10^{-4} M Nb in 12 M HCl, 6.7 ml of cold 6 M HCl, 10.3 ml cold water, and 3 ml of 1.5 M KSCN. The aqueous mixture was extracted four times using 1 ml of 0.05 M TPACl and 25 ml of CHCl_3 for each extraction. Portions of the combined extract were equilibrated, as described previously, for 96 hours.

A third Nb solution in CHCl_3 was prepared by extracting a solution consisting of 10 ml of 2.27×10^{-4} M Nb in 12 M HCl, 55 ml cold 6 M HCl, 26 ml cold water, 4 ml cold 3 M KSCN and 5 ml of 0.05 M TPACl. The mixture was extracted with 100 ml of CHCl_3 for 4 minutes. The aqueous phase was later analyzed by the procedure described in Section 11 to determine the quantity of Nb remaining unextracted. Portions of the CHCl_3 solution were equilibrated for 70-72 hours.

A fourth Nb solution in CHCl_3 was prepared by extracting a solution consisting of 12 ml of 2.27×10^{-4} M Nb in 12 M HCl, 51 ml cold 6 M HCl, 28 ml water, 4 ml 3 M KSCN, and 5 ml of 0.051 M TPACl. One hundred ml of CHCl_3 were used to extract the Nb, and the equilibration time was 72 hours. The data for the four experiments are shown in Tables XVIII, and the results are discussed in the following section.

29. Extraction and Behavior of Cobalt-Thiocyanate Complexes;

Model for Comparison with Niobium

A. Preparation of a Chloroform Solution of the Cobalt-Thiocyanate Complex.

A two ml aliquot of a Co solution, 0.260 mg Co/ml as $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, was added to a separatory funnel in addition to 5 ml of cold water, 5 ml of 1.5 M KSCN, and 1 ml of 0.05 M TPACl. The blue mixture was extracted with $12\frac{1}{2}$ ml of chloroform by shaking for three minutes. After removal of the organic phase, the aqueous phase was extracted again with $12\frac{1}{2}$ ml of chloroform after adding 1 ml of TPACl, and the two extracts were combined. The spectrum of the Co solution was obtained over the region 720-260 μ .

B. Dilution of Cobalt Solutions with Chloroform.

Four ml and 1.0 ml aliquots of the original extract were diluted to 5.0 ml with chloroform. Spectra were obtained

as well as measurements at 625 μ on the D.U.

C. Removal of Water From Cobalt Extracts.

A 5 ml portion of the original extract and a 5 ml portion of the diluted extract (2 ml diluted to 10 ml) were placed in volumetric flasks, to which equilibrators caps containing CaSO_4 (Drierite) were affixed. The extracts, as well as two control samples, were placed in a drawer in order to remove them from the sunlight, and were allowed to equilibrate for 78 hours. Spectra of the dried extracts and controls were obtained as well as single wave-length measurements at 625, 320, and 317 μ . The results are shown in Table XVII .

CHAPTER IV

RESULTS AND DISCUSSION

1. Preliminary Work

The possible extraction of niobium as a thiocyanate complex ion-pair of TPACl was first realized during a previous investigation of the extraction of tungsten with TPACl.⁷⁹ The fact that niobium interfered strongly with the spectrophotometric determination of tungsten, in that the niobium was co-extracted with tungsten, suggested that the extraction of niobium might be worthy of investigation. Initial studies with solutions containing only niobium revealed that TPACl could indeed be used to precipitate a thiocyanate complex of niobium and that the aqueous insoluble ion-pair could be extracted into chloroform; however, the extracted species did not obey Beer's Law.

The work described here was undertaken with the purpose of studying the extraction of the TPACl ion-pair with chloroform in order to develop a quantitative analytical procedure for niobium, to establish the composition of the extracted complex, and to study the extraction equilibria.

The initial extracts of the niobium thiocyanate complex were unstable in that the absorbance at the absorption maximum

increased as a function of time, and the absorbance from 360 to 330 m μ also increased.

In order to discover the source of the problem, blank solutions were prepared as previously described. It was found that the potassium thiocyanate decomposed quite readily at the high acid concentrations used, and some of the decomposition product was evidently extracted into the chloroform. The decomposition products interfered with the absorbance of niobium since the thiocyanate products absorb in the same spectral region as niobium, i.e. from 390 m μ into the ultraviolet. The specific source of trouble was pin-pointed to be the mixing step in which potassium thiocyanate solution was mixed with 6 to 10 M hydrochloric acid. Sufficient heat was generated upon mixing to initiate the decomposition reaction. In order to eliminate the decomposition of KSCN, the solutions were chilled to 3 to 5°C prior to mixing, and furthermore, the addition of potassium thiocyanate to acid more concentrated than 5 to 6 M was avoided.

2. Visible Spectra of Niobium in Organic Solvents

Spectra of the niobium thiocyanate complexes in commercial chloroform, ethanol-free chloroform, and 9/2 chloroform acetone mixtures are shown in Figures 1 and 2, pages 50 - 51.

(The term, commercial chloroform, is used to designate commercially

available reagent grade chloroform which contains 5% ethanol added as a preservative). It is observed that the absorbance band in the chloroform-acetone mixture or ethanol-free chloroform is sharper and more symmetrical than in commercial chloroform, especially in the region 260-330 μ . The absorption band in any of the above named solvents is wide enough that the wavelength of maximum absorbance is easily reproduced and Beer's law is followed quite well even at high concentrations of niobium. At the ultraviolet edge of the visible bands, the absorbance starts rising rapidly and continues to rise into the TPA peaks which occur at 270, 266, and 260 μ . However, in 9/2 chloroform-acetone mixtures the sharp increase in absorbance is also attributed to acetone, which absorbs at 330-320 μ .

When the spectra are compared more closely it is obvious that the absorbance at 390 μ in ethanol-free chloroform (or 9/2 chloroform-acetone) is greater than in commercial chloroform, but is less at 340-360 μ than in the latter solvent. The lower absorbance in the region 340-360 μ is attributed to a lower concentration (or negligible amount) of a second niobium complex in ethanol-free chloroform (or 9/2 chloroform-acetone). Additional evidence for the existence of the second niobium complex in commercial chloroform is presented and discussed in Sections 29 and 30.

ABSORPTION SPECTRA OF THE THIOCYANATE COMPLEX
OF NIOBIUM IN VARIOUS SOLVENTS

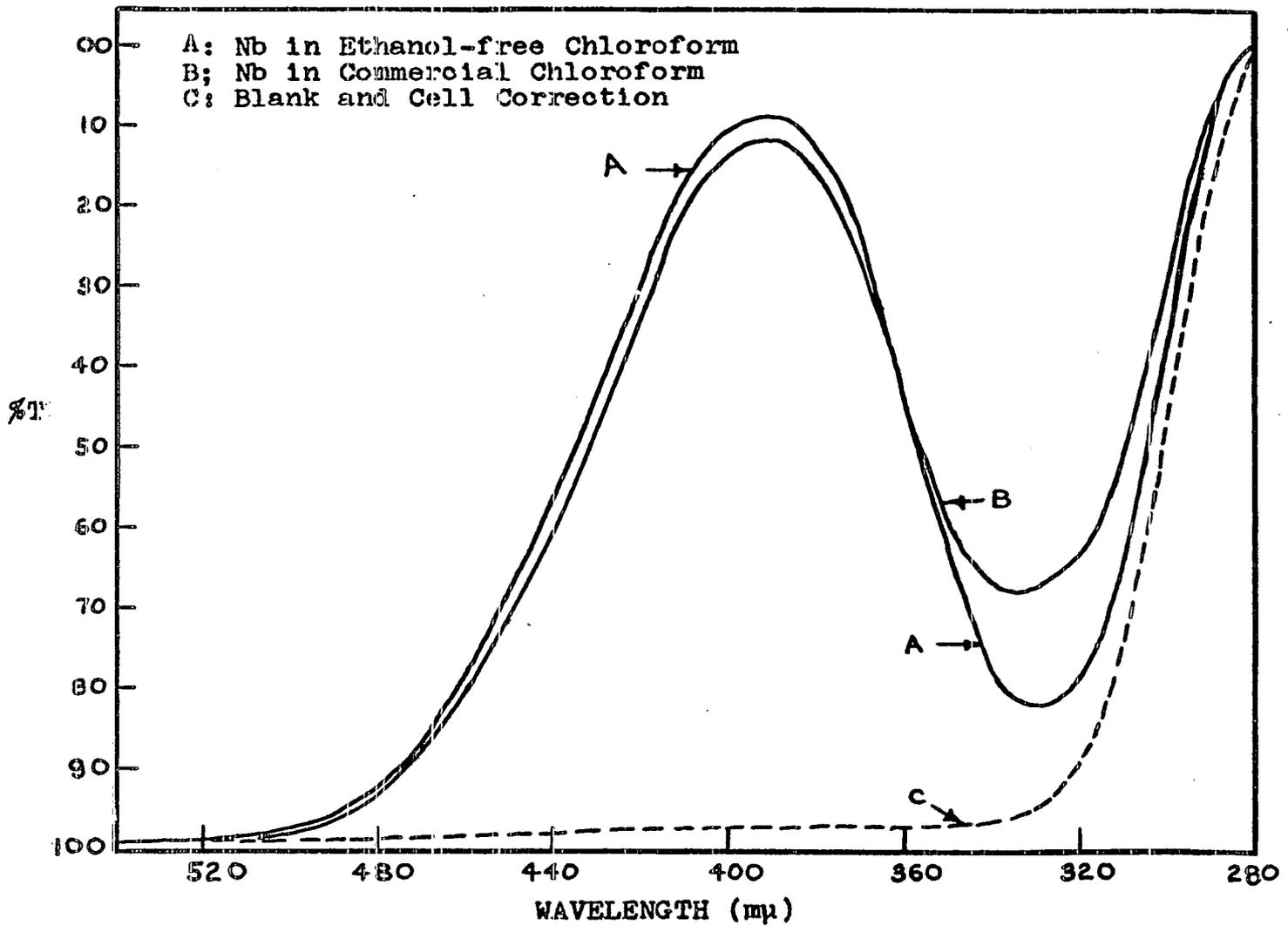


FIGURE 1

A: Nb in Ethanol-free Chloroform
B: Nb in Commercial Chloroform
C: Blank and Cell Correction

ABSORPTION SPECTRA OF THE THIOCYANATE COMPLEX
OF NIOBIUM IN VARIOUS SOLVENTS

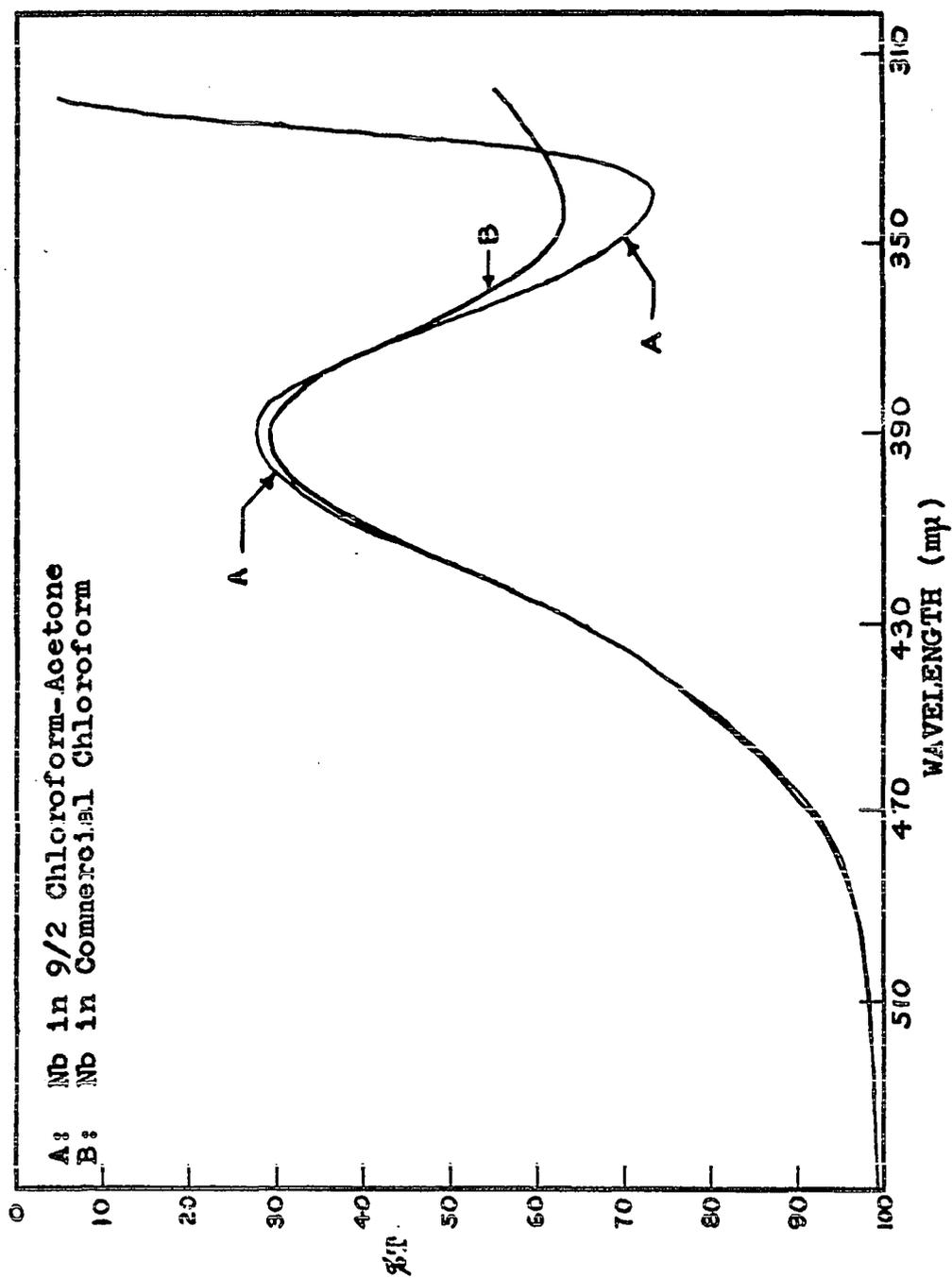


FIGURE 2

3. Extraction Variables

Since preliminary investigations had shown that niobium extracts failed to obey Beer's law, a thorough investigation of the extraction variables was made in order to establish the optimum conditions for the extraction of niobium from aqueous solutions into chloroform and chloroform-acetone mixtures.

The extraction variables were studied by determining the influence of the various reagents on the efficiency of extraction of niobium. The effects of hydrochloric acid, potassium thiocyanate, TPACl, and equilibration time were studied individually by varying the concentration of the reagents, one at a time, and noting the absorbance of the extract.

In Figure 3, page 53, and Curve B of Figure 5, it is apparent that the concentration of hydrochloric acid in the aqueous phase is not critical; however, it was kept within the range 3-5 M in the analytical procedure as the hydrolysis of tantalum and tungsten is likely to occur at low acid concentrations; whereas at concentrations above 5 M a partial decomposition of potassium thiocyanate is likely. At lower acid concentrations the fraction of niobium extracted decreases, probably because of hydrolysis of the niobium species to forms of niobic acid. At the higher acid concentrations (above 5 M) the percentage niobium extracted again decreases. This behavior

EXTRACTION EFFICIENCY OF NIOBIUM VERSUS
HYDROCHLORIC ACID CONCENTRATION
CHLOROFORM SYSTEM

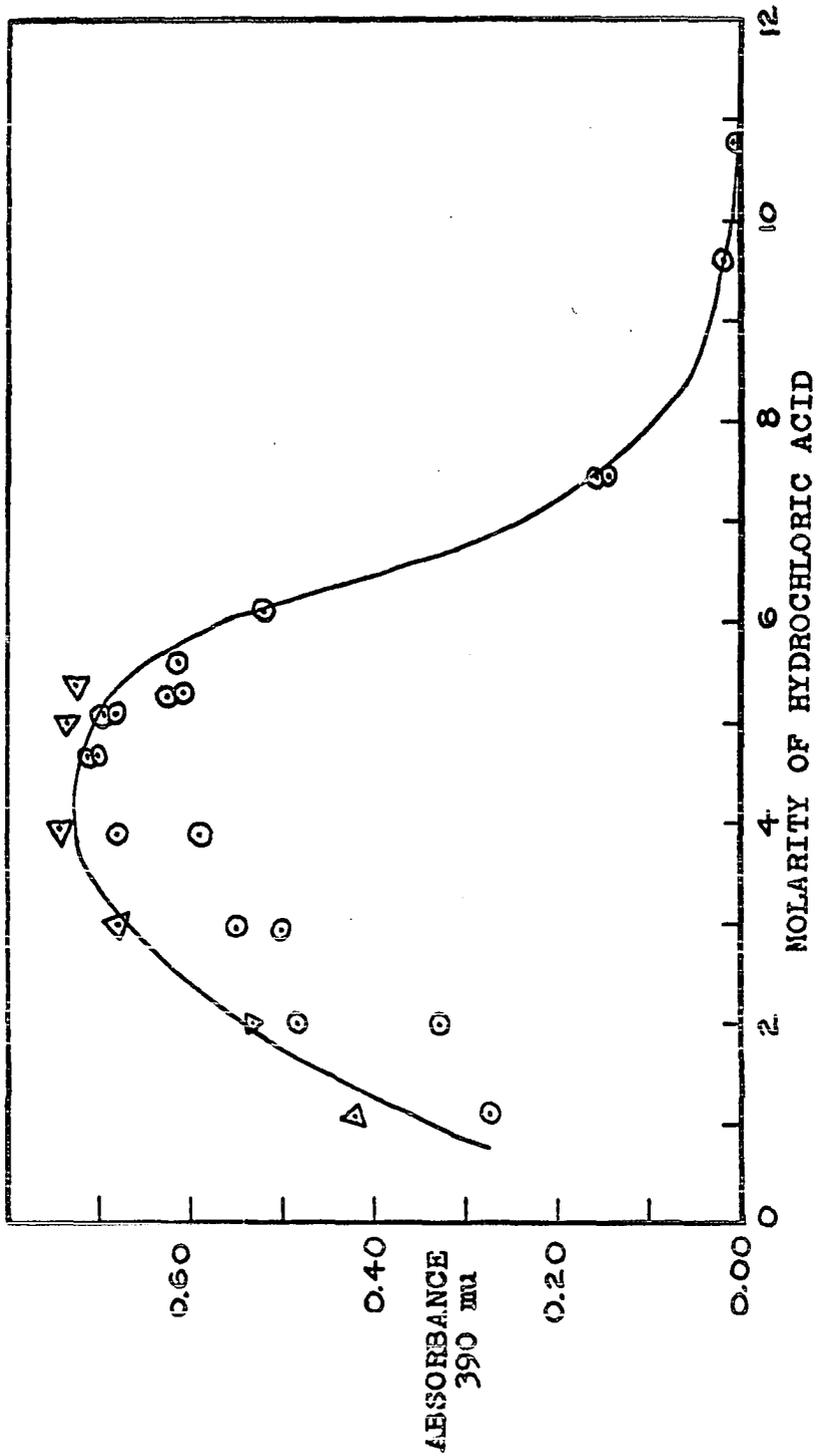


FIGURE 3

of niobium can be explained by considering the distribution curve of niobium on the anion exchange resin, Dowex-2, as a function of hydrochloric acid concentration.⁸⁰ The distribution coefficient, K_d , defined as the ratio of concentrations of niobium on the resin and in solution, is a minimum in 2 to 6 M hydrochloric acid, and increases sharply at both extremes of the stated concentration range. This behavior toward the resin suggests that neutral, cationic, or less stable anionic species are present in 2 to 6 M hydrochloric acid at greater concentrations than at the extremes of the acid range. It has been suggested⁸¹ that niobium exists in hydrochloric acid in the form of one or more of the following ions: NbOCl_4^- , NbOCl_5^- , $\text{Nb}(\text{OH})_2\text{Cl}_4^-$, and $\text{Nb}(\text{OH})_2\text{Cl}_5^-$. The complex ion, $\text{Nb}(\text{OH})_2\text{Cl}_4^-$ has been independently established and its anionic nature proven.⁸² Additional evidence for more than one chloride complex of niobium was obtained from the elution curve of niobium. The three separate peaks which were observed by Huffman *et al.*⁸³ when a 10 M hydrochloric acid solution of niobium was passed onto Dowex-2, followed by elution with 7 M hydrochloric acid, suggests that when equilibrium is reached several species can exist at the same time. Kraus⁸⁴ has concluded that in the case of tantalum and niobium, the species are adsorbed on the resin as chloro complexes at high acidities, but at low acidities

they are retained as hydrolyzed species.

In correlating the extraction behavior of niobium which is reported in this work with its anion exchange behavior, it is suggested that the cationic, neutral, and/or lower chloro complexes present in 2 to 6 M hydrochloric acid are more readily substituted by thiocyanate and subsequently extracted as the arsonium ion-pair; alternately, the increase in chloride concentration, 6 M or greater, may be quite effective in increasing the distribution ratios of TPACl and TPASCN over that of the niobium complex.

It is interesting to note that very little niobium is extracted from 10-12 M hydrochloric acid. This behavior of niobium may be of value in devising a new scheme for the separation of niobium from tungsten, molybdenum, and iron. Molybdenum and iron could be extracted as the chloride complexes, and tungsten is reduced and extracted as the thiocyanate complex or chloride complex, during which niobium is masked as a chloride (or fluoride) complex; afterwards the niobium is demasked and is extracted as the thiocyanate complex species.

The extraction efficiency of niobium as a function of TPACl concentration is indicated in Curve A, Figures 4 and 5. It is apparent that for a minimum number of extractions 0.15 to 0.2 millimoles of TPACl are required with commercial chloroform, and 0.025 to 0.05 millimoles are required with 9/2 chloroform-

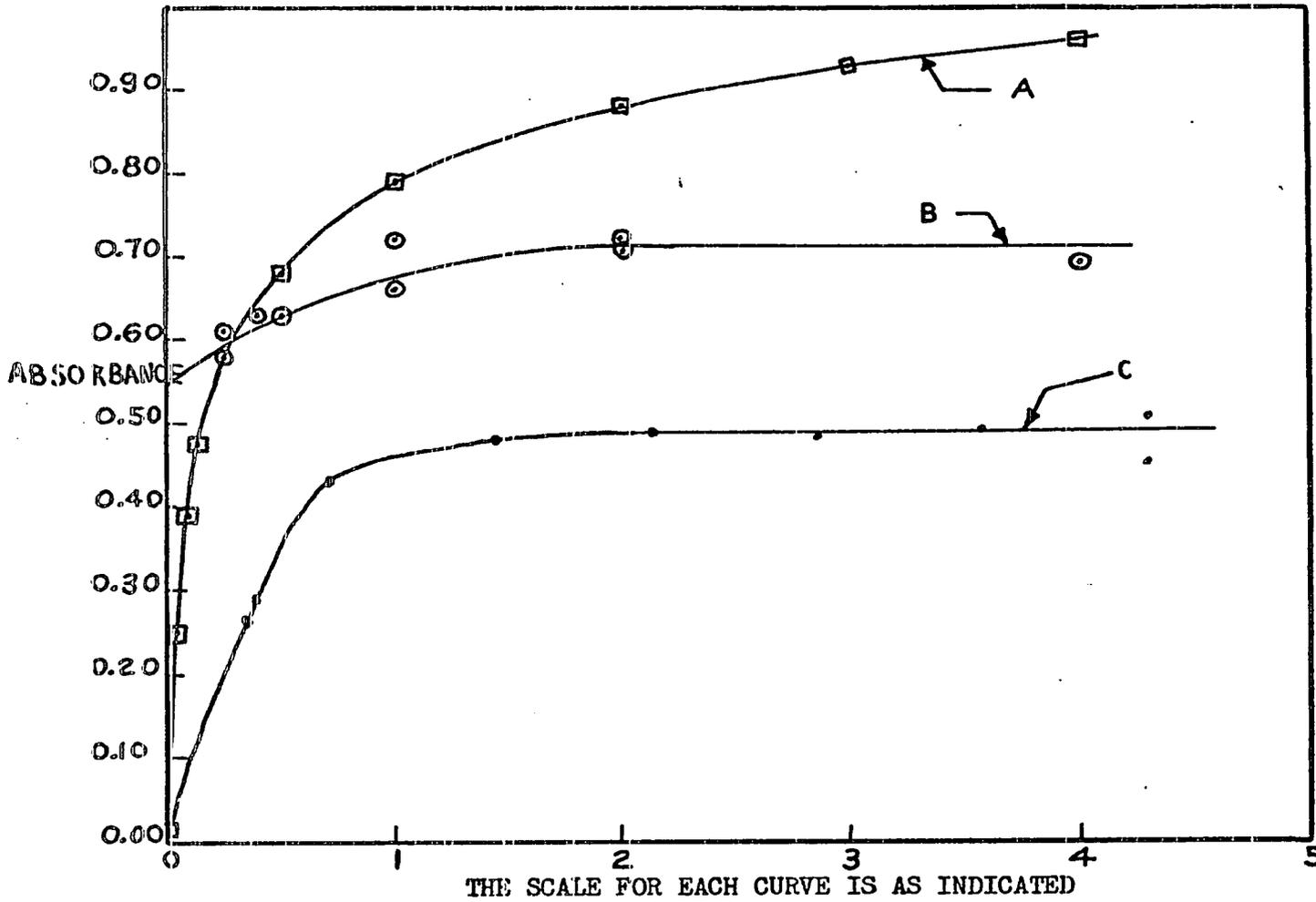
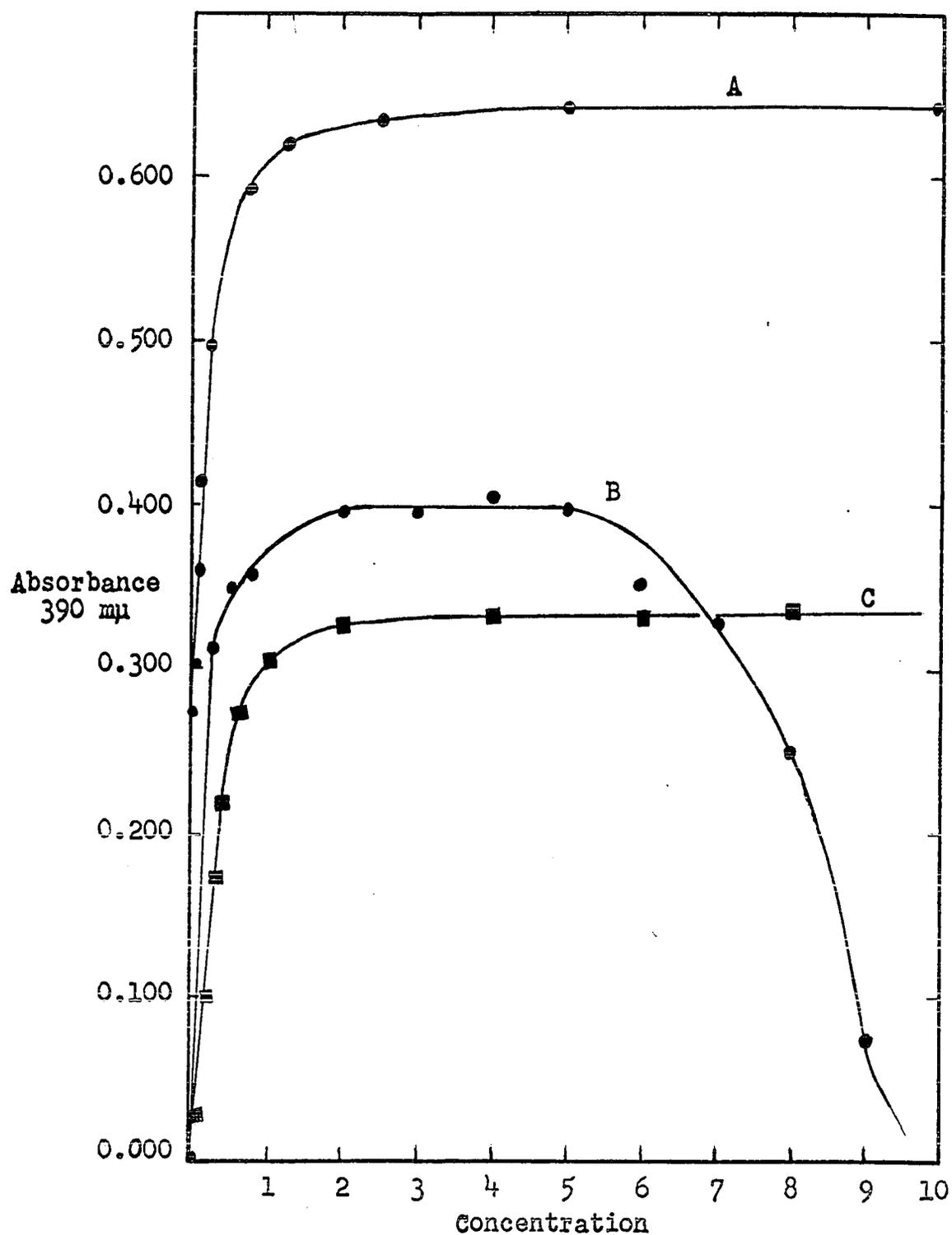


FIGURE 1

THE SCALE FOR EACH CURVE IS AS INDICATED
 A: (millimoles TPACl) x 20
 B: (Molar concentration of KSCN) x 10
 C: (Equilibration time) x 0.5, minutes

EXTRACTION EFFICIENCY AS A FUNCTION OF REAGENT CONCENTRATION



The concentration scale of each curve is indicated below

A: (Millimoles TPAC added) \times 100

B: Molar concentration of HCl

C: (Molar concentration of KSCN) \times 0.1

FIGURE 5

TABLE I

EXTRACTION EFFICIENCY OF Nb VERSUS EQUILIBRATION TIME

Time, min.	Absorbance, 590 m μ	Acidity, M
0.5	0.610, 0.580	2.83
1.0	0.630	3.84
2.0	0.660, 0.721	2.83
4.0	0.706, 0.722, 0.693	2.83, 2.83, 3.84
8.0	0.689	2.83

TABLE II

EXTRACTION EFFICIENCY OF NIOBIUM VERSUS THIOCYANATE
CONCENTRATION, CHLOROFORM SYSTEM

KSCN, M	A ₃₉₀	KSCN, M	A ₃₉₀	KSCN, M	A ₃₉₀
0.000	0.010	0.010	0.090	0.008	0.047
0.036	0.260	0.016	0.228	0.012	0.129
0.072	0.432	0.020	0.303	0.020	0.261
0.143	0.480	0.024	0.395	0.024	0.341
0.214	0.492	0.030	0.518	0.0312	0.446
0.285	0.485	0.040	0.550	0.040	0.535
0.357	0.491	0.040	0.508	0.060	0.629
0.428	0.509	0.040	0.535	0.080	0.702
0.428	0.440	0.060	0.627	0.100	0.709
				0.120	0.714
4 min. equilibration time		3 min. equilibration time		3 min. equilibration time	
5.7×10^{-4} mmole Nb taken		4.54×10^{-4} mmole Nb taken		4.54×10^{-4} mmole Nb taken	

TABLE III

EXTRACTION EFFICIENCY OF Nb AS FUNCTION OF TPACl
CONCENTRATION, CHLOROFORM SYSTEM

Millimoles TPACl	Absorbance, 390 m μ
0.2000	0.963
0.1500	0.928
0.1000	0.879
0.0500	0.757, 0.790
0.0250	0.676
0.0200	0.631, 0.627
0.0125	0.580
0.0075	0.475
0.0050	0.390
0.0035	0.333
0.0025	0.252
0.00125	0.149
0.0000	0.001

acetone solutions. It is interesting to note that the chloroform system requires considerably more TPACl for maximum efficiency of the extraction of niobium.

The role of potassium thiocyanate in influencing the extraction of niobium is indicated in Curve C of Figures 4 and 5. The optimum concentration of thiocyanate is 0.2 M or greater; however, if the concentration is much greater than 0.6 M there is a problem from the decomposition of thiocyanate, especially in the chloroform system. In the analytical procedure, which was based on the use of chloroform-acetone mixtures, the thiocyanate concentration was 0.6 M.

The influence of hydrochloric acid on the extraction of niobium was the first variable to be investigated in the chloroform system. As can be seen (Figure 3) there was considerable scattering of the data points. The source of this problem was discovered to be due to an insufficient equilibration time. The results of extraction efficiency as a function of equilibration time (Curve B, Figure 4) indicate that the aqueous and nonaqueous phases should be shaken for at least 4 minutes. Other studies on the chloroform-acetone system showed that a 1 to 2 minute equilibration time was satisfactory.

A considerable portion of the early investigations was carried out using chloroform as the extraction solvent. It was

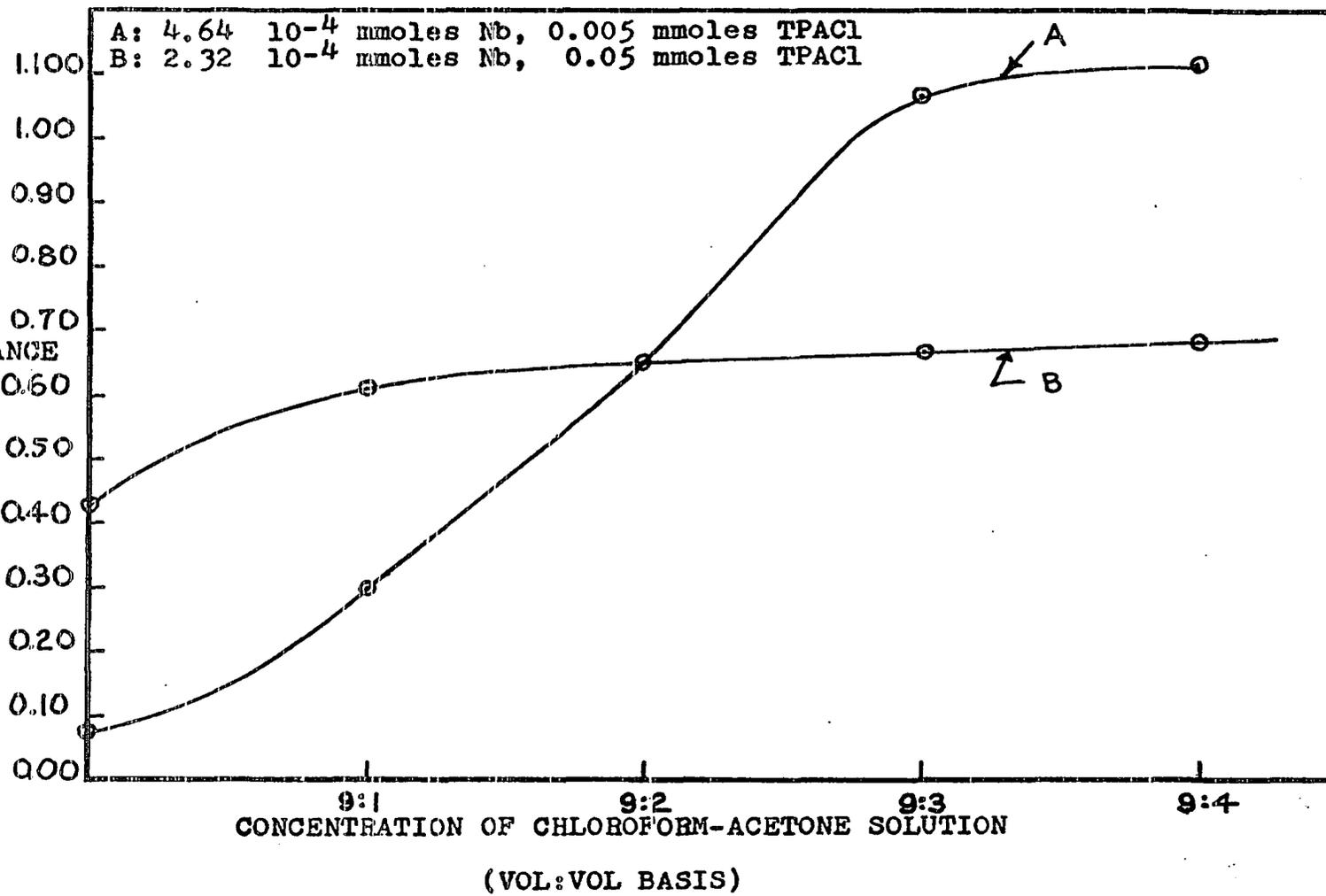


FIGURE 6

not until the investigation of diverse ions was under way that the advantage of a chloroform-acetone mixture was discovered.

Preliminary investigations with stannous chloride as a reductant in a H_3BO_3 -KF - thiocyanate-hydrochloric acid medium containing niobium revealed that niobium was poorly extracted from the medium, but upon the addition of small quantities of acetone, the fraction removed per extraction was increased significantly.

The results of extraction efficiency as a function of chloroform-acetone ratio, shown in Figure 6, page 62, indicate that a 9/2 mixture is the optimum ratio, provided the niobium/TPACl ratio is approximately 0.005 or less. Curve B, which is for a ratio of 0.093 indicates that the optimum conditions for extraction of niobium are complex functions of all the parameters. At low ratios of chloroform to acetone 9:4, 9:5, etc., the aqueous and nonaqueous phases separate very slowly after equilibration.

The advantages of going from a relatively inert solvent, chloroform, to a reaction solvent in the case of niobium are: the molar absorptivity of the complex ion is increased by approximately 17%, the quantity of TPACl required for optimum extraction is reduced by a factor of four, the equilibration time is decreased from four minutes to one to two minutes, and the distribution ratio of niobium is increased from 70% to greater than 90%, and as a consequence, the number of

extractions required for complete extraction of the niobium is reduced from 3 or 4 to two.

Preliminary investigations of diverse ions were conducted as outlined in Section 12, page 28, of the experimental section. Iron(III), molybdenum(V, VI), and tungsten(V, VI) interfered strongly, forming thiocyanate complexes that were extracted with the niobium complex. At this point several hypothetical schemes were outlined for eliminating the interferences of molybdenum, iron, and tungsten. The separation scheme that looked most promising involved the reduction of iron(III) to iron(II), molybdenum(VI) to molybdenum(V), and tungsten(VI) to tungsten(V), after which niobium was masked as a fluoride complex, and molybdenum(V) and tungsten(V) were separated from the niobium by extracting the former ions as their thiocyanate complexes. It appeared that the most important part of this scheme was the masking and demasking of the niobium.

The results of investigations made on the masking and demasking step are shown in Table V, and they indicate that three ml of 0.1 M potassium fluoride will prevent the extraction of niobium, whereas three ml of 1.0 M potassium fluoride completely prevent the extraction of 2.28×10^{-4} mmole of niobium. Of the three demasking agents studied, aluminum(III), beryllium(II), and boric acid, it appears that saturation of the aqueous niobium containing solution with boric acid is most effective in destroying

TABLE V

EFFECT OF VARIOUS REAGENTS ON EXTRACTION OF NIOBIUM

Absorbance	Explanation
0.340	Control
0.397	Control
0.365	Control
0.368	Salting-out Agent; 3 ml of 1 M NH_4Cl
0.363	Salting-out Agent; 3 ml of 1 M NH_4Cl
0.367	Salting-out Agent; 3 ml of 0.1 M H_3BO_3
0.127	Masking Agent; 1 ml of 0.1 M KF
0.025	Masking Agent; 3 ml of 0.1 M KF
0.004	Masking Agent; 3 ml of 1.0 M KF
0.111	Efficiency of AlCl_3 in Demasking Nb
0.150	Efficiency of BeCl_2 in Demasking Nb
0.233	Efficiency of H_3BO_3 in Demasking Nb
0.255	Demasking with H_3BO_3 ; took 0.3 mmole KF
0.197	Demasking with H_3BO_3 ; took 3.0 mmole KF

the niobium fluoride complex. The reactions for formation of the tetrafluoroborate ion from boric acid and fluoride have been described by Coursier et al.⁸⁵ in their paper which reports the extraction of tetrafluoroborate with TPACl.

Another separation scheme investigated (Section 15-Expt.) involved the reduction of iron(III), molybdenum(VI), and tungsten(VI) with hot stannous chloride, followed by the simultaneous extraction of niobium and tungsten as the thiocyanate complexes. Niobium was subsequently stripped from the chloroform extract by backwashing with an aqueous hydrochloric acid-ammonium fluoride solution. The niobium fluoride complex was then destroyed using boric acid, after which the niobium was extracted as the thiocyanate complex. When this scheme was actually applied to a niobium mixture, a chloroform insoluble green-yellow precipitate was found to be present in the tungsten-free solution of niobium which also was saturated with boric acid. The absorbance of the extract was much lower than expected for the amount of niobium taken. Further investigations revealed that pure niobium solutions, when heated with stannous chloride and subsequently treated with potassium fluoride, boric acid, TPACl, and potassium thiocyanate would always produce a green-yellow precipitate that was insoluble in chloroform. However, when the heating step only was omitted the green-yellow precipitate was soluble in chloroform. It was finally discovered that mixtures

of stannous chloride and stannic chloride in the presence of potassium fluoride form precipitates with TPACl that are insoluble in chloroform, and in some manner the stannous and stannic ions apparently reacted with niobium to make its arsonium salt insoluble in chloroform.

At this point of the investigations it was discovered that the insoluble arsonium salts mentioned above were soluble in chloroform-acetone mixtures, and the decision was made to investigate the use of such a mixture as the extracting solvent. The results of using a chloroform-acetone mixture have been compared with chloroform earlier in the discussion, and it is apparent that the mixture is clearly superior as an extracting solvent in the case of niobium. It is suggested that the mixture is a better solvent primarily because of its higher dielectric and polarity, which in turn more readily dissolves the arsonium salt of niobium; however, more complex factors which cannot be ruled out are: (1) a different complex species may be formed in the presence of acetone which contains acetate ligands, presumably in the outer sphere as adducts, and (2) acetone partitions into the aqueous phase to exert a salting-out effect.

Interferences

After establishing optimum values for the extraction

variables, a detailed investigation of interferences was made using the procedure in Section 20-Experimental. The results are summarized in Table VI.

The interference studies revealed that many of the elements that commonly occur with niobium in steels and alloys do not interfere in the slightest with the new method. Furthermore, it is significant that tantalum can be present in a 118-fold excess without interfering. The analytical procedure is adequate to prevent the interference of molybdenum, tungsten, and iron when they are present in ratios of 45/1, 4/1, and 107/1, respectively, compared to niobium on a gram/gram basis. When larger quantities of tungsten are present it will be necessary to use a strong reductant to completely reduce the tungsten(VI) to tungsten(V) prior to its removal in the separation step.

When titanium is present, a precipitate of a thiocyanate complex forms with the TPA ion. Prolonged shaking will cause the precipitate to decompose due to preferential extraction of TPASCN, tetraphenylarsonium thiocyanate, from the aqueous phase.

Oxidizing agents such as oxides of nitrogen interfere with the determination of niobium by causing the oxidation of thiocyanate ion. In such cases the absorbance of the extract increases as a function of time, especially in the spectral region of 350-360 μ , which is characteristic of the thiocyanate decomposition products. For this reason it is mandatory to remove

TABLE VI

INTERFERENCES IN THE EXTRACTION AND DETERMINATION OF
 NIOBIUM WITH TPACl

(Nb taken: 21.3 ug; Absorbance = 0.336 ± 0.002)
 (Percentage error in absorbance is $\pm 0.596\%$)

Diverse Element	Quantity (ug)	Ratio of Diverse element to Nb	Absorbance (± 0.002)	Percent Error
Co	479	22.4	0.336	0.000
Mn	400	18.8	0.333	-0.892
Cr	400	18.8	0.336	0.000
Ni	482	22.6	0.334	-0.596
Cu	1000	47.0	0.335	-0.296
Ti	79.3	3.7	0.336	0.000
Ti	396	18.8	0.414	+23.2
V	204	9.6	0.334	-0.596
Sn	1000	46.9	0.179	-53.0
Ta	2520	119	0.341	+1.49
*Mo	998	45.8	0.336	0.000
W	18.4	0.9	0.337	+0.298
W	92	4.3	0.337	+0.298
Fe	2280	107	0.336	0.000

* Two extractions, each consisting of $\frac{1}{2}$ ml of TPACl and 7 ml. of chloroform-acetone, were required to remove the Mo.

all nitrogen oxides from the solutions prior to making an analysis. It is not necessary to remove nitric acid, as no interference from small quantities has been observed.

The nature of this new method for niobium is such that the method can be modified easily for the analysis of niobium in special material, since the use of alternate reducing agents and masking agents for eliminating the interference of diverse ions will permit many modifications. For example, the determination of niobium as traces in tungsten can be made using a zinc amalgam to reduce the tungsten prior to its extraction from the masked niobium. Also, niobium can be determined in molybdenum alloys by making successive extractions on the aqueous solution containing the masked niobium until the molybdenum concentration is reduced below the level of interference. It is further suggested that the determination of niobium in large quantities of titanium should be feasible by extracting the niobium and traces of the titanium, which has a much smaller distribution ratio, the traces of titanium being later removed from the organic extract by backwashing with fresh 3-4 M hydrochloric acid.

Calibration Curves

A. 9/2 Chloroform-Acetone Solution, with Masking and Separation Steps.

A calibration curve of absorbance as a function of niobium concentration was prepared (Results in Figure 7, Table VII) using the analytical procedure of Section 20-Experimental.

The concentration of niobium in the organic extract was calculated assuming complete extraction of the niobium from the aqueous phase. Beer's law was followed over the entire concentration range investigated, 0.17 to 3.2 mg niobium/liter. The specific absorptivity of $388 \pm 2 \text{ (g Nb/l)}^{-1} \text{ cm}^{-1}$ was determined by a least squares fit of 35 data points on the calibration curve. (The specific absorptivity of 388 corresponds to a molar absorptivity of $36000 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$). The intercept of the line at zero niobium concentration occurred at an absorbance of 0.005. The absorbance of the blank is caused by the excess TPASCN present in the extract.

B. 9/2 Chloroform-Acetone Solution Without Masking and Separation Steps

The calibration curve was constructed during preliminary investigations of the solvent. The data, shown in Table VIIb was plotted and a molar absorptivity of $41600 \text{ M}^{-1} \text{ cm}^{-1}$ was

BEER'S LAW CURVE FOR NIOBIUM EXTRACT IN
9:2 CHLOROFORM-ACETONE AT 390 m μ

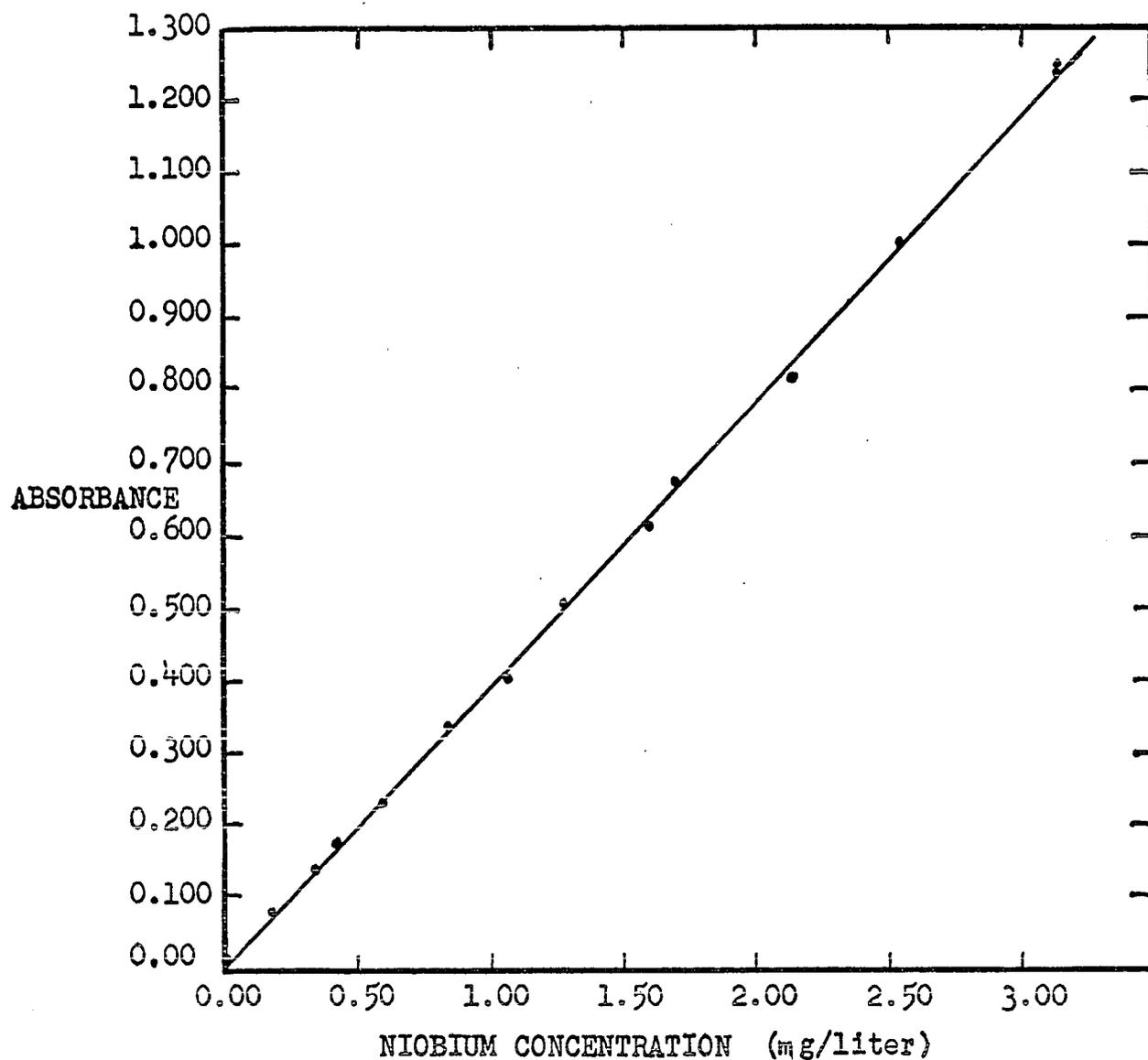


FIGURE 7

obtained.

C. Commercial Chloroform, without Masking and Separation Steps

A least squares analysis of the data in Table IV gave a line of slope $30,900 \text{ M}^{-1} \text{ cm}^{-1}$, with an intercept of 0.004. The procedure used is outlined in Section 11-Experimental.

D. Commercial Chloroform, with Masking and Separation Steps

The data in Table VIIc were plotted and the slope of the line was determined to be $28100 \text{ M}^{-1} \text{ cm}^{-1}$. The experimental procedure is given in Section 15-Experimental.

The concentration of niobium in the organic phase in all four procedures was calculated assuming that all the niobium was extracted into the solvent after making the number of extractions indicated for each procedure. In each of the above cases the completeness of extraction of niobium was checked by making an additional extraction of the aqueous phase after the required number had been made, and the absorbance of the extra extract was compared with that expected for a blank solution. In all cases the extraction of niobium was complete prior to the extra extraction. Hence, the difference between the molar absorptivities in the various solvents cannot be due to incomplete

TABLE VII

BEER'S LAW DATA FOR Nb, 9/2 CHLOROFORM-ACETONE SYSTEM
WITH MASKING AND SEPARATION STEPS

(Concentration, g Nb/ml) x 10 ⁷	Absorbance, 390 mμ
00.000	0.013, 0.011, 0.008, 0.006
1.691	0.076, 0.075
3.381	0.139, 0.137, 0.135
4.226	0.175
5.917	0.232
8.452	0.337, 0.337, 0.337, 0.337, 0.336 0.335, 0.335
10.57	0.412, 0.405, 0.395
12.68	0.514, 0.505, 0.489
15.85	0.630, 0.618, 0.608, 0.600
16.91	0.675, 0.675
21.14	0.818, 0.818
25.35	1.000
31.69	1.250, 1.240

TABLE VII b

DATA FOR BEER'S LAW PLOT OF NIOBIUM IN 9/2 CHLOROFORM-
ACETONE SOLUTION WITHOUT MASKING AND
SEPARATION STEPS

(Molar Conc., Nb) x 10 ⁺⁵	A, 390 mμ
0.000	0.010, 0.011
0.774	0.332, 0.330
1.547	0.665, 0.661
2.320	0.971, 0.975

Volume of organic phase after extraction was 14.7 ml.

TABLE VII c

BEER'S LAW DATA FOR NIOBIUM ; CHLOROFORM
SYSTEM WITH MASKING AND SEPARATION STEPS

[Molar Conc. of Niobium] X 10 ⁵	Absorbance, 390 mμ
0	0.010, 0.011
0.2274	0.075
0.4548	0.138, 0.136
0.6367	0.195
0.9096	0.265, 0.275, 0.279, 0.273
1.137	0.328
1.364	0.392, 0.393
1.705	0.488

TABLE IV

DATA FOR BEER'S LAW CURVE, CHLOROFORM
SYSTEM, 390 m μ

(Molar Conc., Nb) X 10 ⁵	Absorbance
0.00	0.004, 0.006, 0.012
0.910	0.283, 0.284, 0.284
1.37	0.428, 0.424, 0.424
1.82	0.572, 0.568
2.27	0.706, 0.704, 0.702, 0.709

A least squares analysis made on the above points gave a slope of 30,900 M⁻¹ cm⁻¹ with an intercept value of 0.004.

extraction of the niobium, but on the contrary the differences can be attributed to changes in the relative concentrations of the extracted species. Any variation of the conditions will shift the position of equilibrium between the niobium complexes in solution, and consequently the ratio of the concentrations of the two complexes will be different.

In designing the experimental procedure used to obtain the data for a given calibration curve, a constant quantity of all reagents (except niobium) was added, and the same number of extractions was made for each analysis of the standard solution.

Careful control of the experimental conditions showed that Beer's law was obeyed in each solvent, and the precision as indicated by the standard deviation of the absorptivity was quite good.

Alloy Analysis

The new analytical method for niobium was tested for accuracy, precision, and interferences by application to the analysis of several steels and alloys. The results of the analysis of five steels and heat-resisting alloys, all of which were obtained from the National Bureau of Standards, NBS, are shown in Table VIII. The analytical procedure described in

TABLE VIII

ANALYSIS OF NBS STANDARD STEEL AND ALLOY SAMPLES

NBS	% Nb		Difference	Standard Deviation	Number of Samples	Sample description and % Composition
	Reported	Found				
101e	0.013	0.017	+0.004	+0.001	7	Steel: W(0.06), Mo(0.43), Sn(0.02), V(0.04), Mn(1.8), Ni(9.5), Cr(18)
123b	0.75	0.753	+0.003	+0.007	11	Steel: W(0.18), Ta(0.2), Mo(0.2), V(0.05), Ti(0.006)
345	0.231	0.225	-0.006	\pm 0.003	6	Steel: Mo(0.12), Ta(0.002), V(0.04), Mn(0.22), Cu(3.4) Ni(4.2), Cr(16)
167	3.15	3.12	-0.03	\pm 0.01	8	Heat-resisting alloy: Ni(20), Co(43), Cr(20) Mo(3.9), W(4.5), Fe(2.1), Ta(0.08), V(0.03), Cu(0.04)
168	2.95	2.91	-0.04	\pm 0.04	9	Heat-resisting alloy: Mn(1.5), Fe(3.4), Cu(0.04), Ni(20), Co(41), Cr(20), V(0.03), Mo(4.0), W(4.0), Ta(0.95), Ti(0.06), Fe(3.4)

Section 20-Experimental was used to analyze the five samples.

The alloys contained some or all of the metals, cobalt, copper, titanium, nickel, chromium, molybdenum, tungsten, tantalum, vanadium, manganese, and iron, in addition to niobium. The results of the analyses are listed in Table VIII as well as the elemental composition of the alloys. A comparison of the results reported by NBS, and those found with the new method show that the method is as accurate as any of the procedures reported upon by the Bureau of Standards, and the precision as found from the standard deviation of the samples is quite good.

The major time factor in alloy analysis is sample dissolution. In all the above cases the samples were dissolved by heating in concentrated hydrochloric acid, to which one ml portions of concentrated nitric acid were added occasionally to assure complete solution and oxidation. In order to prevent the interference of nitrogen oxides, as mentioned previously, it is desirable to keep the addition of nitric acid to a minimum. Furthermore, a high ratio of nitric acid to hydrochloric acid is quite likely to cause precipitation of tungstic, tantalic, and niobic acids, especially if their concentration is high. Therefore, as much of the steel as possible is dissolved in hot concentrated hydrochloric acid. When dissolution of the sample is complete, the solution is boiled for 10-20 minutes to remove most of the nitrogen oxides. It

is not necessary to remove the nitric acid completely. After boiling, the hot solution is cooled for just a few minutes, then is transferred to a volumetric flask and partially diluted to volume with concentrated hydrochloric acid. After cooling, the solution is diluted to the mark, after which the solution should be tested for the presence of oxides of nitrogen by making an extraction on a portion of the sample with chloroform. If the extract has a yellow-brown color, the aliquot of the sample should be repeatedly extracted until the chloroform layer is colorless.

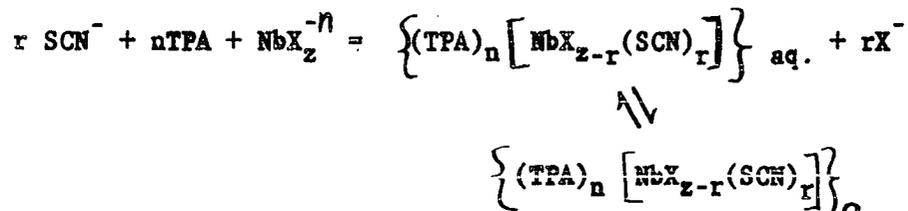
Composition of the Extracted Niobium Salt

A. Variational Analysis

The investigations described in Sections 8, 9, and 16-Experimental not only furnish data which can be interpreted to establish the optimum conditions for extraction of niobium, but when the data are treated as described below, the composition of the extracted complex with respect to thiocyanate and TPA can be deduced. The data for the chloroform and 9/2 chloroform-acetone systems are shown in Tables IX to XIII.

The composition of the complex species in the various solvents was deduced by means of a method previously described by Murphy and Affsprung.⁸⁶ The defining equations which relate the absorbance, A , to the TPA/niobium ratio, n , or the SCN/niobium, r ,

are based on the reaction:



where X is the hydroxy or chloride ligand which can be neglected in the equilibrium since their concentration will be relatively large and constant, and the subscript, o, indicates the organic layer and, aq., the aqueous phase. The equilibrium expression corresponding to the above reaction is:

$$K_o = \frac{(\text{Nb})_o}{(\text{SCN})_{\text{aq.}}^r (\text{TPA})_{\text{aq.}}^n (\text{NbX}_z^{-n})_{\text{aq.}}}$$

$$\text{where } (\text{Nb})_o = \left\{ (\text{TPA})_n \left[\text{NbX}_{z-r}(\text{SCN})_r \right] \right\}_o$$

Consideration of the distribution ratios and ionization constants of TPACl, TPASCN, and KSCN make it possible to write K_o in terms of the formal thiocyanate and TPA concentrations and the absorbance, after which the following expression is obtained:

$$\log \left(\frac{A}{A_o - A} \right) = \log K_5 + r \log \left[(\text{SCN})_t - rA/a \right] + n \log \left[(\text{TPA})_t - nA/a \right] \quad (1)$$

A_o is the expected absorbance for complete extraction of the niobium taken, and "a" is $41600 \text{ M}^{-1} \text{ cm}^{-1}$ for the 9/2 chloroform-acetone system, and $30900 \text{ M}^{-1} \text{ cm}^{-1}$ for the chloroform system. If the thiocyanate concentration, $(\text{SCN})_t$, is large compared to the niobium

concentration, and is held constant for a series of extractions in which the TPA concentration, $(\text{TPA})_t$, is varied, then

$$\log \left[\frac{A}{A_0 - A} \right] = \log K_6 + n \log \left[(\text{TPA})_t - nA/a \right] \quad (2)$$

As a first approximation, a plot of $\log \left(\frac{A}{A_0 - A} \right)$ versus $\log (\text{TPA})_t$ or \log (total millimoles TPA) produces a straight line of slope n .

When the TPACl concentration is held constant and the thiocyanate concentration is varied, then

$$\log \left(\frac{A}{A_0 - A} \right) = \log K_7 + r \log \left[(\text{KSCN})_t - rA/a \right] \quad (3)$$

$$\text{Since } rA/a \ll (\text{SCN})_t, \log \left(\frac{A}{A_0 - A} \right) = \log K_8 + r \log V_{\text{KSCN}} \quad (4)$$

The data were plotted according to equations (4) and (2), and are shown in Figure 8, 10, and 9, 11, respectively. In the 9/2 chloroform-acetone system, the data from the experiments for higher concentrations of niobium were adjusted in the log concentration values by adding -0.250 and -0.925 respectively to each value for the TPA/niobium and thiocyanate/niobium ratios in order to reduce all the values to a single plot.

In Figure 9, the points are experimental and the line is drawn through the points with a slope of two, which indicates a thiocyanate/niobium ratio of two. The TPA graph, Figure 8, is more complicated to interpret since a positive deviation occurs

TABLE IX

DATA FOR VARIATIONAL ANALYSIS OF TPA/Nb RATIO
9/2 CHLOROFORM-ACETONE

A	A _{Blank}	$\frac{A}{A_0-A}$	$\log \left[\frac{A}{A_0-A} \right]$	millimoles TPACl	$\log \left(\frac{\text{mmole}}{\text{TPACl}} \right)$	$\log (\text{mmole})$ + (-0.25)
1.320	0.025	--	--	0.2000	--	--
1.292	0.019	57.9	1.76	0.1000	-1.00	-1.25
1.292	0.015	71.0	1.85	0.1000	-1.00	-1.25
1.277	0.017	36.0	1.56	0.0500	-1.30	-1.55
1.277	0.015	38.2	1.58	0.0500	-1.30	-1.55
1.249	0.015	20.2	1.31	0.0250	-1.60	-1.85
1.231	0.015	15.4	1.19	0.0200	-1.70	-1.95
1.166	0.015	7.99	0.90	0.0100	-2.00	-2.25
1.078	0.014	4.61	0.66	0.0050	-2.30	-2.55
1.013	0.014	3.38	0.53	0.0040	-2.40	-2.65
0.947	0.014	2.58	0.41	0.0030	-2.52	-2.77
0.860	0.014	1.88	0.27	0.0020	-2.70	-2.95
0.700	0.014	1.13	0.05	0.0010	-3.00	-3.25
0.662	0.014	1.00	0.00	0.0008	-3.10	-3.35
0.600	0.014	0.82	-0.09	0.0006	-3.22	-3.47
0.552	0.014	0.71	-0.15	0.0002	-3.70	-3.95
0.497	0.014	0.59	-0.23	0.0002	-3.70	-3.95
0.440	0.014	--	--	0.00	--	--

The symbol, (⊙), represents above set of data in Figure 8.
Nb taken: 2 ml of 2.27×10^{-4} M Nb; Collected 14.7 ml of extract.

TABLE X

DATA FOR VARIATIONAL ANALYSIS OF TPA/Nb RATIO
9/2 CHLOROFORM-ACETONE

A	A _{Blank}	$\frac{A}{A_0-A}$	$\log \frac{A}{A_0-A}$	millimoles TPACl	\log	m moles TPACl
0.656	0.011	--	--	--	--	--
0.650	0.011	91.3	1.96	0.1000		-1.00
0.646	0.011	57.6	1.76	0.1000		-1.00
0.642	0.011	39.3	1.59	0.1000		-1.00
0.644	0.008	63.6	1.80	0.0500		-1.30
0.634	0.006	34.8	1.54	0.0250		-1.60
0.623	0.005	22.0	1.34	0.0125		-1.90
0.591	0.005	9.78	0.990	0.0075		-2.13
0.595	0.005	10.5	1.02	0.0075		-2.13
0.494	0.005	3.11	0.49	0.0025		-2.60
0.499	0.005	3.24	0.51	0.0025		-2.60
0.416	0.004	1.76	0.25	0.00125		-2.90
0.419	0.004	1.80	0.26	0.00125		-2.90
0.361	0.004	1.24	0.09	0.00075		-3.13
0.329	0.004	1.01	0.00	0.00025		-3.60
0.302	0.004	0.855	-0.068	0.00015		-3.82
0.280	0.004	0.745	-0.128	0.00005		-4.30

The symbol, \odot , is used in Figure 8 to represent the above data. Nb taken: 2 ml of 1.14×10^{-4} M Nb.

TABLE XI

DATA FOR VARIATIONAL ANALYSIS OF SCN/Nb RATIO
9/2 CHLOROFORM-ACETONE

A	$A_{\text{corr}} = A - .008$	$\frac{A}{A_0 - A}$	$\log \left[\frac{A}{A_0 - A} \right]$	ml. of 0.3 M KSCN	$\log V_{\text{KSCN}}$	$\log \frac{V_{\text{KSCN}}}{V_{\text{KSCN}}} + (-0.925)$
0.655	0.647	----	----	----	----	----
0.618	0.610	16.45	1.22	5	----	-0.23
0.618	0.610	15.52	1.19	5	0.699	-0.23
0.592	0.584	9.26	0.97	4	0.602	-0.32
0.545	0.537	4.89	0.69	3	0.477	-0.45
0.459	0.451	2.30	0.36	2	0.301	-0.62
0.285	0.277	0.75	-0.13	1.2	0.079	-0.85
0.225	0.217	0.51	-0.30	1	0.000	-0.93

Nb taken: 2ml of 1.14×10^{-4} M Nb ; Least squares slope = 2.13

3.0 M KSCN

0.336	0.328	---	---	4	---	---
0.331	0.323	64.6	1.81	3	0.48	---
0.331	0.323	64.6	1.81	2	0.30	---
0.334	0.336	161.0	2.21	2	0.30	---
0.326	0.318	31.8	1.50	1	0.00	---
0.304	0.296	9.25	0.966	0.5	-0.30	---
0.274	0.266	4.29	0.633	0.3	-0.52	---
0.221	0.199	1.54	0.188	0.2	-0.70	---
0.175	0.167	1.04	0.017	0.15	-0.82	---
0.180	0.172	1.07	0.029	0.15	-0.82	---
0.103	0.095	0.408	-0.389	0.10	-1.00	---
0.059	0.051	0.184	-0.735	0.07	-1.16	---
0.033	0.025	0.083	-1.080	0.05	-1.30	---

Nb taken: 5ml of 2.27×10^{-4} M Nb ; Least squares slope = 1.98

TABLE XII

DATA FOR VARIATIONAL ANALYSIS OF TPA/Nb RATIO
CHLOROFORM SYSTEM

A	A _{corr}	$\log \left[\frac{A}{A_0 - A} \right]$	millimoles TPACl	$\log \left[\frac{\text{m mole}}{\text{TPACl}} \times 100 \right]$
0.963	0.955	--	--	--
--	0.936	--	--	--
0.928	0.920	1.76	0.150	2.18
0.879	0.871	1.13	0.100	2.00
0.790	0.782	0.71	0.050	1.70
0.769	0.761	0.64	0.050	1.70
0.676	0.669	0.40	0.0205	1.40
0.636	0.628	0.32	0.020	1.30
0.631	0.623	0.30	0.020	1.30
0.580	0.572	0.20	0.0125	1.10
0.541	0.533	0.12	0.0100	1.00
0.475	0.467	-0.002	0.0075	0.88
0.390	0.382	-0.161	0.0050	0.70
0.336	0.328	-0.268	0.0035	0.54
0.252	0.244	-0.453	0.0025	0.40
0.149	0.141	-0.752	0.00125	0.10
0.008	--	--	0.00125	
0.014	--	--	0.150	

TABLE XIII

DATA FOR VARIATIONAL ANALYSIS TO DETERMINE MOLAR RATIO
OF THIOCYANATE TO NIOBIUM , CHLOROFORM SYSTEM

A	(A-0.006)	$A_0 - A$	$\frac{A}{A_0 - A}$	$\log \left[\frac{A}{A_0 - A} \right]$	Vol. KSCN (0.12M)	Log V KSCN
--	0.936	0	--	--	--	--
0.714	0.708	0.228	3.10	0.49	15.0	1.18
0.709	0.703	0.233	3.01	0.48	12.5	1.10
0.702	0.696	0.240	2.90	0.46	10.0	1.00
0.629	0.623	0.313	1.99	0.30	7.5	0.88
0.536	0.530	0.406	1.30	0.11	5.0	0.70
0.446	0.440	0.496	0.885	-0.05	4.0	0.60
0.341	0.335	0.601	0.556	-0.25	3.0	0.48
0.261	0.255	0.681	0.374	-0.43	2.5	0.40
0.202	0.196	0.740	0.265	-0.58	2.0	0.30
0.129	0.123	0.813	0.151	-0.82	1.5	0.19
0.047	0.041	0.895	0.046	-1.34	1.0	0.00
0.006	--	--	--	--	2.0	--
0.004	--	--	--	--	12.5	--
0.627	0.621	0.315	1.97	0.29	7.5	0.88
0.550	0.544	0.392	1.39	0.14	5.0	0.70
0.535	0.529	0.407	1.30	0.11	5.0	0.70
0.518	0.512	0.424	1.21	0.08	4.0	0.60
0.395	0.389	0.547	0.71	-0.15	3.0	0.48
0.303	0.297	0.639	0.470	-0.33	2.5	0.40
0.228	0.222	0.714	0.310	-0.51	2.0	0.30
0.090	0.084	0.852	0.099	-1.00	1.25	0.10

TPACl taken : 1 ml of 0.02M

Slope = 2.00

PLOT FOR DETERMINING STOICHIOMETRIC MOLAR
RATIO OF TPA TO NIOBIUM
9/2 CHLOROFORM-ACETONE

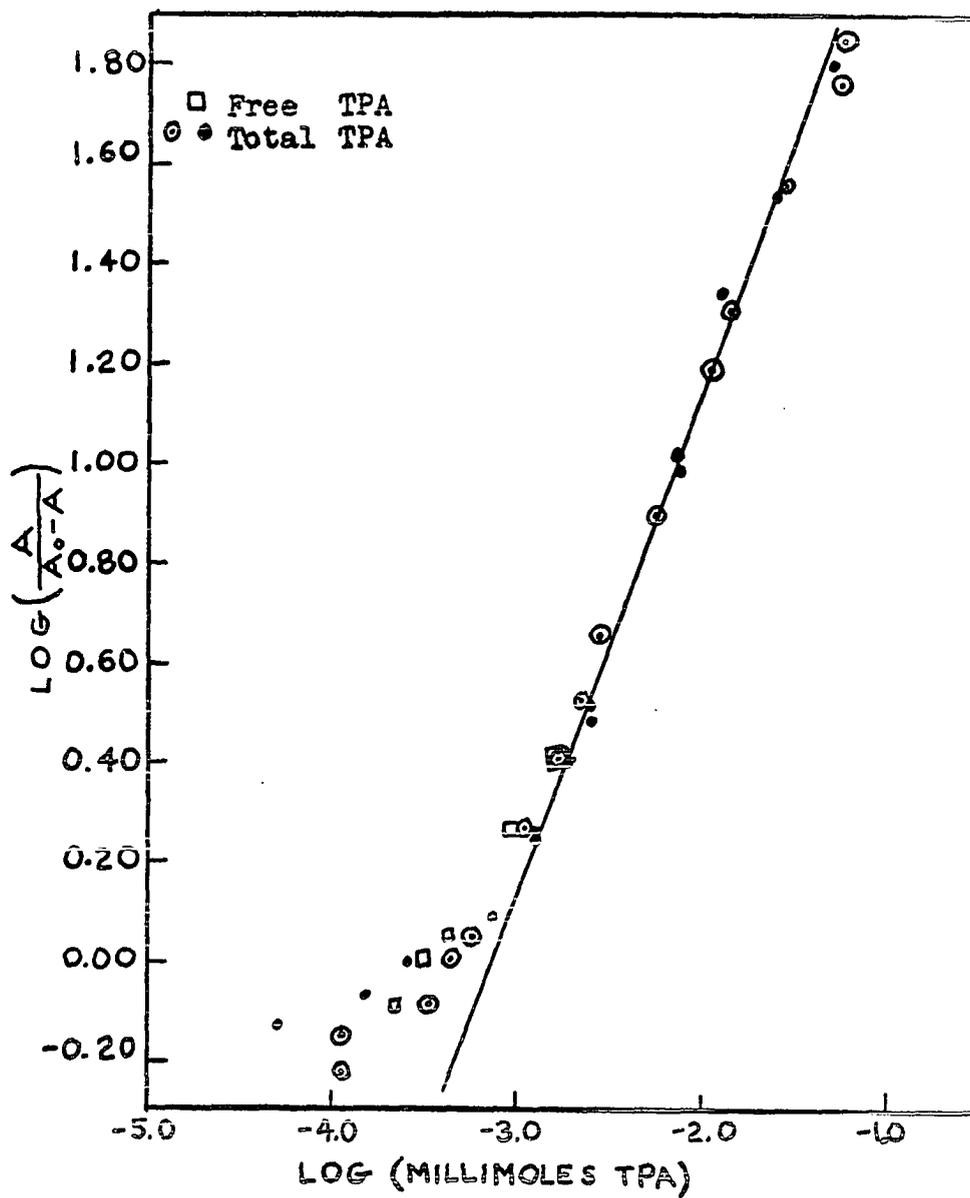


Figure 8

PLOT TO DETERMINE MOLAR RATIO OF THIOCYANATE
TO NIOBIUM, 9/2 CHLOROFORM-ACETONE

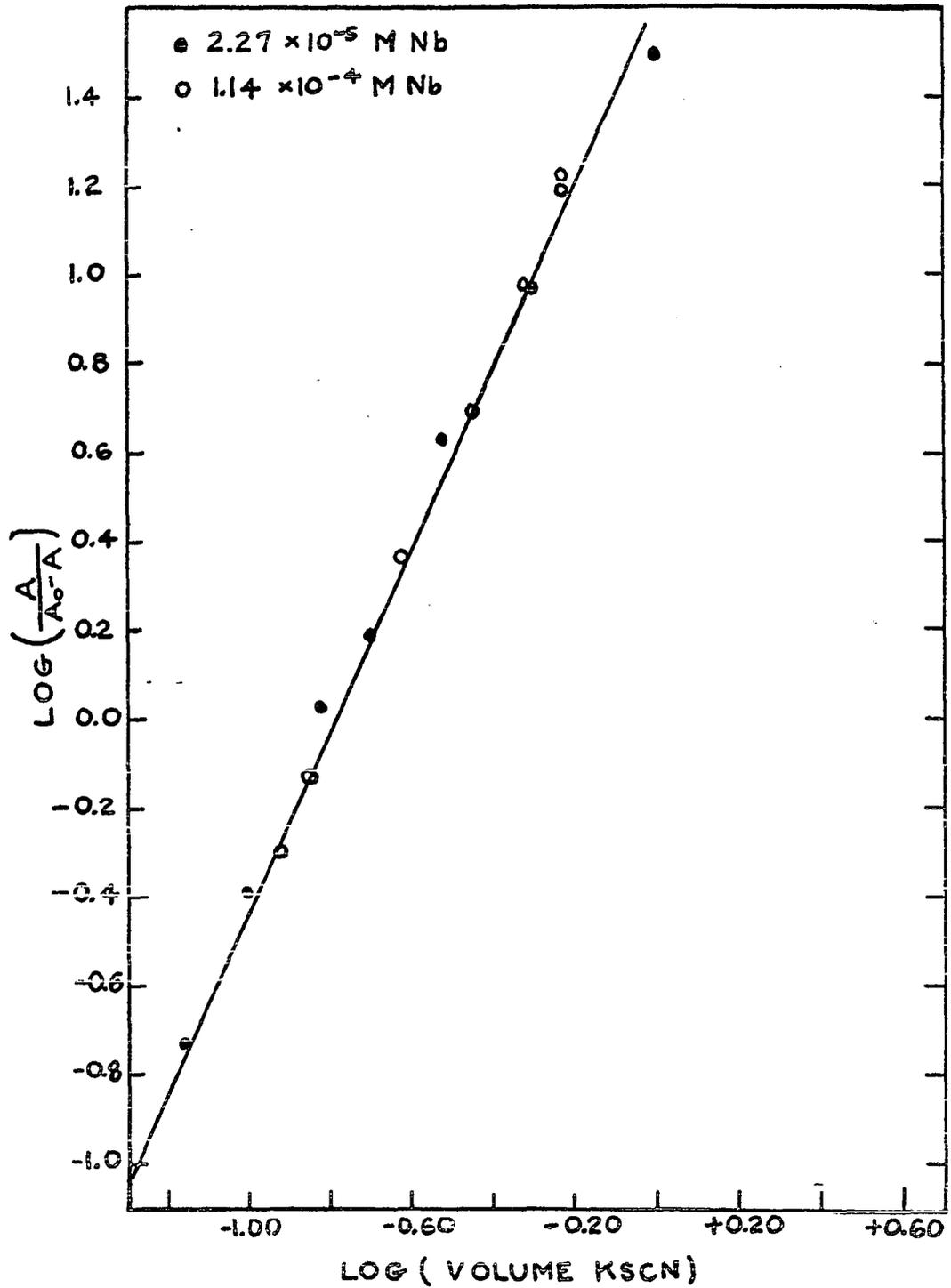


FIGURE 9

PLOT FOR DETERMINING MOLAR RATIO OF TPA TO NIOBIUM

CHLOROFORM SYSTEM

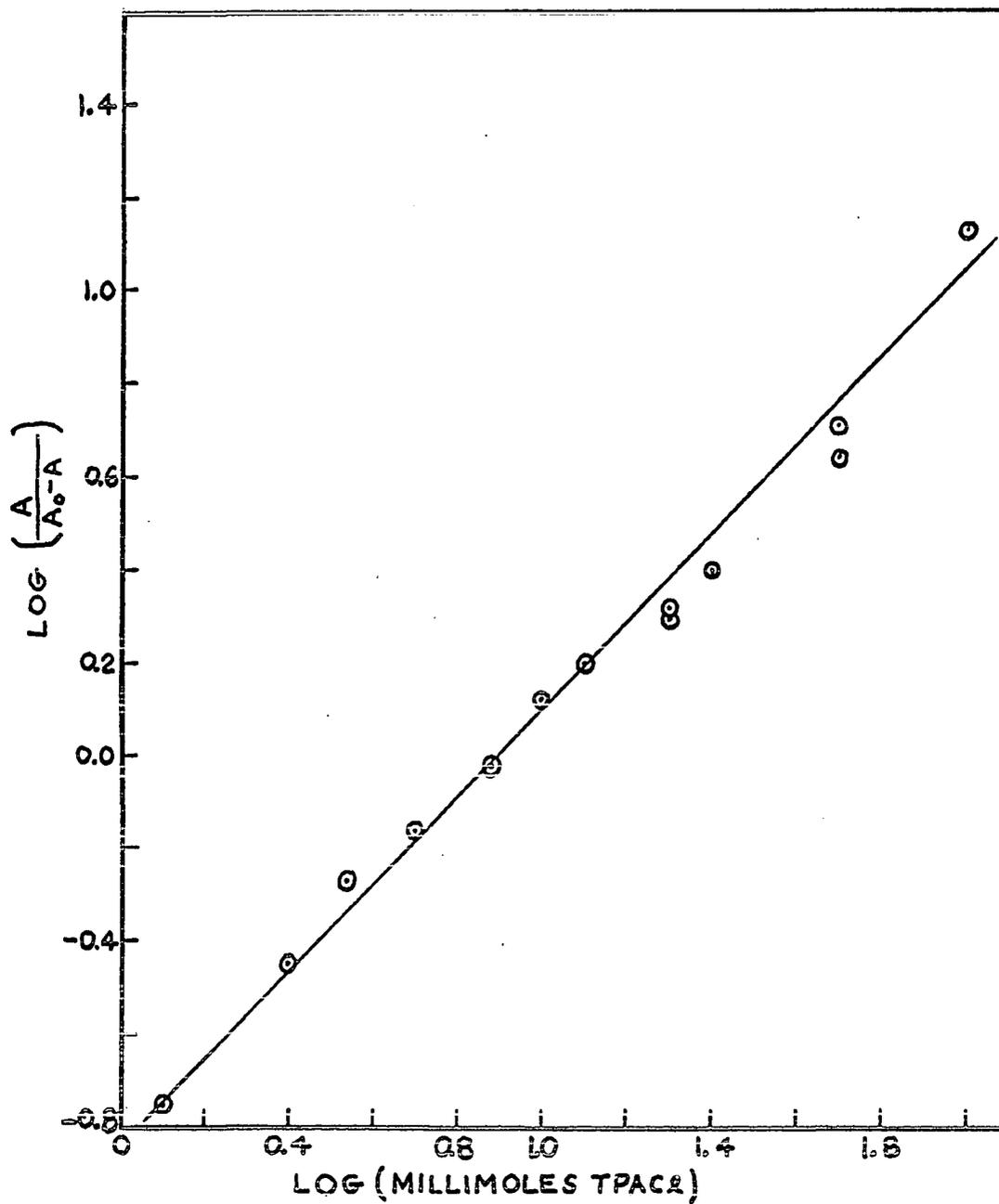


FIGURE 10

PLOT FOR DETERMINING MOLAR RATIO OF
THIOCYANATE TO NIOBIUM
CHLOROFORM

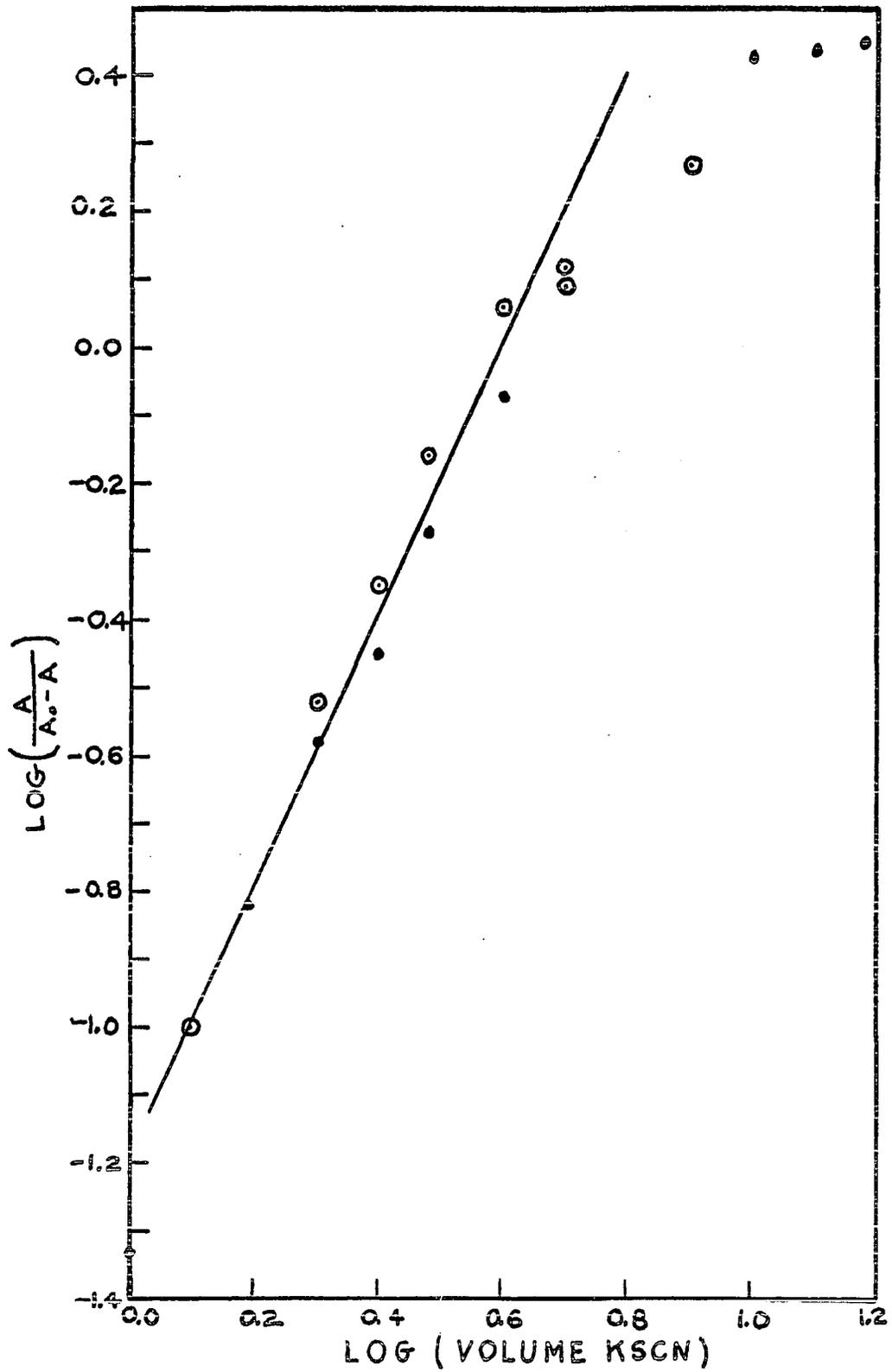


FIGURE 11

at very low TPA concentrations. Neglecting the lower portion of the curve, a line of slope unity is drawn through the data points. The agreement between the experimental points and the line of slope unity indicate a TPA/niobium ratio of one. The results then indicate that the formula for the extracted species is $\left\{ (\phi_4As)^+ [Nb(SCN)_2X]^- \right\}$, where X may be chloride, oxo, or hydroxy ligands, and niobium is present as niobium(V).

The positive deviation of the TPA graph at very low TPA concentrations is caused by coextraction of niobium as the free thiocyanatoniobic acid along with the arsonium ion-pair. The presence of the free thiocyanatoniobic acid has been verified by performing an extraction on a niobium solution in the absence of TPACl. The absorbance of the extract was 0.440 at 390 mμ, and the shape of the spectrum was identical to that of the TPACl extract. At higher TPACl concentrations the extraction of the thiocyanatoniobic acid is negligible since the partition coefficient of the TPA complex is much greater, as inferred from the solubilities of the two species in water and the organic solvent. Corrections for simultaneous extraction of the free acid were not applied since quantitative values for the partition coefficients of the two complexes are not available. Since the extraction of free thiocyanatoniobic acid does not occur when commercial chloroform is used as the extraction solvent, the

TPA/niobium and thiocyanate/niobium ratios were determined in chloroform.

The TPA/niobium graph, Figure 10, has a slope of 0.95, indicating a stoichiometry of 1 to 1 for TPA and niobium. The line in the thiocyanate/niobium graph, Figure 11, has a slope of two. The negative deviation of high thiocyanate concentrations is explained as follows: In general, the variational method of determining stoichiometry in complexes is applicable in those regions of a curve of absorbance as a function of reagent concentration, $A = f(c)$, where the absorbance changes rapidly as the concentration of reagent is varied. The highest three points of Figure 11 are on or very near the plateau of the $A = f(c)$ curve, and consequently would be expected to deviate from the straight line drawn in Figure 11. To further illustrate the point that the plateau of the curve of $A = f(c)$ is not applicable, one can consider those points for which there is no change in absorbance for variation of the reagent concentration; in this case the slope of the variational plot would be zero.

In constructing the TPA/niobium graphs, Figure 8 and 10, a preliminary graph of $\log (A/A_0 - A)$ versus \log (millimoles TPACl) is usually made to determine a value for the integer n , and then $\log (A/A_0 - A)$ is plotted versus $\log \left[(TPA)_t - nA/a \right]$. The latter value for the concentration of free TPA, i.e., TPA not bound in the metal ion-pair usually gives a better fit of the

data points. In Figure 8 the symbol, \square , shows that the values of the free TPA differ from the total TPA values only at very low TPA concentrations (0.003 millimoles of TPACl). At higher concentrations of TPACl the log values of free or total TPA concentration are superimposed, thus making corrections unnecessary for several of the data points.

Infrared Spectra

The infrared spectra of TPASCN, TPACl, KSCN, the arsonium thiocyanate salts of niobium(V), tungsten(V), titanium(IV), cobalt(II), and chromium(III) were obtained in KBr discs on the Beckman IR-8 infrared spectrophotometer. The spectra are shown in Figures 12-15, and the important absorption bands are tabulated in Table XIV. Upon comparing the salts, it is apparent that the band at $2056 \pm 2 \text{ cm}^{-1}$ is due to the $\text{C}\equiv\text{N}$ stretching frequency. The transition metal salts are all probably contaminated with TPASCN, hence the $\text{C}\equiv\text{N}$ band of TPASCN is present in the niobium, tungsten, and chromium spectra as a distinct peak. The niobium salt differs from all the others in that it shows three distinct bands in the $2000\text{-}2100 \text{ cm}^{-1}$ region, whereas the others show only two bands. The 2090 cm^{-1} band of niobium is assigned as an isothiocyanate stretching frequency, $\text{M}\leftarrow\text{NCS}$, since both chromium and cobalt salts have bands near 2090 cm^{-1} which are known to be isothiocyanate bands. The niobium band at 2016 cm^{-1} as well as the titanium band

TABLE XIV

INFRARED ABSORPTION BANDS OF SEVERAL ARSONIUM SALTS

Salt	(1,2) Wave number, cm^{-1}	Assignment
TPASCN	2056 \pm 2 (V.S.)	$\text{C}\equiv\text{N}$ Stretching frequency $\text{C}\equiv\text{N}$ Stretching frequency; 2020 cm^{-1} (a)
Nb Thiocyanate	2090 \pm 2 (m) 2057 \pm 2 (V.S.) 2016 \pm 4 (V.S.b.) 920 w 888 (w) 800 (V.W.)	$\text{Nb}\leftarrow\text{NCS}$ Vibration* $\text{C}\equiv\text{N}$ Stretching frequency $\text{Nb}=\text{O}$ Vibration
Ti Thiocyanate Salt	2040 \pm 2 (S) 1990 \pm 2 (V.V.S.) 885 (m)	$\text{M}\leftarrow\text{NCS}$ $\text{C}\equiv\text{N}$ Stretching frequency $\text{Ti}=\text{O}$ Vibration
W Thiocyanate Salt	2098 \pm 3 (S) 2050 \pm (V.V.S.) 952 (w)	$\text{W}\leftarrow\text{NCS}$ Vibration* $\text{C}\equiv\text{N}$ Stretching frequency $\text{W}=\text{O}$ Vibration
Co Thiocyanate Salt	2077 \pm 5	$\text{Co}\leftarrow\text{NCS}$ Vibration*
Cr Salt (Pink)	2087 \pm 2 (V.S.) 2054 \pm 2 (S)	$\text{Cr}\leftarrow\text{NCS}$ Vibration* $\text{C}\equiv\text{N}$ stretch in TPASCN
Cr Salt (Violet)	2080 \pm 2090 (V.S.)	$\text{Cr}\leftarrow\text{NCS}$ Vibration*
$[\text{MoO}(\text{NCS})_5]^-$	945	$\text{Mo}=\text{O}$ Vibration (a) $\text{Mo}=\text{O}$ range for several compounds is 850-1000 cm^{-1}
MoOCl_4^-	997	$\text{Mo}=\text{O}$ Vibration (a)

1. The indicated uncertainties are attributed to reading error which is dependent on the sharpness of the peak.

2. Band intensities are denoted as: v. = very; s. = strong; m. = medium; w. = weak; b. = broad.

a. P.C.H. Mitchell, Quarterly Reviews XX 103 (1966).

*Defined as a $\text{C}\equiv\text{N}$ stretching vibration in which the N atom is bonded to the metal atom.

TABLE XV

ISOTHIOCYANATE VIBRATIONS OF ARSONIUM COMPLEX SALTS

Element	$\text{M}-\text{NCS}$ Vibration, cm^{-1}	Examples
Ti	2040	$(\text{TPA})_2 [\text{TiO}(\text{NCS})_4]$
Mo(V)	2066, 2037-2049	$(\text{NH}_4)_2\text{Mo}(\text{NCS})_6$; $(\text{PyH})_3\text{Mo}(\text{NCS})_6^{\text{a}}$
Co(II)	2077 ± 5 , 2058-2079	$(\text{TPA})_2\text{Co}(\text{NCS})_4$; $\text{K}_2[\text{Co}(\text{NCS})_4]$
Cr(III)	2087 ± 2	$\text{TPA}[\text{Cr}(\text{SCN})_4]$; $\text{H}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^{\text{b}}$ $[\text{Cr}(\text{NH}_3)_5(\text{NCS})](\text{NO}_3)_2$, $\text{trans-}[\text{Cr}(\text{en})_2(\text{NCS})_2] \text{Cl} \cdot \text{H}_2\text{O}$
Nb(V)	2090 ± 2	$\text{TPA}[\text{NbO}(\text{NCS})_2\text{X}]$
W(V)	2098 ± 3 ; 2058	$\text{TPA}[\text{W}(\text{NCS})_2\text{X}]$; $(\text{Py})_2\text{W}(\text{OH})_3(\text{NCS})_3^{\text{a}}$
Co(III)	2114, 2122	$\text{trans-}[\text{Co}(\text{NCS})_2(\text{en})_2] \text{Cl} \cdot \text{H}_2\text{O}^{\text{b}}$ $[\text{Co}(\text{NH}_3)_5(\text{NCS})](\text{NO}_3)_2$

(a) P.C.H. Mitchell and R.J.P. Williams, J. Chem. Soc. 1912 (1960).

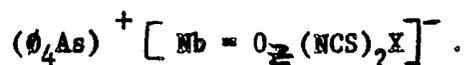
(b) J. Fujita, K. Nakamoto and M. Kobayashi, J. Am. Chem. Soc. 78, 3295 (1956).

PyH = Pyridinium ion en = ethylenediamine

Py = pyridine

at 1990 cm^{-1} are very strong, and their origin remains a mystery.

The metals, niobium, titanium, and tungsten, also exhibited bands in the region $950\text{-}800\text{ cm}^{-1}$, which are likely to be metal-oxygen bands. The bands are assigned as indicated in Table XIV. Hence the infrared spectra indicate that the niobium salt has mixed ligands consisting of isothiocyanato and oxo groups, where the oxo group is double bonded (according to Selbin, ref. 77). Thus the formula of the arsonium salt can be written as:



The ionic character of the $\text{Nb} \leftarrow \text{NCS}$ bonds can be established on a relative basis by comparing the isothiocyanate stretching frequencies of the various salts shown in Table XIV. Fujita, et. al. have compared the spectra of Co(III) and Cr(III) thiocyanate salts with HSCN and deduced that a trend toward higher frequencies for the $\text{M} \leftarrow \text{NCS}$ vibrations in the salts corresponds to an increase in ionic character of the bond, and also an increase in ease of substitution of ligands into the complex. The data in Table XV, which is arranged in the order of increasing frequency, indicate a correlation between higher frequency and a smaller number of thiocyanate ligands in the molecule, which in turn implies less covalent character in the metal-ligand bonds. Thus for the four elements of interest, Ti, Co, Nb, and W, it is suggested that the order of decreasing covalent character as well as number of

INFRARED SPECTRUM OF POTASSIUM THIOCYANATE

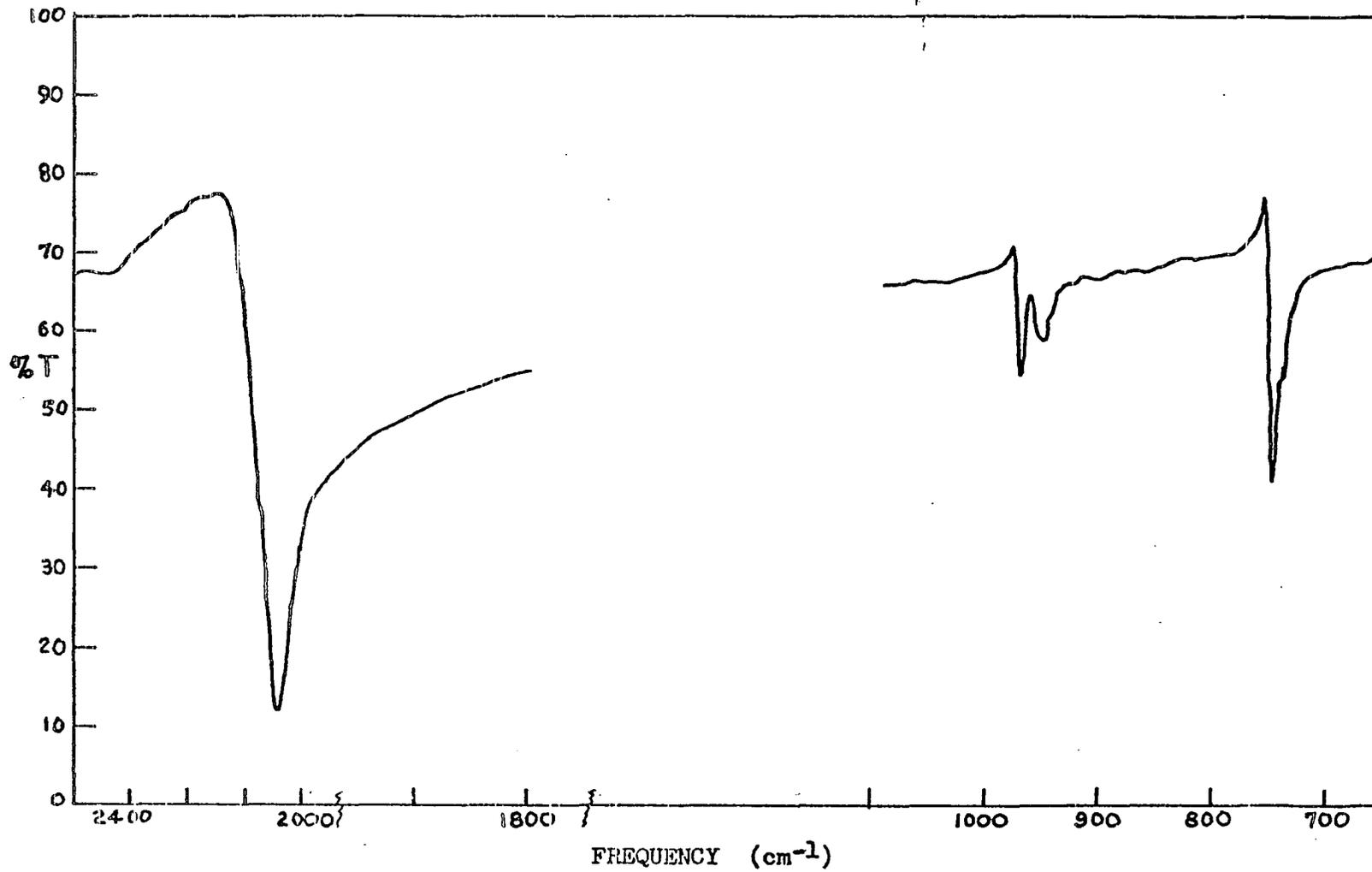
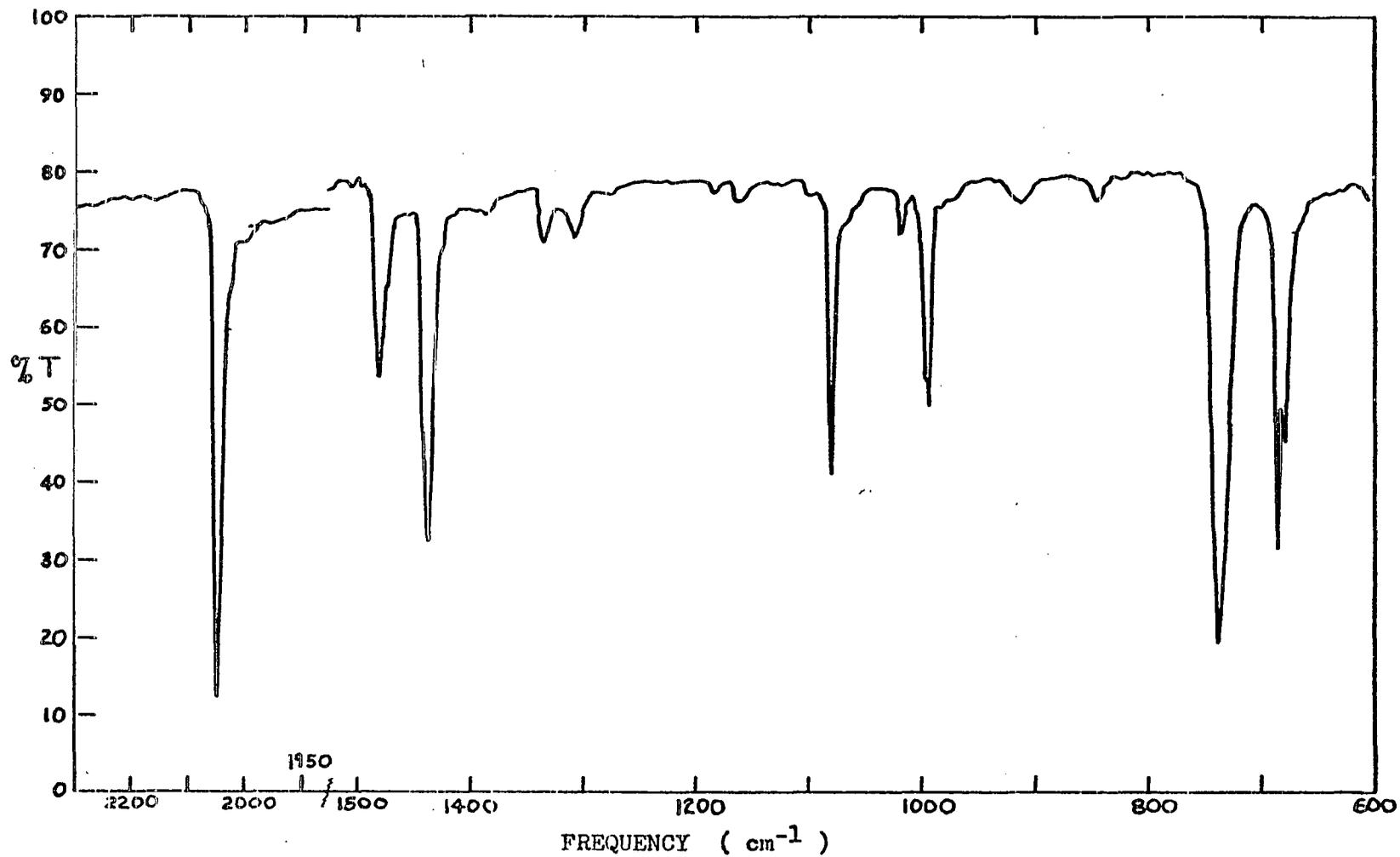


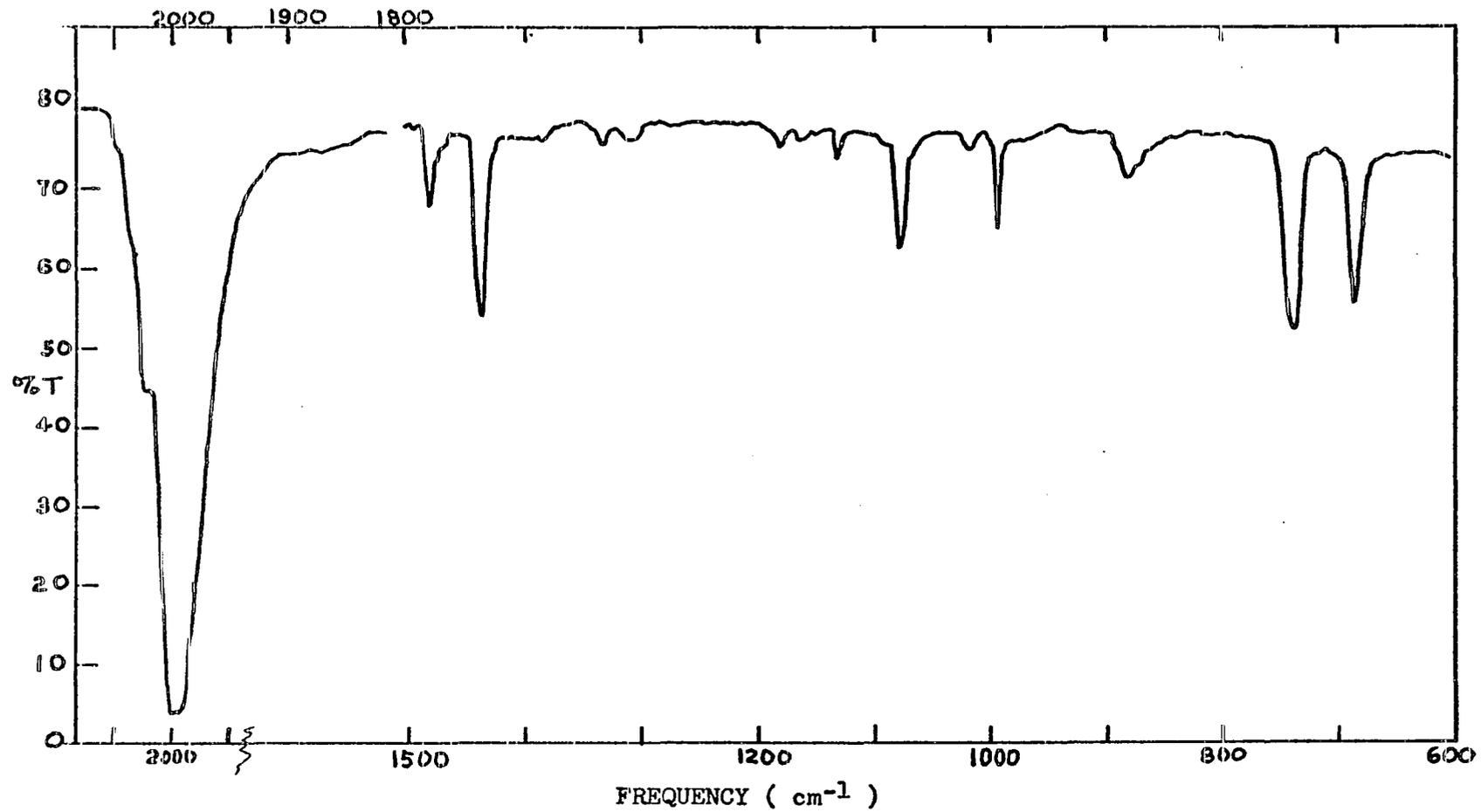
FIGURE 12

INFREARED SPECTRUM OF TETRAPHENYLARSONIUM THIOCYANATE



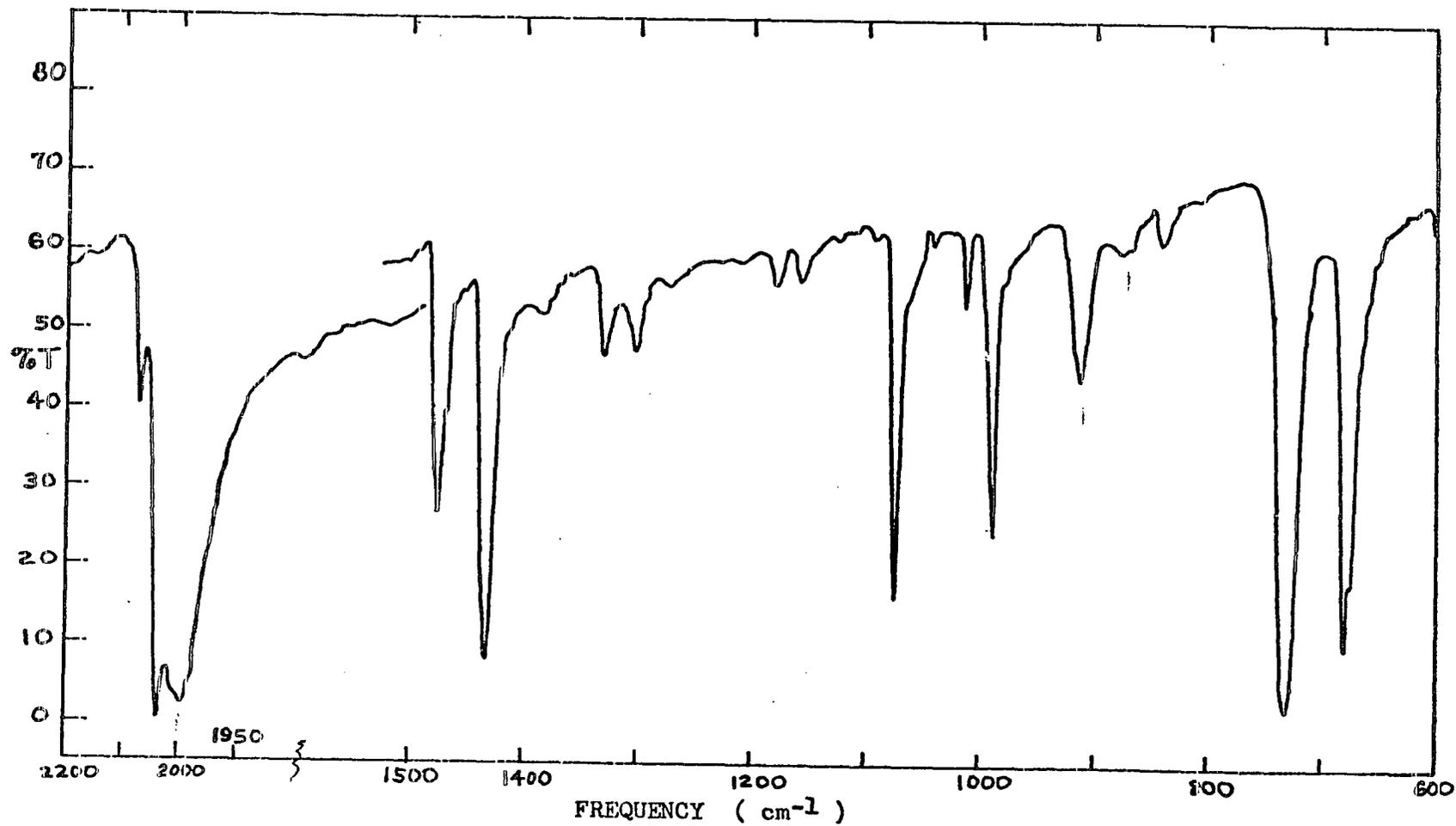
100

Figure 13



INFRARED SPECTRUM OF THE ORANGE SALT CONTAINING TPA AND THE THIOCYANATE COMPLEX OF TITANIUM

FIGURE 11₁



102

INFRARED SPECTRUM OF THE YELLOW SALT CONTAINING TPA AND THE THIOCYANATE COMPLEX OF NIOBIUM

FIGURE 15

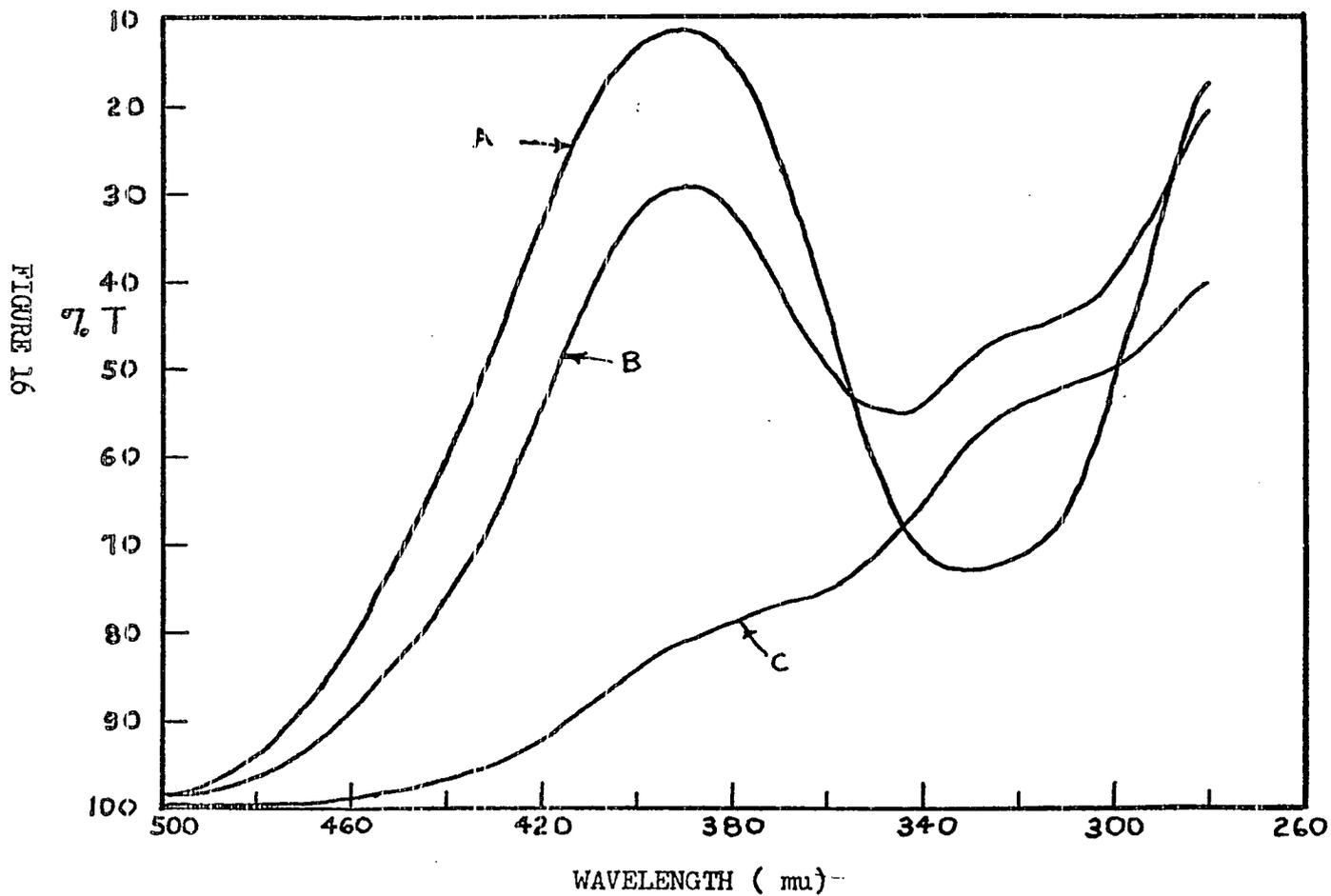
isothiocyanate ligands is: $Ti > Co > Nb > W$.

Dilution of Nb Solutions

Additional information about the niobium equilibria was obtained by means of the dilution experiments described in Section 27-Experimental. Figure 16, which shows the visible spectra of the Nb extract before and after dilution, presents additional evidence for two complexes in the chloroform solution. It is clear that upon dilution, the concentration of one complex decreases (deduced from the decrease in absorbance at 390 m μ) and the concentration of a lower complex increases, as inferred from the increase in absorbance at 320 m μ . Furthermore, the absorbance at 390 m μ before dilution, 0.928, when multiplied by the dilution factor, 0.80, indicates an expected absorbance of 0.742. The observed absorbance of 0.717 (actually 0.550 upon decaying to a constant value) is considerable less than expected, and is suggested to be lower than expected because of a shift in the equilibria. For the case of a 4 to 10 dilution, the discrepancy between the expected and observed absorbances, 0.371 versus 0.098, is even greater.

Upon dilution of a niobium extract the absorbance at 390 m μ quickly decreases, and then decreases at a much slower rate for a period of 5 to 20 minutes, depending on the conditions of extraction. The rate of decrease in absorbance can be used to

- A. Spectrum of Niobium Complex Prior to Dilution
- B. Spectrum of Niobium Complex after Dilution (4 ml dil. to 5 ml)
- C. Spectrum of Niobium Complex after Dilution (4 ml dil. to 10 ml)



EFFECT OF DILUTION UPON THE SPECTRUM OF THE THIOCYANATE
COMPLEX OF NIOBIUM IN CHLOROFORM

FIRST ORDER RATE LAW PLOT FOR DISSOCIATION OF THE NIOBIUM

COMPLEX UPON DILUTION, 390 mu

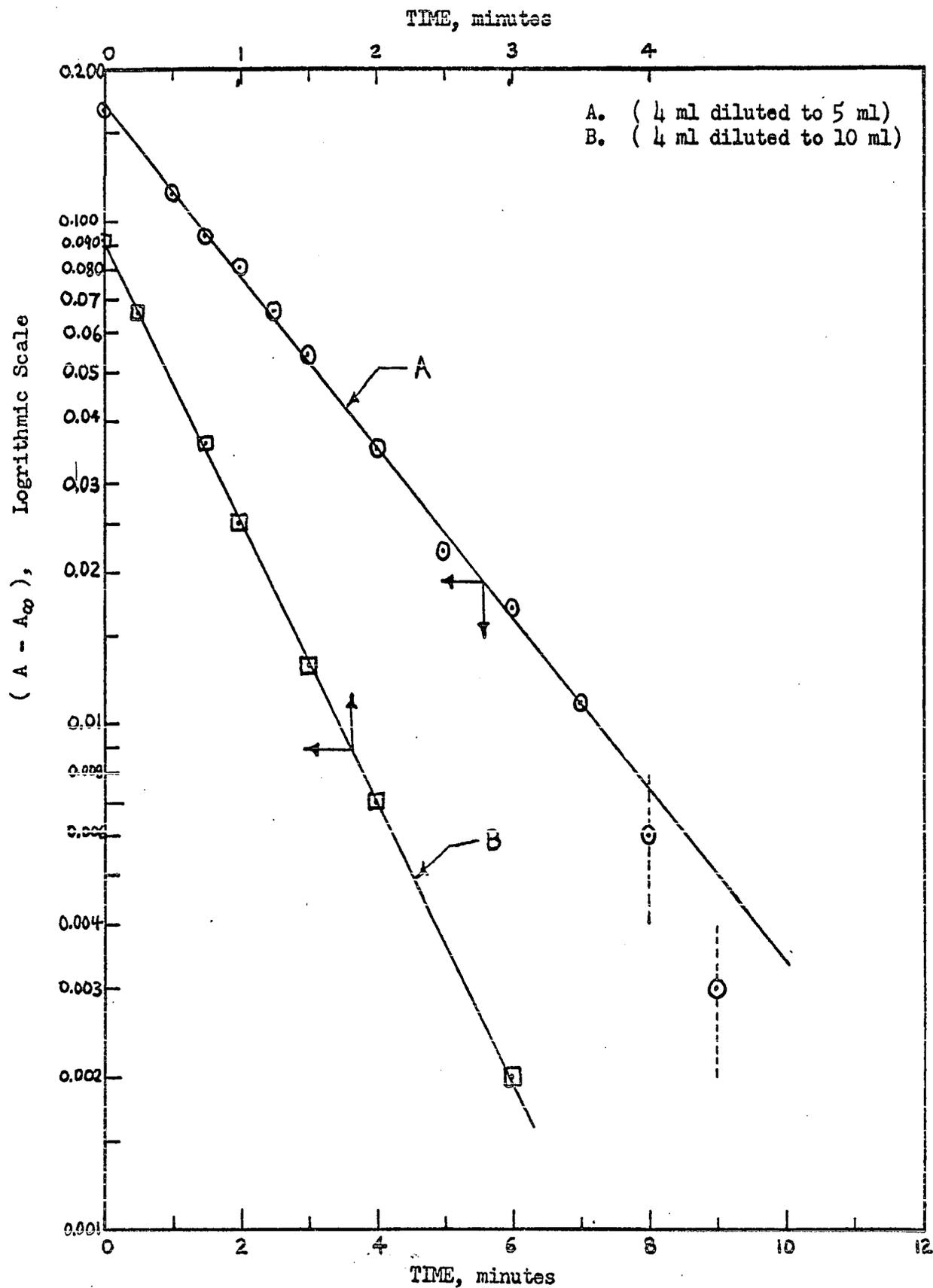


FIGURE 17

TABLE XVI

CHANGE IN ABSORBANCE AS A FUNCTION OF TIME
UPON DILUTION OF CHLOROFORM EXTRACTS

time	A_{390}	$A-A_{\infty}$	time	A_{390}	$A-A_{\infty}$
(Prior to dilution)	0.928	--	0.00	0.190	0.092
0.00	0.717	0.167	0.25	0.164	0.066
1.0	0.663	0.113	0.75	0.134	0.036
1.5	0.644	0.094	1.00	0.123	0.025
2.0	0.631	0.081	1.50	0.111	0.013
2.5	0.616	0.066	2.00	0.105	0.007
3.0	0.604	0.054	3.00	0.100	0.002
4.0	0.585	0.035	4.00	0.098	0.000
5.0	0.572	0.022	8.00	0.098	0.000
6.0	0.567	0.017			
7.0	0.561	0.011			
8.0	0.556	0.006			
9.0	0.553	0.003			
10.0	0.550	0.000			
11.0	0.550	0.000			
14.0	0.550	0.000			

$A_{\text{expected}} = 0.928 \times 0.8 = 0.742$; $A_{\text{expected}} = 0.928 \times 0.4 = 0.371$

obtain information about the kinetics of the dissociation reaction of the higher niobium complex.

The data in Table XVI, were treated by assuming that the dissociation reaction was first order. For such a situation the rate law $\frac{-dc}{dt} = kc$, can be integrated to give $\ln \frac{C_0}{C} = kt = \ln \frac{a}{a-x} = \ln \frac{A_0 - A_\infty}{A - A_\infty}$, where all terms have their usual definition. In particular A_0 is the absorbance at time zero, or in this case the absorbance immediately after dilution. The term A_∞ is the absorbance after an infinite reaction time, or absorbance when the reaction has gone to completion. Plots of $\log (A - A_\infty)$ versus time should be linear if the reaction under investigation is first order. The experimental data were plotted as indicated above, and the linear graphs, Figure 17, indicate that the decomposition of the thiocyanate complex of niobium, which absorbs at 390 mu, is first order with rate constants of 0.380 and 1.28 min.^{-1} . The half-lives, $t_{\frac{1}{2}}$, of the reactions are 1.80 and 1.30 minutes, respectively. The different $t_{\frac{1}{2}}$ values obtained upon dilution of a given niobium solution indicate that the extent of dissociation depends upon the extent of dilution, which would be in agreement with the previous evidence for an equilibria between two niobium complexes. The dissociation of the complex absorbing at 390 mu can be interpreted to be due to reduction of the concentration of free water in the solution, as well as a

reduction of the concentrations of the other reagents.

The experiment was repeated several times with niobium solutions obtained under different extraction conditions, and these results differed considerably from the original results. First order rate constants of 0.352, 0.589, 0.582, and 1.01 min^{-1} were obtained. The half-life varied from 0.541 min to 1.84 min. In all the experiments the scatter in the data was small. Furthermore, no satisfactory conclusions could be drawn concerning the influence of different extraction conditions upon the dissociation of the complex when diluted. More intensive investigations on this aspect of the problem should be worthwhile in elucidating the nature of arsonium complex ion-pairs in nonaqueous media.

In order to compare the behavior of the arsonium ion-pair of niobium with another metal, a cobalt extract in chloroform was prepared, Section 29-Experimental, and then was treated as indicated. Table XVII shows that cobalt extracts can be diluted, and the absorbance of the diluted extract agrees quite well with the expected absorbance. Furthermore there is only a slight change in the absorbance of a cobalt extract upon drying. Hence the ideal or model, cobalt, when compared with niobium indicates that the behavior of niobium upon dilution and drying is unexpected and that the niobium system must be more complicated than the cobalt

TABLE XVII

RESULTS OF DILUTING AND DRYING COBALT THIOCYANATE
EXTRACTS

A 625 μ u	A 320 μ u	A 317 μ u	Explanation
0.656	—	—	Original Co Solution
0.530	—	—	Diluted Extract; (4 ml to 5) expected absorbance = 0.526
0.133	—	—	Diluted Extract (1 ml to 5) expected absorbance = 0.132
0.134	0.852	0.865	Control after 78 hours
0.139	0.881	0.900	Dried extract (1 to 5 dilution)

system. The evidence presented can be interpreted only as an equilibria between two niobium complexes, one of which has the chemical formula $(\text{As})_4^+ \left[\text{NbO}_2(\text{NCS})_2(\text{H}_2\text{O})_1 \right]^-$.

Role of Water in Chloroform Solutions of the
TPA Salt of Niobium

Chloroform solutions of the TPA salt of niobium were prepared by distribution of the complex salt between an aqueous and nonaqueous phase, and consequently small quantities of water were extracted into the nonaqueous phase in addition to the niobium salt, hydrochloric acid, thiocyanic acid, TPASCN, and perhaps TPACl. The water which was extracted into the nonaqueous medium may be present as water of hydration in the various ion-pairs, and/or may be involved to some extent in the complex of niobium with thiocyanate, either in the inner sphere as a ligand, or in the outer sphere as an adduct.

In the experiments described in Section 27 and 28 - Experimental, chloroform solutions of the niobium salt were equilibrated with desiccants and aqueous solutions of known water activities, a_w . The chloroform and constant humidity solutions were enclosed in an air-tight system and were permitted to reach equilibrium by transfer of water through a commonly shared vapor phase. The equilibration process was facilitated by use of

III

EQUILIBRATOR CAP
(full scale)

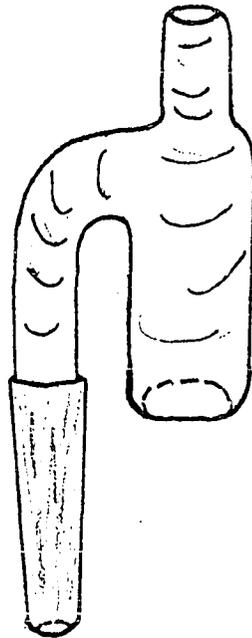


FIGURE 18

equilibrator caps,⁸⁷ Figure 18. The cap is a 3-4 ml closed bottom, open-top cylinder with a side arm attached to a 10-30 inner taper joint. After the appropriate a_w solution is placed in the container, the top is stoppered with a rubber serum stopper, and the filled cap is attached to a volumetric flask or spectrophotometer cell.

The results of a preliminary experiment in which a niobium extract was dried and subsequently equilibrated with an a_w solution indicated that water was important in stabilizing the niobium complex which absorbed at 390 mu. The removal of water from the system caused the absorbance at 390 mu to decrease by 17% from the original value, whereas the addition of water to the dried extract caused the absorbance to increase to slightly more than the original value. The half-life of the drying process was approximately nine hours. A control sample held for the same period as the dried sample showed negligible change in absorbance. After 90 hours a small amount of decomposition occurs in the solution. For this reason equilibrations were limited to approximately 8 half-lives, about 72 hours. The fact that the complex of niobium could be reformed by equilibrating with water showed that the reaction involving the removal and addition of water to the niobium complex was reversible. Furthermore, spectra

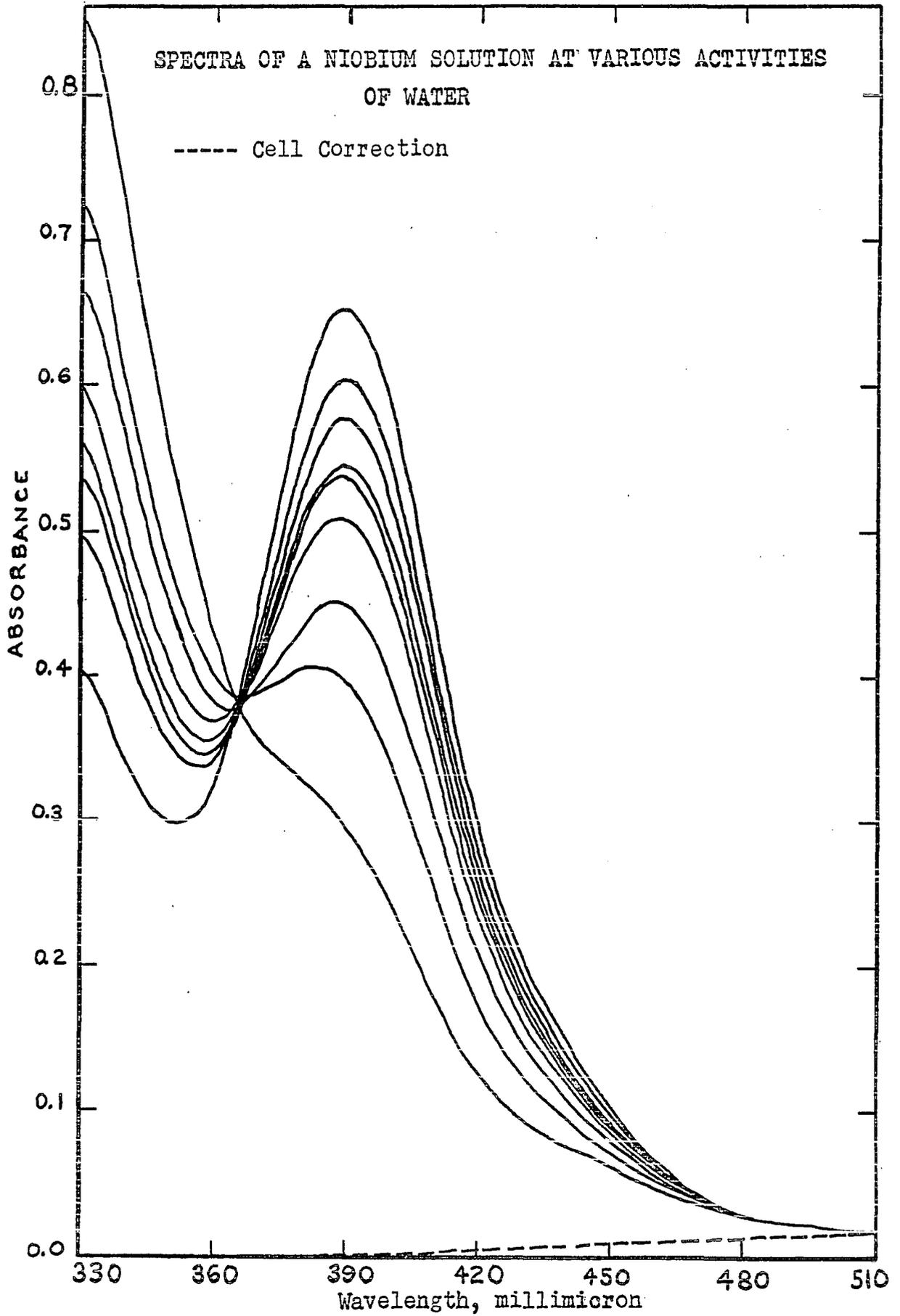


FIGURE 19

taken at different stages of the drying period showed a decrease in absorbance at 390 μ , an increase in the region 360-330 μ , and an isosbestic point at 364 μ . Hence, it is possible to conclude from the spectral information that two niobium complexes are involved in an equilibrium that is dependent on the activity of water in the medium.

In order to deduce the stoichiometry of water in the niobium complexes, niobium solutions in chloroform were prepared at four different formal concentrations of niobium, f_{Nb} , and the absorbance of each solution was obtained as a function of water activity. The spectra of one of the niobium solutions, shown in Figure 19, contains an isosbestic point at 364 μ . The data for the experiment are shown in Table XVIII.

In order to establish a relationship between the two niobium complexes and water, an equilibrium is formulated:



where an anhydrous niobium species, NbX, reacts with water to form a hydrated complex, $\text{NbX}(\text{H}_2\text{O})_n$, both of which absorb at 390 μ , and X represents the other ligands present in the complex species. The formation constant,

$$K' = \frac{[\text{NbX}(\text{H}_2\text{O})_n]}{[\text{NbX}] [\text{H}_2\text{O}]^n} = \frac{C_n}{C_o [\text{H}_2\text{O}]^n}$$

ABSORBANCE OF NIOBIUM SOLUTIONS AT VARIOUS WATER ACTIVITIES

a_w	A	A	A	A
0.000	0.271	0.174	0.222	0.248
0.000	0.273	0.187	0.241	0.260
0.000	-	-	-	0.286
0.000	-	-	-	0.286
0.156	0.375	0.252	0.402	0.426
0.250	0.419	0.288	0.452	0.534
0.400	0.480	0.340	0.547	0.644
0.447	-	0.398	0.584	-
0.498	0.510	-	0.601	-
0.548	-	0.440	0.614	-
0.599	-	0.463	0.623	0.764
0.658	0.549	0.470	0.681	-
0.706	-	0.479	0.659	0.814
0.776	-	0.501	0.706	0.830
0.832	0.569	0.522	0.691	-
0.885	-	0.542	0.732	0.870
0.934	0.618	0.570	0.748	0.909
0.953	-	0.530	-	-
1.00	0.640	0.560	0.754	0.926
	(1)	(2)	(3)	(4)

$f_{\text{Nb}} = 2.22 \times 10^{-5} \text{ M}$ for control solution (2)

used to establish ϵ values.

The concentrations of solutions (1),

(3), (4) are not accurately known but

permit an evaluation of n and K in

equation (4) page 117.

All absorbances were corrected for the reagent blank.

ABSORBANCE OF NIOBIUM SOLUTIONS VERSUS ACTIVITY OF WATER

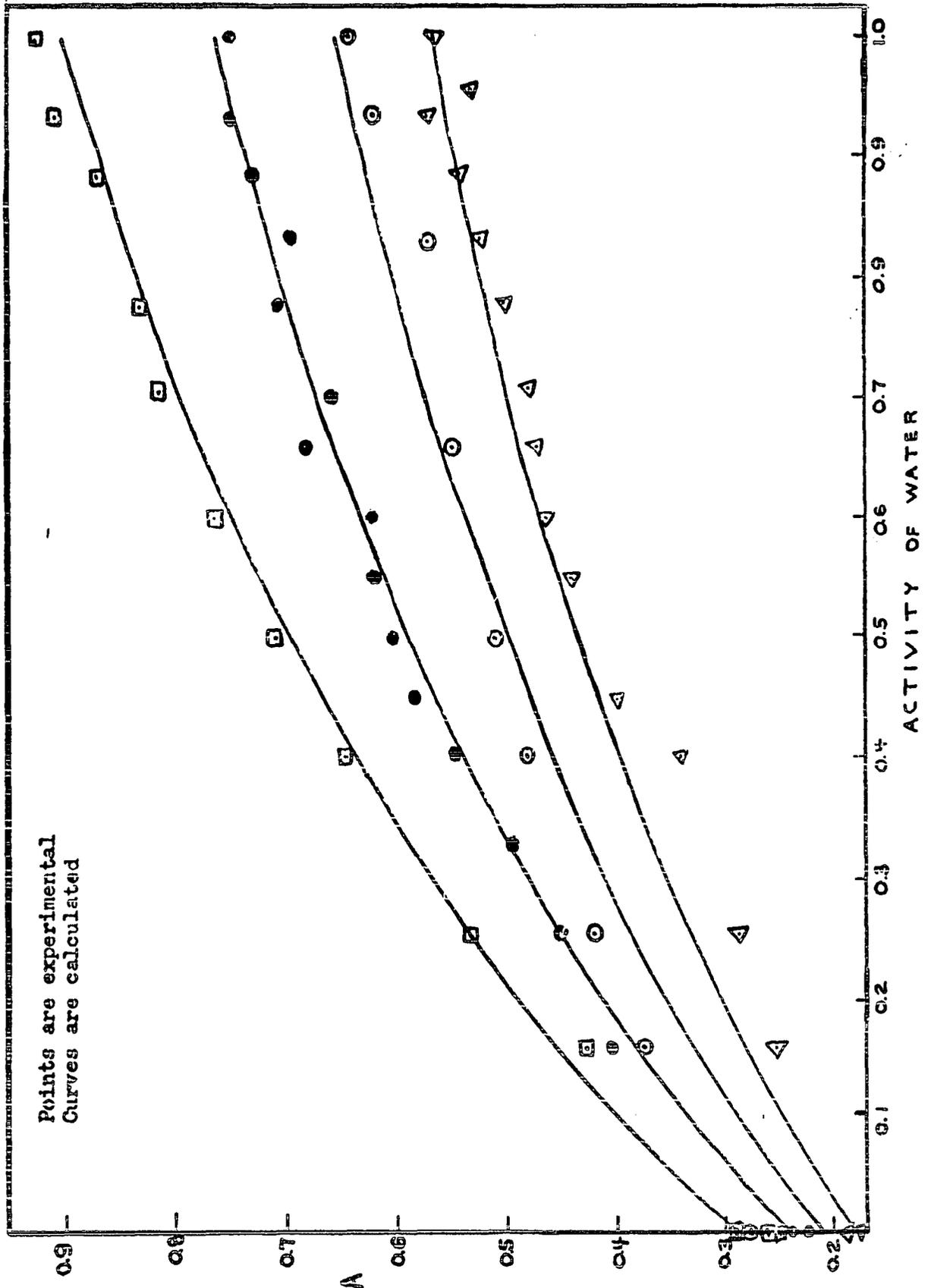


FIGURE 29

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All of the error was forced into A_c , and the calculated root mean square deviation in A_c , RMSD, was subsequently used as a criterion for the choice of n as well as the best value of K . The methods used to obtain the best values of K , ϵ_0 , and ϵ_n are described elsewhere.⁸⁸

When the exponent n was assigned a value of one, the best fitted values obtained for K , ϵ_0 , and ϵ_1 , were 14.1 M^{-1} , $8200 \text{ M}^{-1} \text{ cm}^{-1}$, and $42800 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, for the minimum RMSD, 0.024. A choice of two for the exponent n resulted in K , ϵ_0 , and ϵ_1 , values of $1.4 \times 10^3 \text{ M}^{-2}$, $8650 \text{ M}^{-1} \text{ cm}^{-1}$, and $27000 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, for a minimum RMSD of 0.031. The above formation constants, K , were converted from activity to molar units using a Henry's law constant for water in chloroform which was based on an assumed monomer-trimer equilibrium for the solute, water.⁸⁹

The experimental $A = f(a_w)$ data were further compared with the theoretical curves corresponding to n values of 1 and 2 by superimposing the calculated curve on a plot of the experimental data. Figure 20, which is a plot for $n = 1$, indicated a reasonably good fit for Equation 4. A similar plot for $n = 2$ showed considerable deviation in the a_w range below 0.400. More data points in the a_w region below 0.400 would be desirable as this region is important in establishing the stoichiometry of water in the niobium complexes. However, using the RMSD as a criterion for choosing the most probable chemical species, it was concluded that in the niobium-water system,

the two most probable complexes are an anhydrous niobium complex, $\text{TPA}^+ \left[\text{NbO}_2(\text{SCN})_2 \right]^-$ and a monomer monohydrate, $\text{TPA}^+ \left[\text{NbO}_2(\text{SCN})_2(\text{H}_2\text{O}) \right]^-$. Qualitative analyses, which were made on solid samples of the niobium salt, indicated the absence of chloride ion in the salt. Hence, a stoichiometry of two was assigned to the oxygen group in the complex anion in order to make the ion-pair electrochemically neutral. The infrared spectra, previously discussed, have indicated the presence of at least one oxygen group in the salt. Moreover, several transition metal salts have been reported in which the stoichiometry of oxygen is two in the complex anion (90,91).

Several experiments might be proposed for extending the present study of niobium thiocyanate complexes in nonaqueous solutions. As previously indicated, the formal concentration of niobium was calculated from the absorbance of control aliquots and the molar absorptivity of niobium in chloroform. As there is the possibility of systematic errors in the formal concentration, additional computations would be desirable in which the parameter ϵ_0 is expressed as the quotient of the lower limiting absorbance and the formal concentration of niobium. This would permit the formal concentration to be used as a parameter in addition to K and ϵ_1 , and the RMSD could be calculated with respect to each formal concentration of niobium. An alternate experiment would be to determine the formal concentration of niobium by exhaustive extraction of standard aqueous solutions.

It would also be interesting to study the effect of acetone, ether, and other bases on the niobium thiocyanate complexes. Such studies would be of value in comparing the bases in terms of their relative strengths and would be of help in further elucidating the nonaqueous chemistry of the niobium thiocyanate complexes.

Summary

The analytical procedure which has been developed for niobium fulfills the basic requirements for a good analytical method; its major advantages, in addition to being rapid and sensitive, are that niobium can be determined in large amounts of molybdenum, tantalum, iron, and several other elements, and without modification niobium can be determined in the presence of a five-fold excess of tungsten and titanium. The use of an alternate reducing agent for tungsten and a backwashing step for titanium will permit ready modification of the method for analyzing traces of niobium in tungsten and titanium.

A variational scheme and infrared spectra were employed to determine that one tetraphenylarsonium ion, two isothiocyanato-ligands, and at least one oxo-ligand are associated with each atom of niobium in the extracted species.

Preliminary investigations using a new approach have revealed that water dissolved in the nonaqueous solutions containing the extracted niobium complex play an important role in stabilizing the niobium complex which absorbs at 390 μ . Visible spectra at various water activities reveal that two niobium complexes are in equilibrium with water.

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APPENDIX

THE EXTRACTION OF TITANIUM THIOCYANATE COMPLEXES

WITH TETRAPHENYLARSONIUM CHLORIDE

Introduction

The reaction of titanium(IV) in aqueous hydrochloric acid solution with potassium thiocyanate and TPACl gives rise to an aqueous insoluble salt with a bright orange color.

The thiocyanate complexes of titanium have been previously utilized for its separation and determination. Young and White [Anal. Chem., 31, 393 (1959)] have reported the extraction of Ti(IV) as a thiocyanate complex from sulfuric or hydrochloric acid solutions by means of a cyclohexane solution of tri-n-octylphosphine oxide, TOPO. There is no interference from other quadrivalent metal ions or from anions such as fluoride, phosphate, or oxalate. Beer's law is obeyed up to 1.7 $\mu\text{g Ti/ml}$, and at 432 $\text{m}\mu$, the molar absorptivity is $41,000 \text{ M}^{-1} \text{ cm}^{-1}$. Crouthamel, et al. [C. E. Crouthamel, B. E. Hjelte, and C. E. Johnson; Anal. Chem., 27, 508 (1955)] have investigated the titanium thiocyanate complexes in aqueous acetone media and have found that the development of the complex requires an exacting procedure as the thiocyanate complexes of titanium are relatively weak and unstable.

The molar absorptivity of the titanium complex is $78000 \text{ M}^{-1} \text{ cm}^{-1}$ at 417 μ , the wavelength of maximum absorbance. Also it was reported that the absorbance is markedly temperature sensitive, and varies with temperature in a reversible manner. No recommendations were made concerning the analytical usefulness of the titanium thiocyanate complex in aqueous acetone.

Delafosse [D. Delafosse, Compt. rend., 236, 2313 (1953), 240, 1991 (1955)] has studied the extraction of the complex $\text{Ti}(\text{SCN})_4$ with methyl isobutyl ketone and isoamyl alcohol. The molar absorptivity is $7000 \text{ M}^{-1} \text{ cm}^{-1}$ at 278 μ , in the alcohol. A monothiocyanate complex of titanium has been verified by Tribalat [S. Tribalat, et. al. J. Electroanal. Chem., 1, 443 (1959)] in a polarographic study of the Ti(IV)/Ti(III) couple. The thiocyanate complexes of titanium are reported to be more electroactive (more easily reduced at the Hg drop) than the simple titanium ions [Anal. Chim. Acta, 19, 74 (1958)].

Summary of Experimental Investigations

A. Chloroform System

Preliminary investigations revealed that a solution of $2 \times 10^{-6} \text{ M}$ Ti(IV) in 6 M HCl and 0.75 M KSCN would produce an orange precipitate upon addition of TPACl to the solution. The precipitate was qualitatively analyzed and was found to contain Ti,

SCN, and TPA ions. The precipitate was virtually insoluble in chloroform, and upon vigorous agitation of the solid and chloroform phases the precipitate disappeared due to decomposition and preferential extraction of TPASCN into the chloroform.

More thorough investigations to find an optimum set of conditions for the extraction of the arsonium salt of titanium into chloroform were carried out on a test tube scale. The reagent concentrations (HCl, KSCN, TPACl) were varied over a wide range, one at a time. The HCl concentration was varied from 0.2 to 6 M, KSCN from 0.4 to 5 M, and TPACl up to 0.006 M. Further experiments were conducted in which chloride ion was excluded from the system. A titanium solution in sulfuric acid was prepared as well as a solution of TPAHSO₄. It was eventually concluded that the complex of titanium could not be changed or modified so that the TPA salt would be soluble in chloroform.

Other solvents for extracting titanium were investigated by qualitatively determining the solubility of the titanium salt in the solvent. The solubility of TPACl, TPASCN, and the arsonium thiocyanate salts of titanium and niobium were determined by placing $\frac{1}{2}$ to 1 mg of the salt in a small test tube containing 1 to 2 ml of solvent. The mixture was agitated by shaking vigorously at random intervals. Some of the mixtures were allowed to equilibrate for 12 hours. The results are summarized in Table I.

TABLE I

Qualitative Solubility of TPA Salts in Various Solvents

Solvent	TPACl	TPASCN	Nb Salt	Ti Salt
H ₂ O	sol.	insol.	insol.	insol.
CCl ₄	insol.	insol.	insol.	insol.
CHCl ₃	sol.	sol.	sol.	insol.
C ₂ H ₄ Cl ₂	sol.	sol.	sol.	sol.
C ₂ H ₂ Cl ₄	sol.	sol.	sol.	sol.
C ₃ H ₅ Cl ₃	sol.	sol.	sol.	sol.
Ethyl Ether	insol.	insol.	insol.	insol.
Dioxane	insol.	insol.	-	insol.
Methanol	sol.	sol.	sl. sol.	sl. sol.
Ethanol	sol.	sol.	sl. sol.	sl. sol.
n-propyl alcohol	r.s.	sol.	sl. sol, $\frac{1}{2}$ hr.	-
iso-propyl alcohol	r.s.	sol.	insol.	-
n-butyl alcohol	sol.	sol.	insol.	-
sec-butyl alcohol	sol.	sol.	insol.	-
tert-butyl alcohol	sl. sol.	sl. sol.	insol.	-
iso amyl alcohol	sol.	sl. sol.	v.sl.sol. 12 hr	insol.
acetone	sol.	sol.	sol	sol.
Methyl isobutyl Ketone	sol.	sol.	insol.	insol.
Cyclohexanone	sol.	sol.	v. sol.	v. sol.
Acetophenone	sol.	sol.	sol.	sol.
n-butyl bromide	insol.	insol.	-	-
p-bromotoluene	insol.	insol.	-	-
Benzene	insol.	insol.	insol.	insol.
Hexane	insol.	insol.	-	-
Cyclohexane	insol.	insol.	-	-
Ethyl Acetate	-	-	-	insol.
Heptane	-	-	-	insol.

r.s. = readily soluble

B. Cyclohexanone System

Cyclohexanone was chosen as the second solvent for extracting titanium since the arsonium salt was very soluble in this solvent, and furthermore did not appear to decompose upon standing. The spectrum of the thiocyanate complex of titanium in cyclohexanone showed maximum absorbance at 430 m μ which is close to the value of 418 m μ reported for titanium in acetone. An unfortunate characteristic of cyclohexanone was that relatively large quantities of thiocyanic acid were extracted. High concentrations of thiocyanic acid, especially in cyclohexanone, decompose and polymerize to give rise to products which absorb in the visible and near ultraviolet regions. These products interfered with the absorbance of titanium in that the observed absorbance was not stable, but increased as a function of time. An investigation of reagent blanks, prepared by extracting an aqueous solution containing all components except titanium, revealed that it would be necessary to make absorbance measurements at a predetermined time after the extraction was completed if cyclohexanone was to be used as the extracting solvent. Back-washing the blank extracts with reducing agents and masking agents such as stannous chloride or ammonium bifluoride did not eliminate or reduce the interference from the reagents. An interesting observation was made concerning the back-washing of the blanks with

ammonium bifluoride. When the extracts were back-washed with an aqueous solution containing fluoride, the ketone phase would take on a dark pink coloration which was definitely not due to the formation of a ferric thiocyanate complex ion as no ferric ion was present. Further investigations revealed that the pink color could also be produced by mixing fluoride with dilute aqueous solutions of sulfuric acid and potassium thiocyanate; the pink colored species could then be extracted with cyclohexanone. It is possible that the pink complex was a thiocyanate polymer, possibly containing fluoride ions. The problem of interference from reagent blanks and decomposition of thiocyanic acid in cyclohexanone eliminated any further consideration of this solvent for the extraction of titanium.

C. Tetrachloroethane System

The third solvent to be investigated was 1,1,2,2-tetrachloroethane, TCE. Tetrachloroethane was chosen over 1,2-dichloro-ethane since its density, 1.6 g/ml, is greater than that of dichloro-ethane whose density is 1.26 g/ml, which results in a much better phase separation. The initial investigations of the TCE system were made upon reagent blanks. It was found that blanks which were stable for $\frac{1}{2}$ hour could be obtained from the extraction of an aqueous solution that was 0.75 M in HCl, 0.38 M in

KSCN, and 0.006 M in TPACl. However, it was necessary to use a 5% ethanol-TCE solution as the extracting solvent. The ethanol was added to stabilize the solvent. A preliminary Beer's law curve was obtained by extracting standard titanium solutions with TPACl and TCE. The Beer's law curve had a positive deviation and a limiting molar absorptivity of $17,800 \text{ M}^{-1} \text{ cm}^{-1}$.

The effect of the reagents upon the extraction efficiency of titanium were investigated by a procedure similar to that described previously for niobium. The HCl, KSCN, and TPACl concentrations were investigated over the ranges 0.25 to 7.5 M, 0.2 to 0.75 M, and 0.002 to 0.02 M, respectively. The extraction of titanium was most efficient for HCl concentrations of 3.5 to 4.5 M, KSCN concentrations of 0.5 to 0.75 M, and 0.35 millimoles of TPACl (of 5 ml of 0.07 M TPACl). The above results were obtained from the extraction of 6.6×10^{-8} moles of titanium with 5 ml of TCE. The extraction of titanium with TCE appeared to be good compared to the chloroform and cyclohexanone systems, however the distribution ratio was unfavorable and several extractions (4-5) were required to remove all the titanium from the aqueous phase.

One set of investigations revealed that the titanium precipitate could be readily coagulated by shaking the aqueous solution vigorously prior to adding TCE, and subsequent drop-wise addition of TCE was quite effective in dissolving and extracting

the precipitate as it passed through the aqueous phase. However, if the TCE and aqueous phases were then mixed by vigorous agitation some of the titanium complex dissociated and was back extracted into the aqueous phase. A fading of the yellow color, characteristic of titanium in TCE, was clearly evident upon agitation. The possible extraction of titanium by drop wise addition of TCE was further investigated and a Beer's law plot was constructed. However, the precision was poor, indicating poor reproducibility for the extraction of titanium. This type of extraction was not considered to be worthy of further investigation.

A study of the number of successive extractions required for the complete extraction of titanium shed some light upon the problem of extracting titanium with TCE. It was learned that the extraction was highly dependent upon the quantity of TPACl used for each extraction. Previous investigations of the cobalt, gold, and tungsten systems had revealed that a 50 to 100 fold excess of TPACl was always more than adequate for the extraction of these elements; however, titanium was found to require a 500 to 1000 fold excess of TPACl. An interesting observation made on the extraction of titanium is that when the concentration of TPA is increased considerably there is a shift in the wavelength of maximum absorbance from the 395-406 μ region to 428-430 μ . This shift is presumably due to the formation of a

different titanium complex. When more than 0.35 millimoles of TPACl are used in the extraction procedure the maximum wavelength remains constant. In the procedure described below for the extraction of titanium, the TPACl was dissolved in the 5% ethanol-TCE solution in order to avoid addition of TPACl to the aqueous phase prior to each extraction, which would dilute the aqueous phase and bring about changes in the reagent concentrations.

Procedure for the Extraction of Titanium Thiocyanate Complexes

With TCE

A one ml aliquot of standard 10^{-5} M titanium solution in 12 M hydrochloric acid was added to a 10 ml ground glass stoppered graduate cylinder. After adding 1 ml of 6 M HCl and 1 ml water, the graduate and its contents were chilled in an ice bath, after which one ml of 1.5 M KSCN were added. The aqueous solution was extracted with two ml of 0.1 M TPACl in 5% ethanol-TCE solution by shaking vigorously for $1\frac{1}{2}$ minutes. The organic phase was then removed with a pipette and filtered into a 5 ml volumetric flask. The aqueous phase was extracted twice more with 2 and $1\frac{1}{2}$ ml portions of the organic solvent. The combined extracts were mixed and the absorbance was measured at 428 m μ versus TCE with a D. U. spectrophotometer. The titanium complex obeyed Beer's law, and the molar absorptivity was $64,100 \text{ M}^{-1} \text{ cm}^{-1}$.

Preliminary investigations of diverse elements revealed that iron(III), niobium(V), vanadium(V), tungsten(V), and molybdenum(V) were readily extracted by TCE under the conditions employed for the extraction of titanium. The use of stannous chloride as a reductant for iron and molybdenum was prohibited since it was experimentally established that preferential extraction of stannous chloride complexes greatly reduced the extraction of titanium, and thereby interfered with the extraction of titanium.

In view of the poor extractibility of titanium with TPACl and TCE, the numerous interferences, and the high reagent blanks, it is concluded that the extraction of titanium as an ion-pair with TPA is not an analytically feasible procedure. However, it should be worthwhile to investigate other organic cations such as triphenylsulfonium, methyl triphenylarsonium ion, and related phosphonium ions as extracting ions for the thiocyanate complexes of titanium. Another possibility would be to study mixed solvents such as acetone-TCE solutions. Alternate cations or modified solvents may increase the distribution ratio of titanium to a more favorable value.

Titanium thiocyanate complexes in aqueous acetone are quite temperature sensitive, and the change in wavelength of maximum absorbance with the concentration of the extracting ion, TPA, indicates that the composition of the thiocyanate complexes

may be a function of water activity in a manner similar to the niobium thiocyanate complexes and an investigation of this effect could lead to important and interesting findings.