MURPHY, Jack Warren, 1939–
THE USE OF TETRAPHENYLARSONIUM
CHLORIDE IN THE EXTRACTION OF A
TUNGSTEN–THIOCYANATE COMPLEX.

The University of Oklahoma, Ph.D., 1964
Chemistry, analytical

University Microfilms, Inc., Ann Arbor, Michigan

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

THE USE OF TETRAPHENYLARSONIUM CHLORIDE IN THE EXTRACTION OF A TUNGSTEN-THIOCYANATE COMPLEX

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

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Norman, Oklahoma

1964

THE USE OF TETRAPHENYLARSONIUM CHLORIDE IN THE EXTRACTION OF A TUNGSTEN-THIOCYANATE COMPLEX

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ACKNOWLEDGEMENTS

My sincerest thanks and appreciation are extended to Dr. Harold E. Affsprung for his guidance, consolation, instruction, encouragement, inspiration, and friendship during this research.

I also wish to acknowledge with much appreciation and gratitude the help and encouragement given me by my mother in preparing the manuscript.

The research was supported in part by the National Science Foundation.

DEDICATED TO

JESUS CHRIST,

MY

SAVIOR AND GOD

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THE USE OF TETRAPHENYLARSONIUM CHLORIDE IN THE EXTRACTION OF A TUNGSTEN-THIOCYANATE COMPLEX

CHAPTER I

INTRODUCTION

Arylonium salts have been the subject of extensive investigation because of their wide applicability as analytical reagents. These salts have been found useful in volumetric, gravimetric, electrochemical, and spectrophotometric methods and are of interest especially as cations of ion-pairs which may be extracted from water into non-aqueous solvents. Bock and Beilstein (1) have studied the distribution of ion-pairs of tetraphenylarsonium ion with a number of inorganic anions between water and chloroform, and analytical procedures involving the extraction of complex anions of tantalum (3), gold (2), and cobalt (4) into chloroform as tetraphenylarsonium ion pairs have been described. Arylonium salts are of interest particularly in the analysis of complex metal ions because of the selectivity possible using a solvent-solvent extraction of an ion-pair. The extractability of a metal anionic species as an arylonium pair is a function of the nature of the cation, the nature of the extracting solvent, the anion forming the complex with the metal, the acid strength of the aqueous medium and the ionic strength of the aqueous medium. By judicious variation of these parameters, it is possible to achieve separation of one metal or group of metals from another group prior to a final determination.

Another desirable property of the extraction analyses using arylonium salts is the simplicity and rapidity of the experimental procedures involved. In many cases, metals which are difficult to separate by precipitation or extraction techniques alone, or which are separated only by exercising extreme care to control the conditions, are easily and completely separated by a single precipitation and subsequent extraction of the onium ion salt. In the analysis of alloys, such a technique can eliminate a major portion of the time and work normally required for an analysis. If a separation is not complete in one extraction, the use of an organic extracting solvent which is heavier than water greatly simplifies the process of repeated extractions. Fortunately, in this light, chloroform and carbon tetrachloride are good solvents for many arylonium ion pairs.

Analysis of the separated organic layer can be achieved by many methods, but spectrophotometry is perhaps the simplest technique and for this reason is used whenever possible. Metals forming complexes which absorb in the visible or near ultraviolet are most useful, for arylonium ions absorb quite strongly at wavelengths less than 290 mμ, and if an isolated absorption maximum can be found, analysis is easy and rapid.

Illustrative of the rapidity and simplicity of the methods is the tungsten determination discussed here. The analysis of W in an alloy containing W and any other metals is accomplished in less than an hour (including time for dissolution of sample). Since a number of transition metals offer formidable analytical problems, as evidenced by the complicated methods now in use for them, the investigation of the uses of arylonium salts as reagents for the transition metals can be very fruitful in leading to the establishment of faster and more precise methods for their determination.

There exist at present very few analytical methods for tungsten which are sufficiently selective to be employed in the general analysis of tungsten-bearing alloys. In general, the gravimetric methods are plagued by lengthy and tedious separation steps, and volumetric and colorimetric methods are, or have been, hampered by myriad interferences and by a lack of reproducibility. Some of the methods now used are quite acceptable for certain kinds of samples, and simple wet analysis of many different alloys can be achieved. Improvements in the gravimetric procedures have greatly facilitated the complete separation of tungsten from molybdenum and vanadium. Dams and Hoste (5) reported that coprecipitation from molybdenum and vanadium was greatly reduced if tungstic oxide was precipitated homogeneously by the thermal decomposition of peroxytungstate in nitric acid medium. Pesis (6) reported that pyrazoline derivatives, such as diantipyrinyl-o-hydroxyphenylmethane, could be used satisfactorily in determining tungsten gravimetrically in ferrotungsten alloys. Two recent volumetric methods for tungsten have the usual advantage of rapidity over the gravimetric methods, but the interferences are severe. Witnit and Magee (7) reduced tungsten (VI) to tungsten (V) in HCl with bismuth amalgam and titrated with ceric sulfate. They obtained excellent results and utilized the method for the analysis of steels; however, Mo seriously interfered with the determination. Luke (8) devised an indirect volumetric method for tungsten.

The most widely used wet methods for tungsten are the spectrophotometric methods where tungsten forms colored complexes with various chelating agents and inorganic anions. One of the better and more recent reagents is toluene - 3,4 - dithiol, developed by Hobart and Hurley (9) for use in the analysis of W and Nb in niobium alloys. This is a fine method, for very few, if any, interferences have been noted. Halmekoski (10) has described the use of catechol derivatives in the determination of W and Mo in a mixture and has achieved good results, but Fe(III), Ti(IV), UO_2^+, and VO_3^- interfere. Bhuchar (11) has reported the use of thioglycollic acid in the spectrophotometric microdetermination of tungsten and other metals. Mc Eveney (12) recommends quinol as a reagent for analyzing W, Nb, and Ti separately or simultaneously.

An extensive review of the state of analytical chemistry of tungsten has been published by Busev, Tiptsova, and Khlistova (13).

The most commonly used and extensively investigated spectrophotometric procedure for tungsten is the thiocyanate method. This method consists of reducing the tungsten from the VI state in concentrated HCl to a lower oxidation state, apparently W (V) as recently shown by Gottschalk (14). The reduction is achieved with any one of a number of reagents such as $SnCl_2$ in concentrated HCl, various amalgams, $TiCl_3$, or metallic reductors. Some of these reducing agents actually produce W (III) which is apparently oxidized to W (V) by thiocyanate ion later in the procedure. The thiocyanate forms a bright yellow complex with the reduced tungsten which is the basis of the method. Spectrophotmetric analysis may be carried out either on the yellow aqueous solution, a mixture of acetone with the aqueous solution, or on an isoamyl alcohol or ether extract.

Difficulty has been encountered with the thiocyanate method since the complex is unstable, and time measurements are often necessarily included in the analyses. It has been reported that Nb, V, Ta, and Ti interfere with the thiocyanate determination of tungsten. Niobium (V) forms a yellow thiocyanate complex which may be masked with oxalic acid (15). Titanium and tantalum also form colored thiocyanates, but the molar absorptivities of these complexes at 400 mμ are much lower than that of the tungsten complex, and consequently these two elements offer little interference unless present in high concentration. Hobart and Hurley (9) further discuss some of the disadvantages of the thiocyanate methods. They conclude that, "Thiocyanate methods in general suffer from a lack of selectivity, from poor stability, and from unpredictable interelement effects." Anil and Rahamon (16) have recently reported the separation of tungsten (VI) from other metals using 100% tributylphosphate to extract the tungsten from concentrated HCl. The tungsten is then analyzed by the thiocyanate method.

Thus, while some of the methods mentioned above are rapid and simple, some are comparatively selective, and some are quite sensitive, none of the commonly applied methods combines all of these qualities in a generally applicable analytical procedure. A method which does combine all of these qualities is greatly needed and was the goal of the work reported upon here.

The extra selectivity given the thiocyanate method by the tetraphenylarsonium ion-pair precipitation and extraction is apparently adequate to remove all interferences except niobium, and the interferences of the complex of this ion can be completely masked by fluoride ion. The method has been applied to a number of tungsten-containing alloys containing widely varying amounts of W, and excellent results were achieved in every case. When little difficulty is met in dissolving the steel samples, analyses can be run from start to finish in 45 minutes to an hour.

The aqueous tungsten-thiocyanate complex was first reported by Gentry and Sherrington (17) to be tervalent with the composition WOSCN. In 1954, Crouthamel and Johnson (18) hypothesized that the complex contained pentavalent tungsten, but they offered little supporting evidence. In 1962, Gottschalk (14), using the variational method of Asmus (19), concluded that the tungsten was pentavalent and had the composition $[W(OH)_2(SCN)_4]^-$ in water and $[W(OH\text{-}OR)_2(SCN)_4]^-$ in organic solvents such as alcohols, ketones, and esters. The composition and valency proposed by Gottschalk are reasonable considering that many tungsten (V) thiocynate complexes have been reported. Funk and Bohland (20) have recently prepared compounds of various organic amines with the following tungsten complexes: $[WO(NCS)_5]^=$, $[WO(NCS)_4]^-$, $[WO_2(NCS)_3]^=$, $[W(OH)_3(NCS)_3]^-$, $[WO(OH)_2(NCS)_2]^-$.

With complexes containing the $(SCN)^-$ radical, the question arises as to whether the linkage to the metal is as a thiocyanate,

$(\text{-SCN})^-$, or an isothiocyanate, $(\text{-NCS})^-$. Mitchell and Williams (21), in a study of the infrared spectra of a number of inorganic thiocyanates and isothiocyanates, concluded that the isothiocyanates have a C-N stretching frequency between 2105 cm^{-1} and 2060 cm^{-1}, while the corresponding thiocyanate frequency is at 2145 cm^{-1}. Thus an infrared spectrum of the complex should easily distinguish between the two structures. Funk and Bohland reported all of their compounds as isothiocyanates on this basis.

A conclusive determination of the composition of the extracted species in the analytical method presented here is difficult because the pure compound has not been isolated. Variational schemes may allow partial analysis, but determination of the complete composition depends on total elemental analysis. This is because of the uncertainty in the oxygen species attached to the metal. As seen in the compounds reported by Funk and Bohland listed above, both O- and OH- groups are commonly attached to the metal. The presence of one of these groups is usually assumed in order to give a charge and mass balance to the complex. The compositions of the compounds reported by Funk and Bohland were determined solely by total elemental analysis of W, C, H, N, and S. No consideration was given to the spatial structure of the complexes. The determination of the oxidation number of tungsten compounds by silver reduction was reported in 1915 by Rosenheim and Dehn (22). They treated aqueous solutions of $K_3W_2Cl_9$ and $K_4W(CN)_8$ with ammoniacal silver nitrate and weighed the resulting silver metal. Funk and Bohland (20) recommend either this method or a cerate titration to determine the tungsten oxidation number.

The use of silver (I) as an oxidizing agent is preferred to the use of other oxidants, for stronger oxidants may attack thiocyanate, and oxidants of comparable oxidizing power of silver cannot be used in titrations because they are too weak. Silver can be used despite its low reduction potential because a large excess can be added and the stoichiometry of the redox reaction determined gravimetrically.

CHAPTER II

PURPOSES

The investigation reported upon had three principal goals. The primary aim was to perfect an analytical procedure specific for tungsten utilizing the chloroform extraction of the tungsten-thiocyanate complex with tetraphenylarsonium as the precipitating ion.

Second, it was desired to elucidate the stoichiometry of the extraction process and to determine the composition of the extracted species.

Finally, the possibility of applying a similar technique to the analysis of other transition metals, such as niobium and tantalum, was to be studied.

CHAPTER III

EXPERIMENTAL PROCEDURE

1. Apparatus and Materials

Beckman DU and DK-1 spectrophotometers were used for absorption measurements.

Potassium thiocyanate solutions were prepared by dissolving 30 gms. of Baker's Analyzed KSCN in 200 ml. of distilled water and filtering the resulting solution into a brown storage bottle.

Stannous chloride solutions were prepared by dissolving 30 gms. $SnCl_2$ in 225 ml. concentrated HCl.

Tetraphenylarsonium chloride solutions, 0.025 M, were prepared by dissolving the hydrochloride from K and K laboratories in water and filtering into a storage bottle.

2. Spectrum of Tetraphenylarsonium Chloride (TPAC) in Chloroform

0.06438 gms. (1.537×10^{-4} moles) of TPAC were dissolved into 500 ml. of distilled water. A 25 ml. aliquot of this solution was placed in a separatory funnel and extracted three times until a total of 50 ml. $CHCl_3$ resulted. The $CHCl_3$ layers were drawn off and filtered through a small filter paper into a 50 ml. volumetric flask. The absorbance of the solution was measured on the DU at 0.5 to 2 mμ intervals from 250 mμ to 288 mμ at a slit width of 0.1 mm. A plot was made of absorbance vs. wavelength, as shown in Figure 12, page 83.

The absorptivity of the TPAC in $CHCl_3$ was measured at one of the maxima in the spectrum, 265 mμ. This was done by following the above extraction procedure for 5, 10, 15, and 25 ml. aliquots of the 3.074×10^{-4}M TPAC solution. The absorbance of the $CHCl_3$ extracts was then measured at 265 mμ on the DU. A plot was then constructed of absorbance vs. concentration of TPAC in the $CHCl_3$, and the molar absorptivity was calculated assuming complete extraction. (Figure 13, page 84)

3. Extraction of Tungsten into Chloroform

A suitable amount of W(VI) (<2 μmoles) in concentrated HCl was heated nearly to boiling with 2 - 3 ml. of 10% $SnCl_2$ in concentrated HCl to reduce the tungsten. The solution was then chilled in an ice bath to about 5 - 10°C. The chilled solution was quantitatively transferred to a 60 ml. separatory funnel using 5 ml. of chilled 6 - 12 M HCl. 30 drops of 0.025 M TPAC were then added to the separatory funnel forming a white precipitate of tetraphenylarsonium chlorostannate (II). Next, three ml. of 1.5 M KSCN were added, and the solution became cloudy and yellow in color. After about one minute, approximately 10 ml. of $CHCl_3$ were added, and the mixture was shaken vigorously for about 30 seconds. After the layers had separated, the $CHCl_3$ (bottom) layer was filtered into a 25 ml. volumetric flask (to remove suspended H_2O). To the remaining aqueous layer 10 drops of the TPAC solution were added; the mixture was swirled and extracted with another 10 ml. of $CHCl_3$. The mixture was again shaken 30 seconds and the $CHCl_3$ layer filtered into the same volumetric flask as before. The addition of TPAC and extraction with $CHCl_3$ were repeated until the volumetric flask was filled to the mark.

4. Spectrum of Tungsten Extract in $CHCl_3$

Approximately 0.8 μmoles of W(VI) in concentrated HCl were treated as outlined in Section 3. The absorbance of the extract was measured at 1 to 5 mμ intervals from 320 to 385 mμ using the DU and keeping the slit width constant at 0.1 mm. A graph of absorptivity vs. wavelength was constructed and is shown in Figure 1a, page 37.

A greater spectral range of the extract was obtained on the automatically recording DK-1 spectrophotometer. This portion of the spectrum is shown in Figure 1b, page 38. To determine the symmetry with respect to energy of the absorbance band found at 400 mμ, a number of points on the chart were chosen and the reciprocal of the wavelength was computed and plotted vs. the absorptivity. Figure 2 (page 39) shows the resulting plot of absorptivity vs. wavenumber. Further into the ultraviolet region, the excess TPAC and thiocyanate absorb and mask the spectrum of the compound.

5. Beer's Law Calibration for the Absorbance of Tungsten at 406 mμ

10^{-4}M W(VI) in concentrated HCl was prepared in the same manner as described in Section 6. Aliquots from 1 to 10 ml. of this solution were treated with $SnCl_2$, TPAC, and KSCN and extracted with chloroform as outlined in Section 3 above. The absorbances of the solutions were measured at 406 mμ on the DU with a 0.1 mm slit width. A plot was made of absorbance vs. the concentration of tungsten in the chloroform assuming complete extraction. The absorptivity was computed as the least squares slope of this linear curve. The graph is shown in Figure 3, page 41. The data are tabulated in Table 1, page 42.

6. Preparation of Standard Tungsten Solutions

1.1596 gm. (0.00500 moles) ignited WO_3 (99.5% pure) was dissolved in 10 ml. hot concentrated KOH, diluted to 500 ml. with distilled water, and stored in a polyethylene bottle. (A small amount of residue remained after treatment with KOH, so the basic solution was diluted slightly with distilled water and then filtered into a volumetric flask prior to dilution.) 5 ml. of the resulting solution were pipetted into a 500 ml. volumetric flask and diluted to the mark with concentrated HCl. The 10^{-4} M W(VI) in HCl was stored in a 500 ml. glass stoppered Erlenmeyer flask.

7. Interference of Other Metals with Determination of Tungsten

A. Preparation of Metal Solutions

(1) Vanadium. 0.182 gms. (1 mmole) of V_2O_5 (reagent grade) were dissolved in concentrated HCl and diluted to 100 ml. with HCl in a volumetric flask to give 2×10^{-2}M Vanadium (V) ion. 10 ml. of this were diluted to 100 ml. to give a solution 2×10^{-3}M in V.

(2) Molybdenum. 85% Molybdic oxide (MoO_3), 0.1690 gm., was dissolved easily in a few ml. of 0.1 M NaOH and diluted to 100 ml. with water to give a 10^{-2}M solution of Mo.

(3) Niobium. 0.1334 gm. of reagent grade Nb_2O_5 were mixed with solid KOH and heated in a crucible until the KOH had melted. The melt was allowed to resolidify, and then melt and crucible were plunged into a beaker containing 50 ml. of distilled water. The solution was

transferred to a 100 ml. volumetric flask to give a 10^{-2}M solution, and 5 ml. of the resulting solution were pipetted into a 500 ml. volumetric flask and diluted with concentrated HCl to give a solution approximately 10^{-3}M in niobium.

(4) Tantalum. 0.1805 gms. of reagent grade Ta_2O_5 were treated as outlined for Nb_2O_5 in preceding section to give approximately 10^{-4}M Ta_2O_5 in concentrated HCl.

(5) Others. $CoCl_2$, $CrCl_3$, $MnSO_4$, and $NiSO_4$ aqueous solutions were prepared by dissolving enough of the reagent grade salt in distilled water to give 250 ml. of solution containing 1.00 mg. metal/ml.

(6) Iron. $FeCl_3$ was dissolved in 1% HCl to give 7.5 mg. Fe/ml. solution.

B. Determination of Extent of Interference of Metal Ions with the Quantitative Tungsten Analysis

(1) General Procedure. A suitable quantity of one of the metallic solutions prepared as outlined above was pipetted into a beaker. 0.5 μmoles W (VI) in concentrated HCl and 2 ml. 10% $SnCl_2$ in concentrated HCl were added, and the solutions were carried through the reduction-extraction process previously described. The absorbance of the solution was measured at 406 mμ, and the apparent amount of tungsten present was calculated and compared to the actual amount taken. (See Table 5, page 60).

(2) Extraction of Various Metals under Conditions used for Tungsten.

(a) Vanadium. Five ml. of 2 x 10^{-3}M V (V) were treated in the manner described for tungsten with tungsten absent to determine the extent of independent color formation and extraction.

Extraction was attempted with both $CHCl_3$ and $CHCl_3$-C_2H_5OH mixture.

(b) Molybdenum. One ml. of 10^{-2}M Mo(VI) was treated with KSCN solution in the absence of tungsten and $SnCl_2$. Color formation was noted and extraction attempts were made using isoamyl alcohol and TPAC plus $CHCl_3$.

(c) Tantalum. Approximately 2 mg. of Ta(V) in HCl solution were treated in the manner described for tungsten with tungsten absent to determine the extent of independent color formation and extraction. A spectrum of the $CHCl_3$ extract was run on the DK-1.

(d) Niobium. (See Niobium Interference under "Analysis of tungsten bearing alloys") Approximately 0.4 umoles of Nb(V) were treated as in (1). Each $CHCl_3$ portion, after extraction, was then run into another 60 ml. separatory funnel and shaken with 10 ml. of a solution of $NH_4F \cdot HF$ and NaCl of varying concentrations. The fluoride concentration ranged from 0.6 to 6.0 M and the chloride concentration ranged from zero to saturated. NH_4Cl, HCl, $NH_4C_2H_3O_2$, and $(NH_4)_2\ SO_4$ were also used in place of NaCl.

Five ml. of approximately 2 x 10^{-4} molar Nb(V) in concentrated HCl was treated as directed for tungsten to determine the extent of independent color formation and extraction. A similar treatment was carried out in which no $SnCl_2$ was employed, and a spectrum of the $CHCl_3$ extract was run on the DK-1 (Figure 6, page 62).

8. Interference of Nitrates

Five μmoles of W(VI) in HCl were boiled with 2 ml. concentrated

HNO_3 until the brown fumes of nitric oxide were no longer evolved. The resulting solution was carried through the extraction procedure for tungsten. The absorbance of the $CHCl_3$ extract was measured as a function of time.

9. Variation of Extraction Efficiency with Acid Concentration in the Aqueous Layer

Five ml. of 10^{-4} M W(VI) (92 µg) in 12.1 M HCl were reduced by heating with 2 ml. of 10% $SnCl_2$ in 9.8 M HCl. The resulting solution was cooled to 10° C in an ice bath and rinsed into a 60 ml. extraction funnel with 5 ml. of cold HCl solution varying in HCl concentration from 0 to 12 M. 30 drops of 0.025 M TPAC were then added to the funnel, followed by 3 ml. of 1.5 M KSCN. The total aqueous volume was 16.5 ml. with final HCl concentration between 5.1 and 8.8 M. A 4 M HCl concentration in the extract was obtained by washing with 10 ml. distilled water rather than 5 ml.

Twenty-five ml. $CHCl_3$ were then pipetted into the funnel, the mixture shaken vigorously, and the layers allowed to settle. The $CHCl_3$ layer was filtered through a small filter paper into a ground glass stoppered flask, the absorbance measured at 406 mµ, and the percent extraction of tungsten calculated and plotted against acid molarity. (Figure 5, page 47.)

The molarities of HCl used in the wash were 0, 3.1, 6.1, 9.2, and 12.1 to give final acid concentrations of 5.1, 6.1, 7.0, 8.0, and 8.8 M respectively.

Five ml. of the same tungsten stock solution were analyzed as in section 4 to determine the absorbance assumed for 100% extraction.

The acid concentration present in the aqueous layer after extraction was determined by titrating a 1 ml. aliquot of the corresponding aqueous layer with 0.202 N NaOH.

The amount of HCl extracted into pure $CHCl_3$ from HCl in pure water was determined by shaking 25 ml. of $CHCl_3$ with 25 ml. of 9 M HCl and titrating 1 ml. of the acid solution both before and after extraction. (Table 3, page 49).

10. Effect of Chloride Concentration on Extraction Efficiency

(Table 4, page 51)

A. Final HCl Concentration 5 M

Five ml. of W(VI) in 12.1 M HCl were reduced with 2 ml. 10% $SnCl_2$ in 9.8 M HCl by heating and were then chilled in an ice bath. The reduced solution was quantitatively transferred to a separatory funnel with 5 ml. of NH_4Cl solution of varying molarity to control the final chloride ion concentration. Thirty drops 0.025 M TPAC, 3 ml. of 1.5 M KSCN, and 25 ml. $CHCl_3$ were then added and the mixture shaken vigorously. After separation of the layers, the $CHCl_3$ layer was filtered into a 25 ml. volumetric flask through a small filter paper. The absorbance was measured at 406 mμ and the percent extraction was calculated based on 100% extraction for the same amount of tungsten treated as in Section 4.

Molarities of NH_4Cl solution used as wash were 5.6 M (sat), 3.8 M, 1.9 M, and 0.9 M, giving final chloride concentrations of 6.8 M (sat), 6.3 M, 5.7 M and 5.3 M.

B. Final HCl Concentration 4 M

The process was carried out as in A, except that 10 ml. portions of NH_4Cl solution were used as washes giving total aqueous volumes of

21.5 ml. rather than 16.5 ml.

11. Analysis of Tungsten Bearing Alloys (Table 6, page 64)

A. Standard Sample #2

(1) Dissolution of Sample. 0.1126 grams of the steel were weighed into a 250 ml. beaker, treated with approximately 20 ml. of concentrated HCl, and heated on a hot plate. Concentrated HNO_3 was added dropwise (about 2 ml.) to oxidize carbon as formed. When all the original alloy was dissolved and all the carbon removed, the solution was boiled 5-10 minutes longer to remove nitrogen oxides. The sample was then transferred to a 100 nl. volumetric flask and diluted to the mark with concentrated HCl.

(2) Preparation of Sample for Analysis. Approximately 10 ml. of the diluted solution was shaken in a separatory funnel with chloroform to remove any nitrogen oxides still present. The extraction was repeated with fresh chloroform until the chloroform layer was colorless after the shaking.

Two ml. of the $CHCl_3$ washed sample were pipetted into a 50 ml. beaker and treated as for tungsten in Section 2.

The absorbance of the $CHCl_3$ extract was measured at 406 mμ on the DU, and the percent tungsten present was calculated.

B. Standard Sample #4

(1) Dissolution of Sample.

(a) 0.1033 gms. of the steel were dissolved as described for Standard Sample #2. The resulting solution was diluted to 250 ml. in a volumetric flask.

(b) 0.0998 gms of the steel were dissolved as described for Standard Sample #2. The resulting solution was diluted to 250 ml. in a volumetric flask.

(2) Preparation of Sample for Analysis. Two ml. of the diluted sample were pipetted into a 50 ml. beaker and treated as described for tungsten in Section 2.

C. Standard Sample #10

(1) Dissolution of Sample. 0.0927 gm. of Standard Sample #10 were treated as described for Standard Sample #2.

(2) Preparation of the Sample for Analysis.

(a) One two ml. aliquot was treated as for Standard Sample #4 above.

(b) One two ml. aliquot was treated as for Standard Sample #2 above.

D. Standard Sample #11

(1) Dissolution of Sample. 0.0646 gms. of the steel were dissolved as described for Standard Sample #2. The resulting solution was diluted to 250 ml. with concentrated HCl.

(2) Preparation of Sample for Analysis. Same as for Standard Sample #4 (above).

E. Standard Sample #23

(1) Dissolution of Sample. 0.1053 gms. of the steel were dissolved as described for Standard Sample #2 (above).

(2) Preparation of Sample for Analysis. Same as for Standard Sample # 4 (above) using a 1ml. aliquot of steel solution.

F. NBS Steel #50a

(1) Dissolution of Sample. 0.1152 gms. of the steel were dissolved as described for Standard Sample #2 (above). The resulting solution was diluted to 250 ml. with concentrated HCl.

G. NBS Steel #50b

(1) Dissolution of Sample. 0.1149 gms. of steel were dissolved as for steel Standard Sample #2 above. The resulting solution was diluted to 250 ml. with concentrated HCl.

(2) Preparation of Sample for Analysis. Same as for Standard Sample #4 above.

H. NBS Steel # 123b. (Niobium Containing)

(1) Dissolution of Sample. 1.0342 gms. steel were dissolved as described for steel Standard Sample #2 (above). The resulting solution was diluted to 250 ml. with concentrated HCl.

(2) Preparation of Sample for Analysis. The entire diluted sample was pre-extracted with $CHCl_3$ as described for Standard Sample #2 (above).

A 10 ml. aliquot of the residual steel solution was then reduced and the tungsten extracted as in Section 3. After separation, however, the $CHCl_3$ layer was released into another 50 ml. separatory funnel containing 10 ml. of freshly prepared saturated $NH_4F \cdot HF$ solution. The two layers were shaken together for at least two minutes and then allowed to separate. The $CHCl_3$ layer was filtered into a 25 ml. volumetric flask. The process was repeated until the flask was filled.

The absorbance of the $CHCl_3$ extract was measured at 402 mμ, and the percent W in the sample was calculated.

I. NBS Steel #132

(1) Dissolution of Sample. 0.1066 gms. of the steel were treated as described for Standard Sample #2 (above).

(2) Preparation of Sample for Analysis. Same as for Standard Sample #4 (above).

J. NBS Steel #132a

0.0990 gms. of the steel were treated as described for NBS steel #132 (I).

K. NBS Steel #134

0.2094 gms. of the steel were treated as described for NBS steel #132 (I) using two and three ml. aliquots.

L. NBS Steel #153

0.3027 gms. of the steel were treated as described for NBS steel #132 (I).

M. NBS Steel #155

(1) Dissolution of Sample. 0.1631 gms. of the steel were treated with about 25 ml. HCl and 5 ml. HNO_3. Dissolution was difficult and left a heavy brown scum. After extensive boiling (15 minutes), the dissolved sample was diluted to 100 ml. in a volumetric flask.

(2) Preparation of Sample for Analysis. The entire solution was pre-extracted with $CHCl_3$ as described for Standard Sample #2 and was then filtered to remove a silky, white precipitate.

Ten ml. of the sample were then treated as described in Section 2.

N. NBS Heat Resisting Alloy #167

(1) Dissolution of Sample. 0.1020 gm. of the alloy was weighed into a 250 ml. beaker and boiled with 30 ml. concentrated HCl for about one hour. Concentrated HNO_3 was then added dropwise (3 to 4 drops at a time) every 15 minutes until the sample completely dissolved. Concentrated HCl was added to replenish that lost by evaporation. After dissolution, the sample was diluted to volume in a 100 ml. volumetric flask with concentrated HCl. Total solution time was about two hours.

(2) Preparation of Sample for Analysis. 3 ml. aliquots of the diluted sample were reduced, extracted, and washed with fresh, cold, saturated $NH_4F{\cdot}HF$ as described in (H) for NBS steel #123b.

The absorbance of the $CHCl_3$ extract was measured at the absorbance peak close to 400 mμ, and the percent W was calculated.

O. NBS Heat Resisting Alloy #168

Same as for heat resisting alloy #167 using 0.1015 gm. sample.

12. Investigation of Uses of Bismuth and Zinc Amalgams as Reductants for Tungsten

A. Preparation of Bismuth Amalgam (3% Amalgam)

Three gm. of Bi metal granules were dissolved in 100 gm. (7.6 ml.) clean Mercury using a little concentrated HCl to aid amalgamation.

B. Preparation of Zn Amalgam (3% Amalgam)

Zinc amalgam was made by dissolving approximately 3 gm. of zinc granules in 100 gms. (7.6 ml.) clean Hg using dilute H_2SO_4 to aid amalgamation.

C. Reduction of Tungsten with Bi Amalgam and Subsequent Tungsten Extraction

(1) About 5 ml. of 10^{-3} M W (VI) in concentrated HCl were shaken with 100 gm. of 3% bismuth amalgam in a separatory funnel. The amalgam was then run out of the funnel. A portion of the aqueous layer was treated with 25 drops of 0.025 M TPAC and 3 ml. of 1.5 M. KSCN, producing a reddish-white precipitate. The mixture was shaken with $CHCl_3$ and allowed to remain undisturbed for a few minutes. After about five minutes, the $CHCl_3$ layer was red and the aqueous layer colorless. The $CHCl_3$ layer was then separated and shaken with distilled water which changed the color to yellow. The spectrum was recorded on the DU from 385 to 420 mμ.

(2) Approximately 5 ml. of 10^{-3} M W (VI) in concentrated HCl were heated to boiling with 100 gm. of 3% bismuth amalgam. One ml. of the resulting blue solution was placed in a glass stoppered graduated cylinder. 1.5 M KSCN and 0.025 M TPAC were added, and the resulting precipitate was extracted into $CHCl_3$. The spectrum was run on the DK-1.

D. Use of Zinc Amalgam to Reduce Tungsten and Extraction of Tungsten

About 5 ml. of 10^{-3} M W (VI) in concentrated HCl were shaken with 100 gm. of 3% zinc amalgam and a nearly equal volume of distilled water. About one ml. of the resulting red solution was placed in a glass stoppered, 10 ml. graduated cylinder. 0.025 M TPAC and 1.5 M KSCN were added in that order, and the yellow precipitate which appeared was extracted into $CHCl_3$. The spectrum of the $CHCl_3$ layer was run on the DU from 350 to 440 mμ.

E. Spectrum of Aqueous Tungsten Reduced with Zinc Amalgam

Ten ml. of 10^{-3} M W (VI) in concentrated HCl were pipetted into a separatory funnel containing 100 gm. of 3% zinc amalgam. The mixture was shaken for five minutes and the amalgam removed. A spectrum of the HCl layer was run on the DK-1 immediately, after one-half hour, and after four hours.

F. Spectrum of Aqueous Tungsten Reduced with Bismuth Amalgam

Same as (E) using 3% bismuth amalgam instead of zinc amalgam.

G. Calibration Plot for Tungsten Analysis after Reduction with Zinc Amalgam

A quantity of 10^{-4} M tungsten (VI) in concentrated HCl was shaken in a 60 ml. separatory funnel with 3% zinc amalgam for about one minute. An aliquot (between 2 and 15 ml.) of the reduced tungsten solution was pipetted into another separatory funnel followed by a few ml. of chilled concentrated HCl, 1.5 ml. of chilled 0.025 M TPAC; and 3 ml. chilled 1.5 M KSCN in that order. The mixture was repeatedly extracted with 5 to 8 ml. portions of $CHCl_3$ until 25 ml. $CHCl_3$ had been used. The TPAC was replenished after each extraction. The absorbance of the $CHCl_3$ solution was measured on the DU at 406 mμ.

This procedure was carried out for aliquots of 2, 5, 10, and 15 ml. of the tungsten solution, using a freshly reduced tungsten solution for each run.

A plot was made of concentration of tungsten taken vs. absorbance and the absorptivity was calculated.

13. Composition of Extracted Species

A. Preparation of a Yellow Tetraphenylarsonium Salt of the Tungsten-Thiocyanate Complex

(1) From an Aqueous Solution. Approximately 10 ml. of 10^{-3} M W (VI) in concentrated HCl were placed in a 70 ml. separatory funnel. About 5 ml. of 3% zinc amalgam were added and the mixture was shaken for about 5 minutes to insure good mixing. The amalgam was then drained off and 3 ml. of 0.025 M TPAC were added to the funnel. Approximately 5 ml. of 1.5 M KSCN were then added and the mixture was allowed to sit for a few minutes. The resulting solid was caught by vacuum filtration on Whatman #40 paper, was air dried, and was then stored in a bottle.

(2) From an Aqueous-ethanolic solution. About 0.3 gms. of $Na_2WO_4 \cdot 2H_2O$ were dissolved in 10 ml. distilled water and treated with 100 ml. concentrated HCl. This solution was treated with 100 gm. of old, used 3% zinc amalgam. The amalgam was then drawn off. The resulting dark blue solution was chilled in a liter beaker in an ice bath. 150 ml. of 0.025 M TPAC (G.F.SMITH) and 120 ml. of 0.75 M KSCN in 1.1 water-ethanol solution were slowly added simultaneously from separate dropping funnels while the tungsten solution was being stirred rapidly with an automatic stirring device. Addition of reagents required about 5 minutes. After addition of TPAC and KSCN solutions, the mixture was filtered and the

yellow solid caught on a medium sintered glass filter crucible. The yellow salt was transferred to a petri dish, spread, and allowed to dry over P_2O_5 in a desiccator. After drying two days in the desiccator, the precipitate was washed with ethanol, water, and ethanol-water mixtures. The remaining solid was dried on a petri dish over P_2O_5 in a desiccator.

B. Preparation of a Green Salt

(1) Fifty ml. of 10^{-3} M H_2WO_4 in concentrated HCl were heated on a hot plate with 100 ml. 10% $SnCl_2$ in concentrated HCl. The solution was then chilled in an ice bath and placed in a 750 ml. separatory funnel. 200 ml. of cold water and 50 ml. of 0.025 M TPAC were added. 75 ml. of 1.5 M KSCN were then added. Extraction was then made using three 50 ml. portions of $CHCl_3$. The $CHCl_3$ layer was filtered through coarse, porous paper into a beaker, and the filtrate was allowed to stand a couple of hours to allow time for complete precipitation. The crystals were then filtered using a coarse paper and air dried.

(2) Fifteen ml. of 10^{-3} M W (VI) were reduced with $SnCl_2$ and extracted into $CHCl_3$ as previously described. The $CHCl_3$ extract was then repeatedly washed with 10 ml. portions of distilled water until the distilled water washes give a negative test for thiocyanate and chloride and were neutral to pH paper. The chloroform extract was allowed to stand until the green crystals had precipitated. The precipitate was filtered with rapid-filtering paper, air dried, and stored in a weighing bottle.

C. Analysis of Precipitates

(1) Qualitative Test for Chloride. A small amount of the solid was decomposed with concentrated HNO_3 in a test tube. The solution was

centrifuged to settle all the precipitate and $AgNO_3$ solution was added to the supernate.

(2) Gravimetric Determination of Tungsten in the Prepared Salts. 0.336 gms. of a green compound prepared earlier were dissolved in 10 to 20 ml. of concentrated HNO_3 to decompose the compound and precipitate the H_2WO_4. After complete decomposition, the mixture was diluted to about 200 ml. with distilled water. Twenty ml. of 10% cinchonine in 6 M HCl were added, and the solution was heated to 70 to 80 degree Centigrade until the supernatant liquid was clear. The solution was cooled, filtered through Whatman #40 filter paper, and washed 20 times with 1% cinchonine in 0.1 M HCl. The paper and precipitate were ignited in a tared Pt crucible with a Meker burner and weighed.

(3) Spectrophotometric Analysis of Tungsten. 0.0739 gms. of compound were weighed into a beaker and decomposed with five drops of HNO_3, and the solution was evaporated to dryness. The residue was taken up in 6 M NaOH and diluted to 50 ml. in a volumetric flask with distilled water. A 10 ml. aliquot of the basic solution was diluted to 50 ml. with concentrated HCl. A five ml. aliquot was analyzed for tungsten as described in Section 2.

(4) Spectrophotometric Analysis of Tetraphenylarsonium (TPA).

(a) Verification of analysis procedure for TPAC. Two samples (0.0335 gm. and 0.0356 gm.) of reagent grade TPAC were decomposed with a few drops concentrated HNO_3 and diluted to 100 ml. with approximately 1 M HCl. Five ml. of the solutions were extracted into 25 ml. $CHCl_3$, and the absorbance of the $CHCl_3$ extracts was measured at 265 mμ.

(b) 0.0244 gms. of the compound being studied were weighed into a beaker, decomposed with a few drops of HNO_3, digested for a few minutes, diluted to about 20 ml. with 6 M HCl, and diluted to 100 ml. in a volumetric flask with distilled water. A 10 ml. portion of the diluted solution was placed in a 60 ml. separatory funnel and extracted with 25 ml. of $CHCl_3$. The $CHCl_3$ solution was drawn off through a filter paper, and its absorbance was measured at 263 mμ.

(c) Variational method of analysis of As/W ratio and SCN/W ratio.

1. As/W ratio in extract: Five ml. of 10^{-4} M W (VI) in concentrated HCl were heated nearly to boiling with 2 ml. 10% $SnCl_2$ in concentrated HCl, chilled in an ice bath and rinsed into a 60 ml. separatory funnel with 10 ml. of cold, 6 M HCl. X ml. of 5×10^{-3} M TPAC or 5×10^{-4} TPAC were then pipetted into the solution. 3 ml. of 1.5 M KSCN and (5 - x) ml. of cold distilled water were added and the mixture swirled to mix. Twenty-five ml. $CHCl_3$ were added, the mixture shaken, and the layers allowed to settle. The $CHCl_3$ solution was filtered off through filter paper and its absorbance was measured at 406 mμ on the DU. Values of X were 0.5, 1.0, and 2.0 for the 5×10^{-3} M TPAC and 0.5, 1.0, 1.5, and 2.0 for the 5×10^{-4} M TPAC.

The log of the function (A/Ao-A) was plotted against the log of the total TPA concentration. A is the absorbance of a given extraction, and Ao is the absorbance for the normal tungsten extraction with the same quantity of tungsten taken as in the above procedure. The slope of this plot is then determined to the nearest interger as n', and another plot is made of log (A/Ao-A) vs. log (TPA - $\frac{n'A}{a}$). The slope of this line is determined as n, the molar ratio of TPA to tungsten in the extracted species. (See Table 7, page 73 and Figure 7, page 70).

2. Thiocyanate/tungsten ratio in the extracted species: 10 ml. of 10^{-4} M W (VI) (Ao = 0.590) in concentrated HCl were heated with 3 ml. of 10% $SnCl_2$ in concentrated HCl, chilled in an ice bath, and rinsed into a 60 ml. separatory funnel with (10-x) ml. of chilled distilled water. Two ml. of 5 x 10^{-3} M TPAC were then added by pipet. Then X ml. of a KSCN stock solution were added. (Two stock solutions of KSCN were used. Solution 'a' was approximately 0.05 M and solution 'b' was exactly 0.20 as concentrated as 'a'. X was 1, 2, and 3 ml. for 'a' and 3, 4, and 6 ml. for 'b'). Twenty-five ml. of $CHCl_3$ were then pipetted in, and the mixture was thoroughly shaken and allowed to settle. The $CHCl_3$ layer was filtered through a small paper, and its absorbance was measured at 406 mμ.

A plot of log (A/Ao-A) vs. log (X) was constructed and the thiocyanate/tungsten ratio determined as the slope of the plot. (See Table 8, page 77 and Figure 9, page 76).

(d) Attempts at determining oxidation number of tungsten:

1. Using solid compound: 0.1710 gms. of the green

crystals were dissolved in acetone and treated with an excess of aqueous $AgNO_3$. The resulting precipitate was caught on a weighed sintered glass crucible, dried at 100 to 140 degrees C and weighed. The precipitate was then treated with concentrated NH_4OH in the filter and the NH_4OH solution was filtered off. Two NH_4OH washings were done. The residue was dried at 140 degrees and weighed.

2. Using washed extract: Approximately 25 μmoles of W (VI) (25 ml. of 10^{-3} M W (VI) in concentrated HCl) were reduced with $SnCl_2$, treated with TPAC and KSCN in the usual manner and extracted into 100 ml. $CHCl_3$. The absorbance was measured at 406 mμ.

The entire extract was washed with 50 ml. portions of distilled water until the washes gave negative tests for the $AgNO_3$ test for chloride and the ferric ion test for thiocyanate and were neutral to pH paper. The absorbance of the washed extract was quickly measured, and 75 ml. of the solution were pipetted into a beaker. Ethanolic $AgNO_3$ was then added to the yellow solution until the color disappeared. A small excess of $AgNO_3$ was added, and the mixture was stirred and allowed to digest for a few minutes in the dark. The precipitate was filtered through a weighed medium-sintered glass filter and washed with dilute HNO_3, concentrated NH_4OH, dilute HNO_3, distilled water, and ethanol in that order. The filter and contents were dried in the oven at 110° C for about one-half hour, cooled, and weighed.

The oxidation number of the tungsten was computed according to the formula:

$$\text{OX.num.} = 6 - \frac{(\text{WtAg})a_m}{(\text{MWAg})A}\,\frac{1000}{75}$$

3. Spectral studies on $CHCl_3$ extract: 2.5 μmoles of W (VI) in HCl were reduced and extracted into 50 ml. $CHCl_3$ as previously described. The spectrum of the $CHCl_3$ was recorded on the DK-1 spectrophotometer from 1300 mμ to 400 mμ using 1 and 10 cm. cells.

(e) Stability of extracted complex under various conditions:

1. Washing extract with 7 M KOH, 6 M HCl, and distilled water. Four extractions were prepared as described above using 0.5 μmoles W (VI). The $CHCl_3$ solutions were filtered into 50 ml. Erlenmeyer flasks. To three of the flasks were addded, respectively, 2 ml. of 7 M KOH, 2 ml. 6 M HCl and 2 ml. distilled water. One flask was used as a control. The flasks were allowed to sit for an hour and a half with frequent shaking. When no changes were noted in the appearances of the solutions, the flasks were stoppered and allowed to stand overnight. The following morning, spectra were run on each of the layers and the appearance of each layer was recorded.

2. Acid washes of extracted $CHCl_3$ solution:

(a) $HClO_4$ washes. Three samples of 0.5 μmoles of tungsten were each extracted into 25 ml. $CHCl_3$ as described previously. Each sample was washed with 50 ml. of water to back wash the solutions free of all excess H^+, Cl^-, and SCN^- ions. One sample was filtered into a flask, and its absorbance was measured every half hour at 406 mμ on the DU. The two remaining water-washed extracts were washed with 10 ml. of 5.4 M $HClO_4$ and 10 ml. of 2.7 M $HClO_4$, respectively. The acid washed solutions were filtered, and their absorbances were measured at 406 mμ on the DU at irregular time intervals.

(b) HCl washes. Same as procedure (a) using 1.5 μmoles W (VI), an additional 25 ml. water wash, and finally washing with 10 ml. of 6.0 M HCl and 10 ml. 9.0 M HCl, respectively.

(c) Extraction of HCl into $CHCl_3$. Each of the following solutions was extracted with 25 ml. $CHCl_3$, and the $CHCl_3$ layers were then backwashed with 50 ml. of distilled water. The water layers from the backwash were titrated with standard KOH and the number of mmoles of acid extracted was determined for each of the following cases. The data are presented in Table 3, page 49.

(1) 20 ml. concentrated HCl + 5 ml. H_2O

(2) 20 ml. concentrated HCl + 3 ml. 1.5 M KSCN + 2 ml. H_2O.

(3) 20 ml. concentrated HCl + 3 ml. 1.5 M KSCN + 2 ml. 0.025 M TPAC,

(4) 15 ml. concentrated HCl + 3 ml. 1.5 M KSCN + 2 ml. 0.025 M TPAC + 5 ml. 10% $SnCl_2$ in concentrated HCl.

CHAPTER IV

RESULTS AND DISCUSSIONS

1. Preliminary Work

Preliminary investigations on the thiocyanate complex of tungsten were made using various precipitating cations and various solvents. Attempts were made to isolate a salt of the complex thiocyanate-tungsten anions using various large cations. It was found that with tetraphenylarsonium chloride (TPAC) as precipitating agent a tungsten complex could be extracted into chloroform but Beer's law was not followed by the extracted species. A yellowish green salt could also be isolated using TPAC, but the composition of the salt was not constant. The work described here was undertaken at this point to study the extraction with chloroform of the TPAC ion-pair of the tungsten-thiocyanate complex in order to develop a quantitative analytical procedure for tungsten and to determine the stoichiometry of the complex formation and ion-pair extraction.

The method of extraction was the reduction of tungsten (VI) with $SnCl_2$ in concentrated HCl, addition of 0.05 M TPAC, addition of 1.7 M NH_4SCN, and extraction with $CHCl_3$. One of the principal drawbacks of this procedure was the incomplete reduction of the tungsten under the conditions mentioned. Following this method of extraction, Beer's law was not followed, and the deviation was negative. Geld & Carroll (25) reported on the reduction of tungsten prior to complex formation and found that reduction was rapid and complete in greater than 9 M HCl for a large excess of $SnCl_2$ if the tungsten and tin (II) were heated to boiling during the reduction. Application of this process to the scheme of extraction helped considerably, but new problems appeared. While complete reduction and supposedly complete extraction were now possible, it was apparent that the chloroform extracts were highly unstable. The absorbance of the solutions decreased rather rapidly, and the solutions often changed color. Sometimes the yellow chloroform solutions would become red and eventually develop a yellow precipitate, and sometimes the color would simply fade out. The results were such that Beer's law was still not obeyed by the extracts.

To discover the possible sources of the problem, blanks were run using $SnCl_2$ in concentrated HCl, NH_4SCN, and TPAC in water. It was found that the NH_4SCN decomposed in the higher acid concentrations to give yellow solutions or precipitates, and the decomposition was greater at higher temperatures.

To eliminate the decomposition of the thiocyanate, potassium thiocyanate was used in place of ammonium thiocyanate. The potassium thiocyanate is easier to purify and is apparently more stable in acid solutions than the ammonium thiocyanate.

A number of attempts were also made to extract the ion-pair from low acid concentrations by forming the thiocyanate-tungsten complex in 3 to 4 molar HCl and adding tetraphenylarsonium chloride to the resulting yellow solution. Chloroform, isoamyl alcohol, and mixtures of chloroform with ethanol, acetone, and isoamyl alcohol were used as solvents.

Extraction with chloroform at these low acid concentrations was incomplete with considerable emulsification and subsequent precipitation of salts in the separated organic layer. Addition of isoamyl alcohol or acetone to the chloroform prior to the extractions or after the extraction increased the rate of precipitation in chloroform, and acetone caused sharp fading of color during the extraction. A 3:7 ethanol-$CHCl_3$ solution apparently gave some good extractions, but Beer's law was not followed. The precipitate in the $CHCl_3$ layer when ethanol was not used was a chartreuse, crystalline material.

When the above experiments failed to produce the desired results, another attempt at obtaining a workable Beer's law curve was made using higher acid concentrations. The reduced tungsten solutions were chilled to prevent decomposition of thiocyanate, and KSCN was used instead of NH_4SCN. Although the chloroform extracts were not stable indefinitely, a reasonable Beer's law plot was constructed so this procedure was adopted as the standard procedure for extraction of the tungsten. (See Section 3-Experimental). The essential improvements in the method were (a) complete reduction of the tungsten prior to addition of thiocyanate (b) formation of the complex and extraction of the ion-pair in a chilled (10 to 15 degrees) aqueous phase and (c) use of potassium thiocyanate in place of ammonium thiocyanate.

It is good to note further that the most effective extractions were achieved by very vigorous shaking of the chloroform-acid mixtures. Such vigorous shaking is usually not recommended for solvent-solvent extraction where no solid phase is involved. It is apparent in this case, however, that vigorous shaking causes much cleaner and more rapid extraction and a better separation of layers than does the more gentle equilibration technique usually applied for liquid-liquid extraction. For liquid-liquid extractions involving no solid phase, Morrison and Freiser (23) state that the rate of extraction depends mainly on the relative velocity of the particles within each phase, and not upon the surface area contact. For the case where solid is present, however, it is reasonable to assume that the rate of extraction would be principally a function of surface area contact between the dispersed phase and the extracting liquid.

2. Spectrum and Beer's Law

The spectrum in the visible region of the yellow tungsten ion-pair extracted in chloroform is shown in Figures 1 and 2. Figure 1a) presents the spectrum in the usual manner, i.e., molar absorptivity versus wavelength in millimicrons. The position and shape of the region of maximum absorbance with peaks at 406 mμ are quite suitable for a spectrophotometric analysis. The band is reasonably symmetrical and wide enough (half-band width = 23 mμ) that the wavelength of maximum absorbance is easily reproduced without difficulty, and Beer's law is followed quite well even at high concentrations. At the ultraviolet edge of the large visible band, the absorbance starts rising rapidly and continues to rise into the tetraphenylarsonium peaks which appear at approximately 270 and 260 mμ. The tetraphenylarsonium bands are badly distorted, however, because of a strong thiocyanate absorption in this region which increases without a maximum to the chloroform cut-off wavelength at 240 mμ. The spectrum of the blank is shown as the dashed line in Figure 1a). Apparently the ultraviolet absorption of the solution is partially due to the complex. The visible band also shows a bulge on the long wavelength side.

SPECTRUM OF TUNGSTEN EXTRACT

IN CHLOROFORM

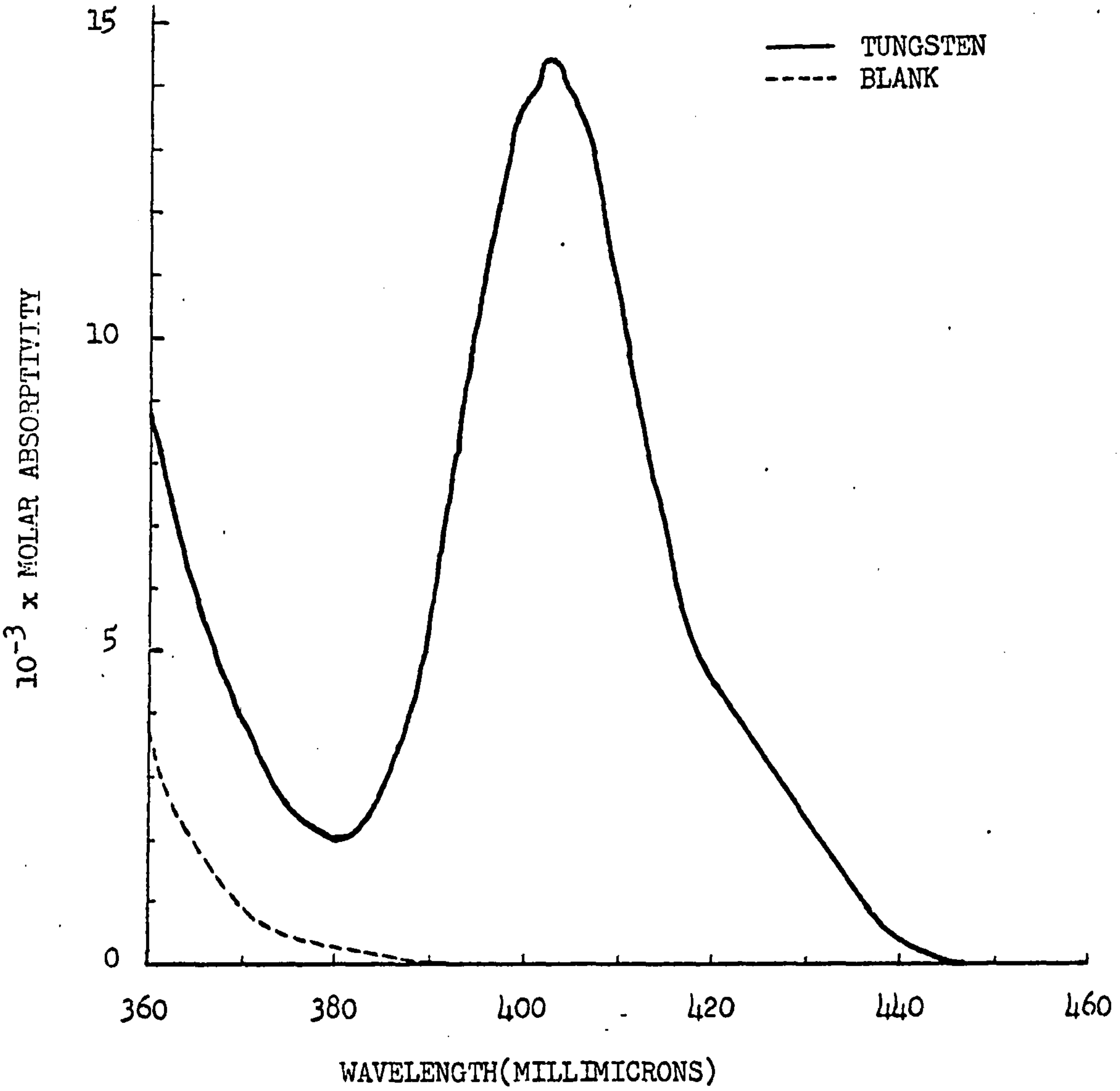


FIGURE 1a

SPECTRUM OF TUNGSTEN EXTRACT
IN CHLOROFORM

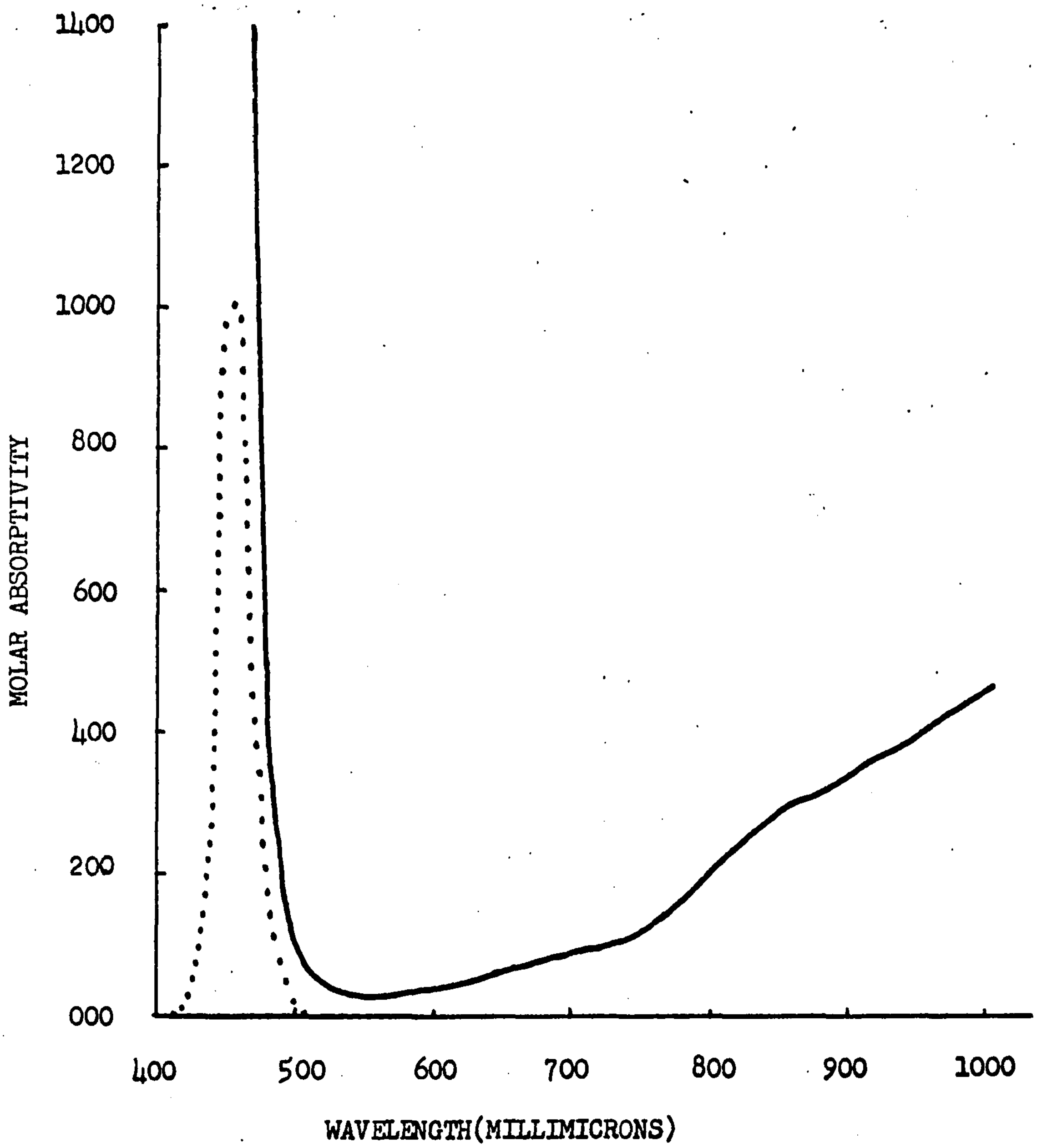


FIGURE 1b

SPECTRUM OF TUNGSTEN EXTRACT IN CHLOROFORM

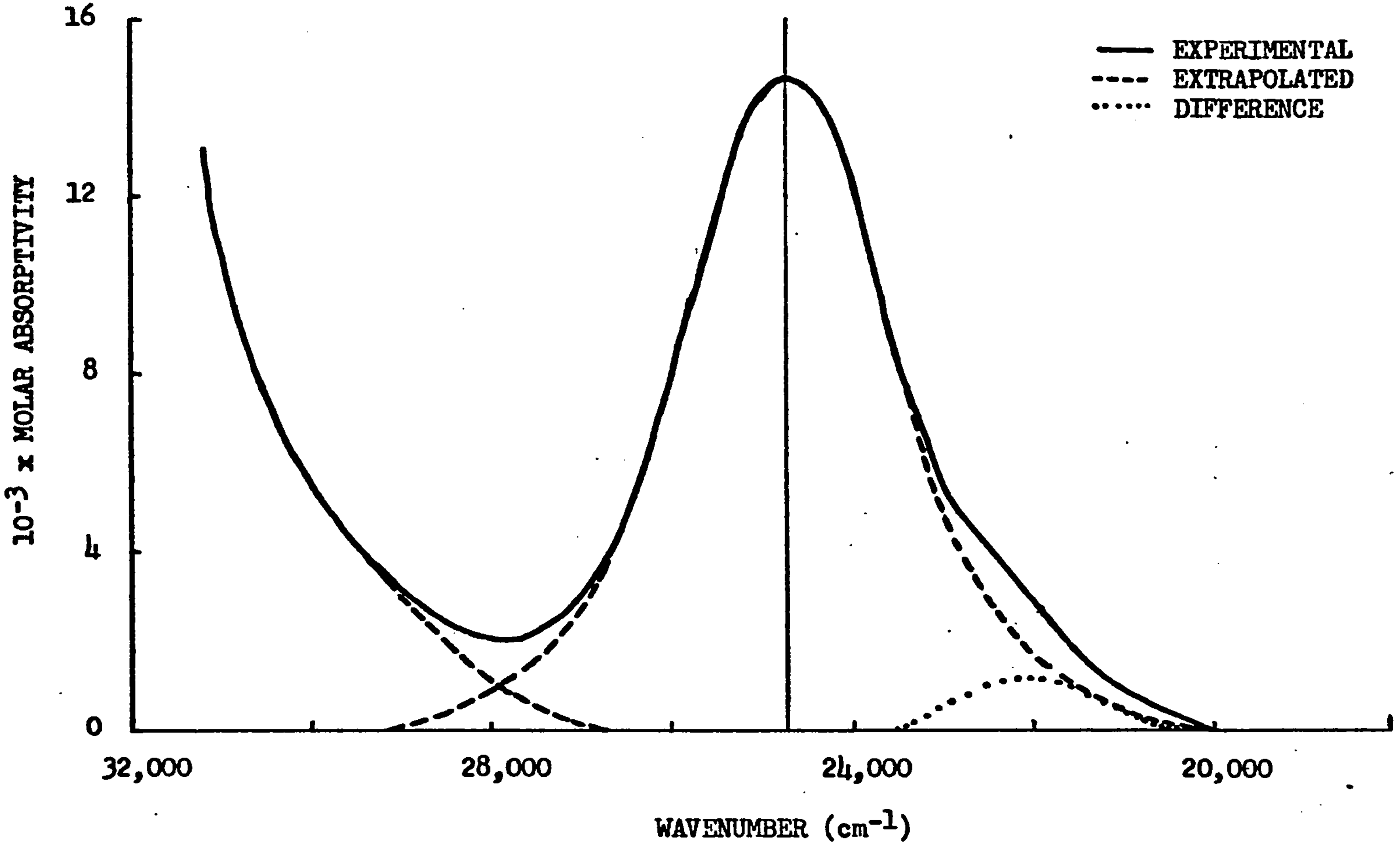


FIGURE 2

Neither the ultraviolet nor the long wavelength absorbance interferes with the peak absorbance of the band at 406 mμ. Thus the use of the maximum at 406 mμ for spectrophotometric tungsten analysis requires no blank and the solvent may be used directly as one spectrophotometric reference.

On the same absorptivity scale as Figure 1a), no additional absorption was detected to 1000 mμ. However, with the scale expanded 20 times (concentrated solutions) a generally increasing absorbance is noted between 600 mμ and 1000 mμ. There are shoulders on this spectrum at about 690 mμ and 850 mμ. This expanded scale spectrum is shown in Figure 1b). It is not feasible to extend the spectrum of the chloroform solution further into the infrared because of solvent absorption.

The spectrum of absorbance versus wavelength was obtained by the method explained in Section 4-Experimental. To calculate the absorptivity at the maximum wavelength, a Beer's law plot was constructed as described in Section 5-Experimental. The extractions for the Beer's law plot all were made initially from approximately 7 to 8 M HCl as a result of the acid variation tests discussed in Section 4-Results & Discussion. The acid variation tests, however, were done for a constant concentration (20 μmolar) of tungsten. It was subsequently found that increased tungsten concentrations required higher HCl concentrations. Thus, for greater than 50 μmolar tungsten, it is necessary to use 10 to 11 M HCl to achieve complete extraction with three equilibrations using a total of 25 ml. $CHCl_3$. Two sets of data, collected one year apart with different tungsten stock solutions and different quantities of tungsten extracted, are both plotted on the same graph in Figure 3. The line was calculated from a least squares analysis of the earlier data. The graph is seen to be

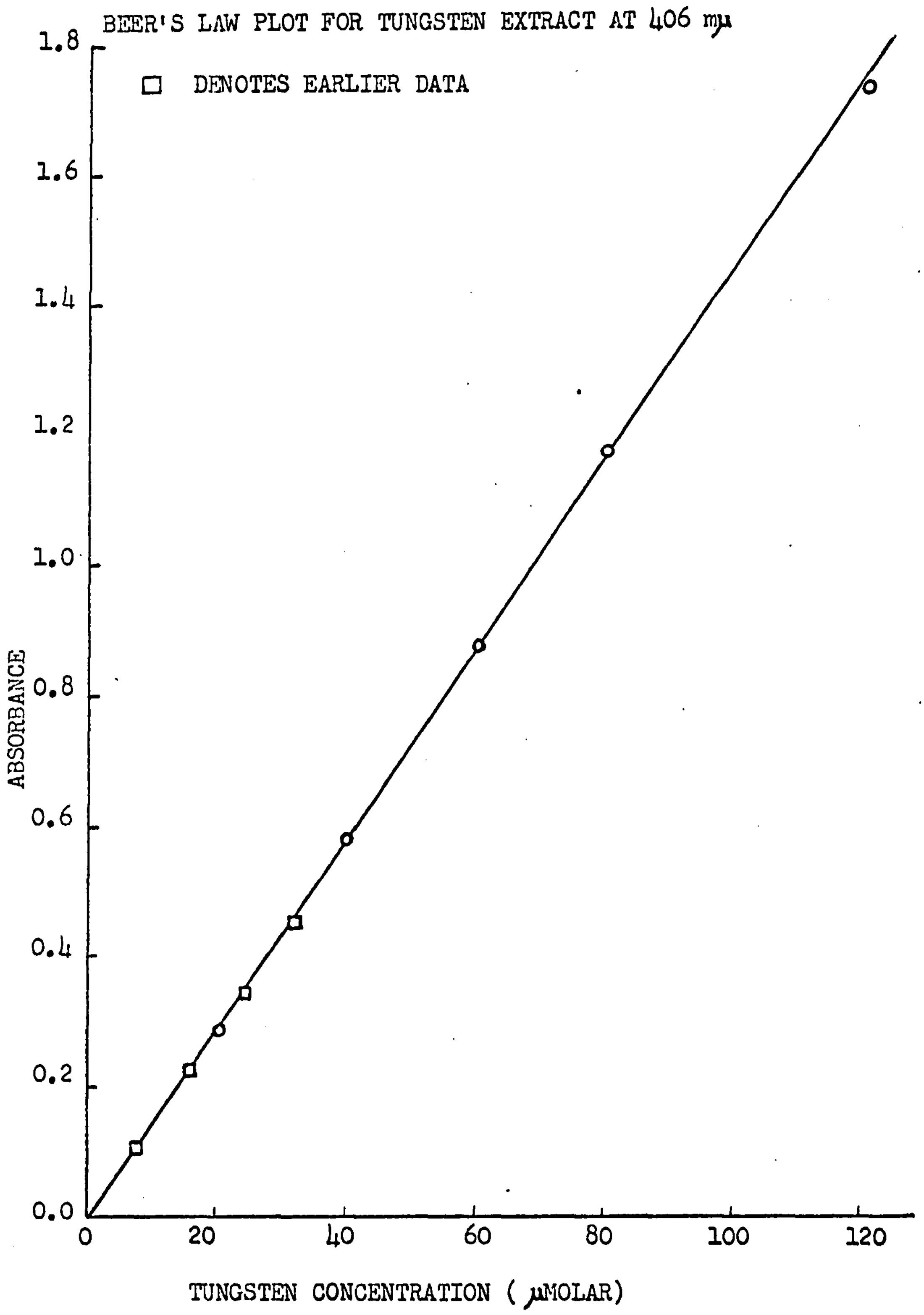

BEER'S LAW PLOT FOR TUNGSTEN EXTRACT AT 406 mμ
□ DENOTES EARLIER DATA
ABSORBANCE
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
120
TUNGSTEN CONCENTRATION (μMOLAR)

FIGURE 3

linear in experimental error out to 120 μmolar (highest concentration tried) and an absorbance of 1.8. The slope of the line is 1.475 x 10^4 $M^{-1}cm^{-1}$. Data are tabulated in Table 1.

TABLE I

BEER'S LAW DATA FOR TUNGSTEN COMPLEX AT 406 mμ

Micromolar Concentration of Tungsten	Absorbance
8	0.119
16	0.237
20	0.294
24	0.355
32	0.471
40	0.598
60	0.890
80	1.184
120	1.754

The absorptivity at a given wavelength was determined by dividing the absorbance at that wavelength by the absorbance measured for the same solution at 406 mμ. The absorptivities were then plotted against wavelength.

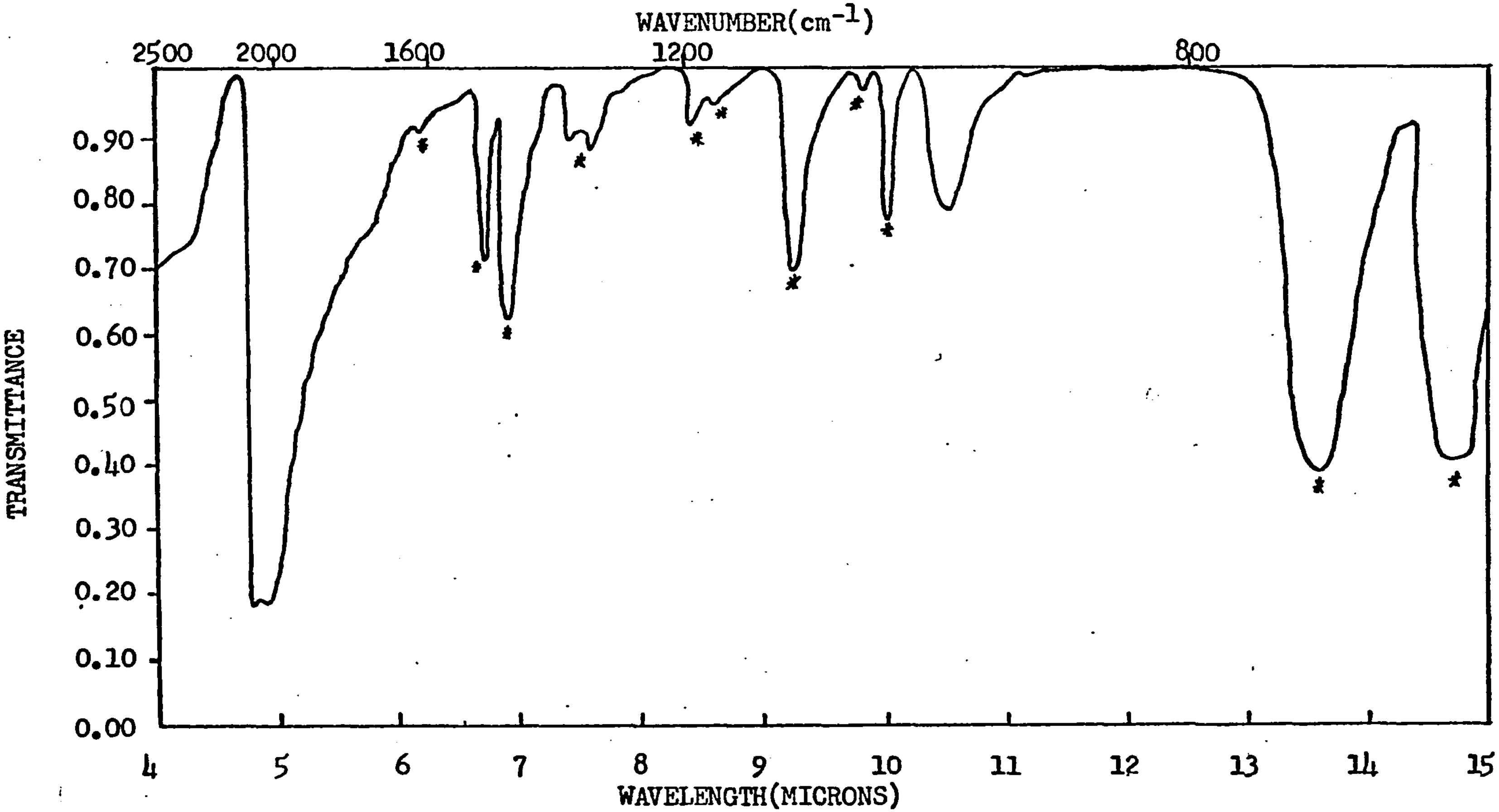
Because of the very high absorptivity of the band whose peak appears at 406 mμ, it is likely that the band is due to a charge-transfer process. Charge-transfer transitions are wholly allowed transitions and often have absorptivities in the thousands and ten thousands.

In attempting to aid in the determination of the structure and composition of the absorbing species, it was thought desirable to study the spectrum due to transitions between d levels split by the ligand field. These transitions are usually singly (Laporte) forbidden transitions and for this reason are characterized by low molar absorptivities. For symmetrical octahedral ligand fields, for example, the molar absorptivities normally are of the order 1 to 200, while tetrahedral complexes may demonstrate absorptivities as high as several hundred. Because of thermal vibrations of the ligands, the field strength at the metal nucleus varies considerably, and thus the difference in energy between two d levels also varies. For this reason, d-d transitions are usually characterized by broad absorption bands. The number and relative position of the bands depend on the electronic structure of the metal, the symmetry of the ligand groupings, and the strength of the ligand fields.

Because of the low absorptivity of d-d transitions, it was thought that the long-wavelength sideband of the main charge-transfer band might be attributable to a d-d transition of the tungsten-thiocyanate anion. To determine the intensity and frequency of the peak of the side band, the entire band was plotted from 340 mμ to 470 mμ as absorptivity versus wavenumber (Figure 2). The solid line is the experimental spectrum. The dashed line is the result of an extrapolation of the main portion of the peak on the ultraviolet side to the shape it would have were the strong ultraviolet band not there also. Since the ultraviolet band was steeper, it was extrapolated to zero absorbance on a smooth line, and the difference between the experimental spectrum and the extrapolated ultraviolet line was taken to be part of the absorbance due to the band at 406 mμ and was plotted as such. Assuming that the absorptivity of the charge transfer band was symmetrical with respect to the light energy, the high energy side of the peak was reflected across the line perpendicular to the wavenumber axis at the position of the band maximum (24,610 cm^{-1}). The reflected portion is shown as the dashed lines on the low energy side of the band. The absorptivity differences between the experimental curve and the symmetrical curve on the low energy side of the band were calculated. This difference was plotted against wavenumber to give the smaller band (dotted lines) in the figure. This curve is also shown as the dotted portion of Figure 1b). The band has an absorptivity of about 1100 $M^{-1}cm^{-1}$, which is much higher than that usually observed for octahedral compounds and higher than that observed for tetrahedral compounds. Furthermore, the half-band width is only 30 mμ. Thus it is not safe to attribute the band to a d-d transition without further information. The two shoulders at 690 and 850 mμ are probably due to d-d transitions in the complex, but the absorption in this region is too general to assign with certainty any definite number and position of bands. For these reasons, no conclusions about the structure or valency of the complex were obtained from the spectrum.

The infrared spectrum of TPAC and of the yellow salt were obtained in KBr discs on the Perkin-Elmer Model 21 infrared spectrophotometer. The spectrum of the yellow salt is shown in Figure 4. Some tetraphenylarsonium thiocyanate is probably present also. Those bands labeled TPAC are present also in the TPAC spectrum. The band at 2100 cm^{-1} to 2050 cm^{-1} is attributed to the C-N stretch of the thiocyanate group.

INFRARED SPECTRUM OF THE YELLOW SALT OF
THE TUNGSTEN-THIOCYANATE COMPLEX AND TPA ION



(ASTERISKS DENOTE TETRAPHENYLARSONIUM BANDS)

FIGURE 4

For tetraphenylarsonium thiocyanate, a sharp band at 2100 cm^{-1} is present. Evidently the broader band of Figure 4 just below 2100 cm^{-1} is attributable to the thiocyanate groups directly attached to the tungsten atom. According to Mitchell and Williams (See Introduction), the linkage for this compound is through the nitrogen. Thus the complex is an isothiocyanate.

The band at 10.5 microns is not present in the spectrum of TPAC or of tetraphenylarsonium thiocyanate; it is therefore probably characteristic of the tungsten compound.

3. Extraction Variables

A. Effect of Hydrogen Ion and Chloride Ion Activities

It was brought out in the Introduction that the efficiency of extraction, i.e., the percent of metal complex extracted into the organic phase, was a function of the acidity of the aqueous phase. Section 9 - Experimental describes the technique employed to determine the relationship between extraction efficiency and acidity. Table 2 tabulates the results of the experiment, and Figure 5 illustrates the data.

It is evident from the graph that the extraction of tungsten is favored by high acid concentrations, the optimum concdntration being in the range 7 to 10 M HCl for the tungsten concentration considered. It should be noted that the abscissa of the graph is the HCl concentration computed from the total mmoles of HCl added to the aqueous phase divided by the volume of the aqueous phase. The HCl concentration of the aqueous phase after extraction is lower due to partitioning of various acids (such as HSCN) between the aqueous and organic phases. This is illustrated in Table 3.

EXTRACTION EFFICIENCY AS A FUNCTION OF HYDROCHLORIC ACID CONCENTRATION

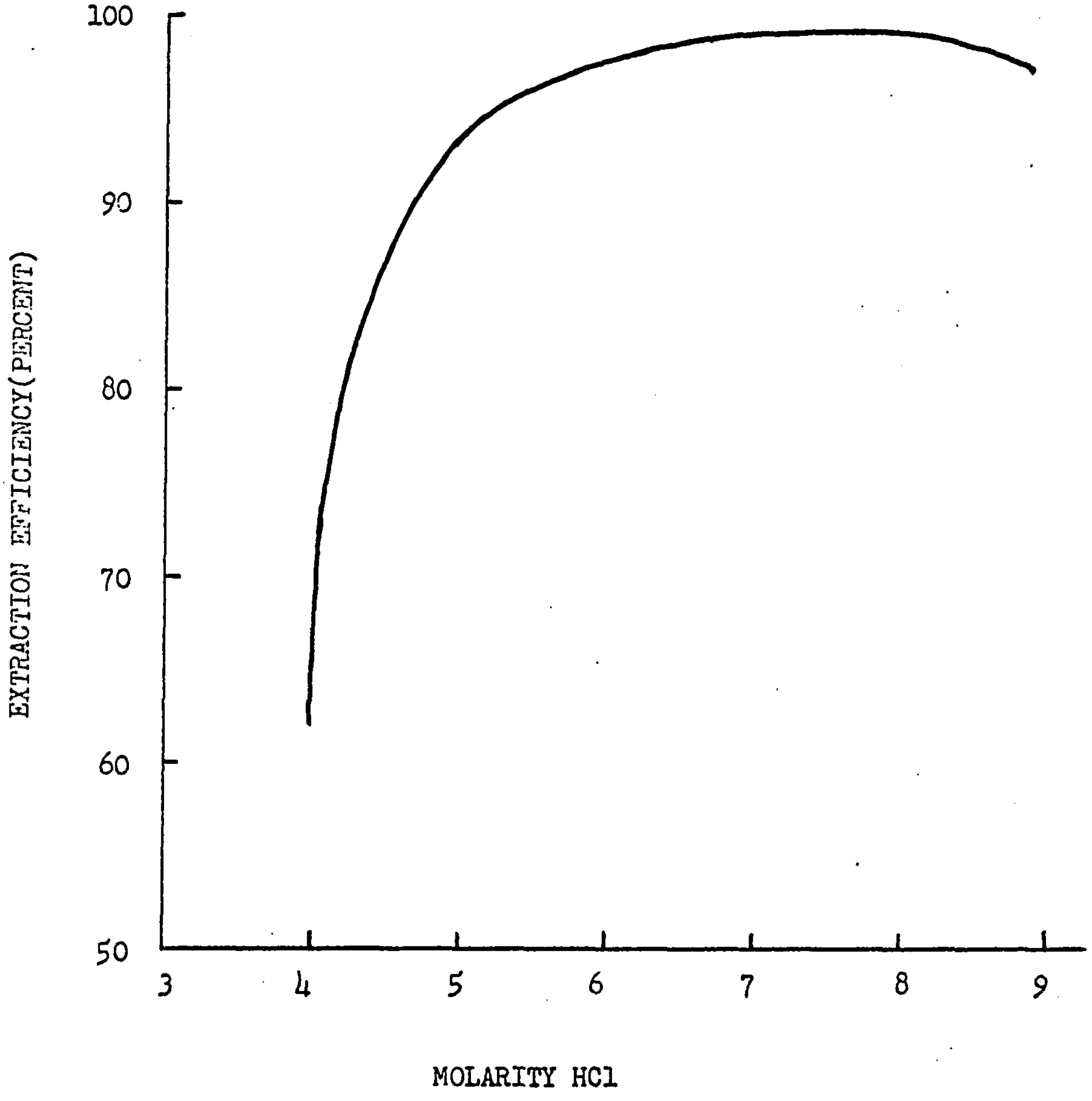


FIGURE 5

TABLE 2

DEPENDENCE OF EXTRACTION EFFICIENCY ON HCL CONCENTRATION

Molar Concentration of HCl	Percent Extraction
4	62.6
5	93.5
6	97.0
7	98.6
8	98.9
8.8	97.3

There is some problem associated with the experimental technique of studying the acid dependence of the extraction. If a quantitiative separation of the tungsten extracted with one aliquot is to be effected, it is necessary to rinse the residual aqueous solution with another portion of the organic solvent to remove suspended drops, etc. However, the rinse aliquot of organic solvent may also extract some amount of tungsten itself, so a rinse is not desirable. The procedure used and described in Section 9-Experimental was to add a given aliquot of chloroform of known volume and measure the absorbance of the separated filtered chloroform layer without diluting further to a known volume. The assumption is that the chloroform volume does not change in the course of the extraction. This is an assumption which is accurate to about five percent, for there is approximately a one milliliter uncertainty in the post-extraction volume of an original 25 ml. aliquot of chloroform. This uncertainty is insignificant for the purposes of the experiment.

TABLE 3

EXTRACTION OF HCl INTO CHLOROFORM

Composition of Aqueous Layer					Millimoles H+ Extracted into $CHCl_3$	Distribution Ratio for H+ ($CHCl_3/H_2O$)
Volume 12 M HCl	Volume 10% $SnCl_2$ in 12 M HCl	Volume H_2O	Volume 1.5 M KSCN	Volume 2.5 mM TPAC		
20	0	5	0	0	0.0590	2.46×10^{-4}
20	0	2	3	0	19.90	0.091
20	0	0	3	2	22.20	0.101
15	5	0	3	2	21.20	0.095

All volumes are in milliliters

240 millimoles of HCl taken for each extraction

One aspect of the acid dependence of the extraction is not indicated on the graph. This is the appearance of a precipitate at low acid concentrations. If the HCl concentration is below 6 M for the extraction, small green crystals form in the extracted chloroform layer after a few minutes. The lower the HCl concentration, the greater the rate of precipitation of the crystals. As the crystals appear, the absorbance correspondingly decreases.

Since the extraction requires a high acidity and HCl was the only acid with which the acidity could readily be achieved without other complicating factors, the study of the chloride dependence of the extraction was seriously hampered. The HCl provided a high chloride ion concentration, establishing a lower limit to the chloride concentration. Furthermore, not many cations will tolerate chloride concentrations of greater than 5 M, so an upper limit to the chloride ion concentration is also established. For these reasons, the tests for effect of chloride ion were limited to varying the chloride concentration with NH_4Cl while maintaining the HCl concentration at 5 M and then at 4 M and checking the percentage tungsten extracted and stability of the extract with respect to the formation of a precipitate. The data are in Table 4 and indicate that a high chloride ion concentration does increase the extraction efficiency and stability of the extract.

Since the thiocyanate is unstable in very concentrated acids, the extracts were made from about 7 M HCl in the analytical procedure. However, for high tungsten concentrations, i.e., greater than 40 μM in tungsten, the higher acid concentrations (9 to 10 M) must be used to prevent the formation of the green precipitate.

TABLE 4

DEPENDENCE OF EXTRACTION EFFICIENCY ON CHLORIDE ION CONCENTRATION

Molarity Chloride	Percent Extracted
5 M HCl	
5.12	88.8
5.42	93.5
6.00	95.6
6.56	99.4
4 M HCl	
5.50	24.4
6.33	66.4

The above results are similar to those obtained for the extraction of an ion-pair of a chloro complex in a strong acid medium. The extraction of the chloro acids of gold (III) and iron (III) with ether and di-n-octyl sulfoxide are examples of this, as is the extraction into chloroform of the ion-pair of TPAC and the tetrachloroaurate (III) anion. This kind of behavior is expected when the formation of a chloro complex in the free acid form is necessary for the extraction. But in the case of the extraction of the tungsten-thiocyanate complex, it is baffling, for qualitative tests have shown the absence of chloride in the precipitated complex. Furthermore, the aqueous complex is most stable in less than 4 M HCl. As mentioned in the Introduction, the aqueous thiocyanate complex of tungsten is also precipitated by TPAC at low acid concentrations. The question of why such a high acidity is necessary for the extraction and stabilization of the tetraphenylarsonium-tungsten-thiocyanate ion-pair remains unanswered.

New light was shed on the problem when it was discovered that a backwash of a chloroform extract with aqueous ammonium bifluoride caused a succession of color changes in the chloroform layer. The intense yellow color of the chloroform solution faded as the chloroform solution was shaken with the fluoride, and eventually the chloroform layer reddened. With continual shaking, however, the chloroform layer again became yellow. A spectrum of the resulting chloroform layer revealed that the absorption maximum of the solution had shifted about 4 mμ to the ultraviolet with no other apparent changes. The following explanation for the changes is hypothesized: the tungsten-thiocyanate complex is extracted into chloroform and rendered stable there by carrying along with it an 'outer sphere' of acid molecules, such as HCl and HSCN. The outer sphere complex is probably quite labile, and thus a high HCl concentration is necessary to insure its quantitative formation. This serves to stabilize the outer sphere complex in the chloroform solution. When the chloroform layer is shaken with aqueous ammonium-bifluoride solution, the acid groups are partitioned between the water and chloroform, causing the outer sphere complex in the chloroform to dissociate. The HF is also partitioned between the chloroform and water and displaces the other acids from the loose complex. The resulting higher field around the complex results in a slightly higher energy for the charge transfer absorption and a corresponding shift in frequency of the absorption band.

A number of experiments were performed which gave results consistent with the above hypothesis, but which were not conclusive. A chloroform extract was backwashed with water until all excess thiocyanate and chloride had been removed and the final wash tested neutral to pH paper. The chloroform extract, stable prior to the backwash, subsequently decreased in absorbance as green crystals formed in the solution. According to the hypothesis, the water washes had removed the acids from the $CHCl_3$ and the outer sphere acid molecules were now dissociating leaving a chloroform-insoluble species which precipitated. This precipitation was slow from dilute tungsten solutions but quite rapid from concentrated solutions.

An obvious extension of the above experiment is to resupply the washed chloroform solution with HCl and determine if the precipitation can be prevented. Unfortunately, (as seen from Table 3) pure, aqueous HCl is extracted only to a very small degree into chloroform, and thus it is impossible to provide a significant activity of acid without some other agent to carry in the acid. Use of another acid which is extracted into chloroform was suggested. Perchloric acid was tried but was found to oxidize the tungsten.

It is conceivable that a basic backwash would hasten precipitation by back-extracting the HCl more effectively. Thus four extractions were made and washed with 6 M HCl, 6 M NaOH, and distilled water respectively. One extract was used as a control and was thus not washed. No precipitation was noticed immediately, so the extracts were kept in contact with their washes overnight. During this period, green particles precipitated from the extract washed with water, no effect was noticed for the control or for the acid-washed extract, and the basic solution had extracted the yellow color from the chloroform layer. The spectrum of the yellow color in the base was not the same as it had been in the chloroform. No precipitation was noticed in the base treated extract. Thus, while the acid apparently had no effect (or perhaps a stabilizing effect) on the extract, nothing could be determined about the effect of a base wash on precipitation. Addition of pyridine to a chloroform extract caused no immediate noticeable change in the solution, but the solution gradually decreased in absorbance.

Spectral results indicate that the species which precipitates from the chloroform extracts has a composition similar to that of the original extracted species, for the crystals are easily soluble in acetone and in solution give a spectrum nearly identical to that of the chloroform extract. However, the absorption maximum is at 400 mμ rather than at 406 mμ.

Considering the tungsten atom to be surrounded by thiocyanate and hydroxyl or oxide primary ligands, one may conceive of acid molecules hydrogen-bonded to the sulfur atom of the thiocyanate groups or the oxygen atom of the hydroxyl or oxide groups.

Possibly, formation of a di- or polymeric tungsten species results from the removal of the acid groups. Polymeric species are known for tungsten (V) (20), and tungsten (VI) polymerizes easily. One dimeric bridge complex, $W_2Cl_9^{\equiv}$, is known for tungsten (III). Thiocyanates also have been reported to form bridge complexes using both a thiocyanate and an isothiocyanate linkage (21).

B. Reduction of Tungsten

Freund, Wright, and Brookshier (24) and Geld and Carroll (25) have extensively discussed the conditions for the reduction of tungsten with stannous chloride. While the experimental conditions were quite nicely discussed, there was no concrete evidence given concerning the oxidation number of the tungsten. The method adopted for reduction of the tungsten prior to its extraction in the case described here was essentially that of Geld and Carroll. The tungsten was heated with a large excess of $SnCl_2$ (1 mmole $SnCl_2$ to 5×10^{-4} mmoles tungsten) in concentrated HCl almost to boiling. The reduced tungsten solution was then chilled in an ice bath and diluted before the thiocyanate was added.

To determine the oxidation number of the tungsten in the complex, an attempt was made to reduce the tungsten to some known oxidation state and test for color formation and extraction. It was also attempted to determine the oxidation state of the tungsten after reduction with $SnCl_2$. Finally, attempts were made to determine the oxidation number of the tungsten in the complex itself.

A potentiometric titration of tungsten (VI) with $SnCl_2$ in hot, concentrated HCl proved ineffective, for no large deflection was observed.

Bismuth amalgam is known to reduce tungsten (VI) to tungsten (V) in concentrated HCl (26), and zinc amalgam is known to reduce tungsten (VI) to red tungsten (III) in concentrated HCl. Extraction of tungsten after reduction with bismuth and zinc amalgams as in Section 12 C&D - Experimental showed that both reductants put the tungsten in a state from which the complex could be formed and extracted into chloroform. Visible spectra of the two extracted solutions were qualitatively identical to those obtained after $SnCl_2$ reduction.

Crouthamel (18) suggested that the thiocyanate oxidizes tungsten (III) to tungsten (V) in acidic medium and claimed, without presenting supporting evidence, that the yellow thiocyanate complex of tungsten was a tungsten (V) complex. Gottschalk (14) showed that Ti (III) reduces W (VI) to W (V) in the presence of thiocyanate. Gottschalk used the method of Asmus to determine the reaction coefficients for the reduction reaction, and also attempted to determine the stoichiometry of the complex formation of thiocyanate with tungsten.

An attempt to verify the oxidation number of the tungsten in the extracted species took on two forms: 1.) treatment of the chloroform extract or the green crystals with silver nitrate and subsequent weighing of the reduced silver metal, and 2.) examination of the spectrum attributable to transitions between d electron energy levels in the tungsten. A discussion of the spectrum studies is found in Section 2 - Results and Discussion.

In the silver nitrate method, stannous chloride could not be used for reduction of the tungsten prior to the extraction, for some tin (II) is extracted into the chloroform along with the tungsten and causes reduction of the silver ion. Using an amalgam for the reduction, however, this problem is eliminated, for the amalgam is separated after the reduction of the tungsten. Even with the use of zinc amalgam as a reductant, two difficulties are evident. First, any thiocyanate and chloride present will be precipitated along with the silver metal, so it is necessary to wash out excessive quantities of these two ions prior to silver nitrate addition. This of course makes the extract unstable so that the amount of tungsten present in solution is in question. Secondly, hexavalent tungsten is formed and may precipitate as the hydrous acid. In the solid compounds, large amounts of thiocyanates and chlorides are not present, and the small amount of these salts precipitated may be removed with an ammoniacal wash. Ethanolic silver nitrate works much faster on the precipitates becasue they are more soluble in ethanol than in water.

No reproducible results were obtained either by treatment of the chloroform extracts or by treatment of the solid materials. The solids did not have a constant composition and apparently contained some other reducing agent in addition to the tungsten, for the weights of silver obtained indicated a change in oxidation number of seven or eight based on tungsten oxidation alone. These results were unrealistic even when a correction was made for precipitated tungstic oxide.

A Beer's law plot of the extracted tungsten using zinc amalgam as reductant was made, and an absorptivity was calculated assuming complete extraction of the tungsten. The absorptivity was 85% of the absorptivity of the complex formed in the analytical method developed with $SnCl_2$.

C. Formation of the Complex and Ion-pair

The aqueous thiocyanate-tungsten complex apparently has a low effective stability constant in fairly concentrated acid. Gentry and Sherrington pointed out that for maximum development of color in thiocyanate-tungsten systems, the HCl concentration would have to be less than

4 M. Freund, Wright, and Brookshier showed that for about 0.1 millimolar tungsten solutions, the thiocyanate concentration had to be greater than 0.2 M for full color development to take place. Thus in order to insure complete complex formation in the strong acid solutions, the aqueous phases in our work were approximately 0.25 M in potassium thiocyanate prior to extraction. However, extraction is still complete with a thiocyanate concentration of 0.03 M. With less than a ten-fold excess of thiocyanate over tungsten, extraction is incomplete. This fact is the basis of the determination of the stoichiometric ratio of thiocyanate to tungsten in the extracted complex.

It was also found that a greater than stoichiometric amount of TPAC was necessary in order to achieve complete extraction. Apparently the ion-pair formed from the tungsten-thiocyanate complex and tetraphenylarsonium ion is moderately soluble in water and thus needs a high concentration of TPAC to suppress its aqueous solubility and favor extraction. Normally a fifty-fold excess of TPAC was added for the quantitative extractions. Since tetraphenylarsonium thiocyanate and chloride are quite readily extracted into chloroform, it is necessary to replenish the TPAC before each chloroform extraction. It is not necessary to replenish the thiocyanate. The dependence of the extraction efficiency on TPAC concentration is used to determine the charge on the extracted anion.

4. Interferences

There are essentially three types of interferences possible in the proposed method of tungsten analysis. These interference types and some examples are discussed below.

a. The interfering substance itself may be extracted into chloroform and absorb light at 406 mμ. While many compounds absorb in this region of the spectrum, very few are likely to be present in tungsten bearing materials and also be extractable into chloroform under the conditions required for the tungsten determination. Thiocyanate decomposition products (thionic acids) may be one source of this type of interference, and thus precautions (such as chilling of solutions) are taken to reduce thiocyanate decomposition.

b. The interfering substance is extracted into chloroform and serves as an oxidizing agent to cause decomposition of the chloroform extract. The biggest problem of this type is the interference of nitrogen oxides. If nitrogen oxides happen to be present in the acid phase (from dissolution of a sample with HNO_3 and HCl), they are easily extracted into the chloroform layer. In the chloroform layer, the nitrogen oxides decompose the yellow solution to a red solution and eventually leave a colorless solution and a heavy yellow deposit.

Apparently, any trace of oxidant present in the chloroform extract will make the yellow complex unstable. It is now believed that the major difficulty encountered in obtaining a satisfactory Beer's law calibration line was due to the use of glassware which had not been thoroughly cleaned and thus had traces of oxidant of various kinds present.

In the analysis of some alloys, a scum is present after dissolution with HNO_3 and HCl. If the analysis is continued without further treatment of the acid solution, the extract is very unstable and the red color appears rapidly.

These interferences are easily eliminated by the following steps:

(1) Thoroughly clean all glassware with aqua regia, water, acetone, and chloroform in that order.

(2) When the presence of nitrogen oxides is suspected, repeatedly pre-extract the acid solution (without reduction, addition of thiocyanate, or addition of TPAC) with chloroform until the chloroform layer shows no trace of brown coloration. This chloroform extraction removes the nitrogen oxides. This same procedure should be followed for the solutions which have a brown scum, but filtration is also necessary to remove heavy silky precipitates in some cases.

c. The interfering substance forms a chloroform extractable species with thiocyanate or chloride and TPAC which absorbs at 406 millimicrons. This is the most common type of interference in an extraction analysis. The beauty of the proposed method for tungsten is that it is nearly free of interferences of this type. Ten metals commonly occurring with tungsten in various forms were tested by the method of Section 7 - Experimental, and only niobium was found to interfere significantly. The data are presented in Table 4.

The amazing selectivity of the method can be attributed to the combination of selection steps in the process of the analysis. First, the tungsten is reduced, and then the thiocyanate complex is formed. The $SnCl_2$ used to reduce the tungsten also reduces Fe (III) to Fe (II) and Mo (VI) and Mo (V) to Mo (III). While the higher oxidation states of these two metals form strong, interfering thiocyanate complexes, the lower oxidation states are harmless as far as the tungsten analysis is

INTERFERENCE OF OTHER METALS WITH TUNGSTEN DETERMINATION

Metal	Metal	Abs. (±.002)	γ W (found)	Error(γ)	Error(%)	γ W (taken)
V	250	0.297	91.6	-0.4	-0.3	92.0
Mo	1000	0.302	93.2	+1.2	+1.3	92.0
Co	1000	0.297	91.6	-0.4	-0.3	92.0
Cr	1000	0.296	91.4	-0.6	-0.6	92.0
Mn	1000	0.296	91.4	-0.6	-0.6	92.0
Ni	1000	0.297	91.6	-0.4	-0.3	92.0
Fe	7500	0.298	92.0	0.0	0.0	92.0
Ti	1800	0.300	92.6	+1.4	+1.5	91.2
Ta	9100	0.296	91.4	+0.2	+0.3	91.2
Nb*	37	0.298	92.0	0.0	0.0	92.0
Nb	37	0.462	106.8	+14.8	+16.1	92.0
None	----	0.298	92.0	___	___	92.0

*Chloroform extract washed with 10 ml. aqueous solution of 3 M $NH_4F \cdot HF$ in 6 M NaCl.

concerned. A number of the other metals still form thiocyanate complexes at this point - notably Co (II), Ni (II), Ti (IV), Nb (V), and Ta (V). Next the tungsten ion-pair with TPAC is precipitated. V (V), Co (II), Ti (IV), Ta (V), and Nb (V) also show precipitates at this point, as does Sn (II). The final step of the regular procedure is the chief separation step, for at the high acid strengths, the only colored species extracted are Nb (V) and the tungsten ion-pair. Some Sn (II) is also

SPECTRUM OF NIOBIUM EXTRACT IN $CHCl_3$

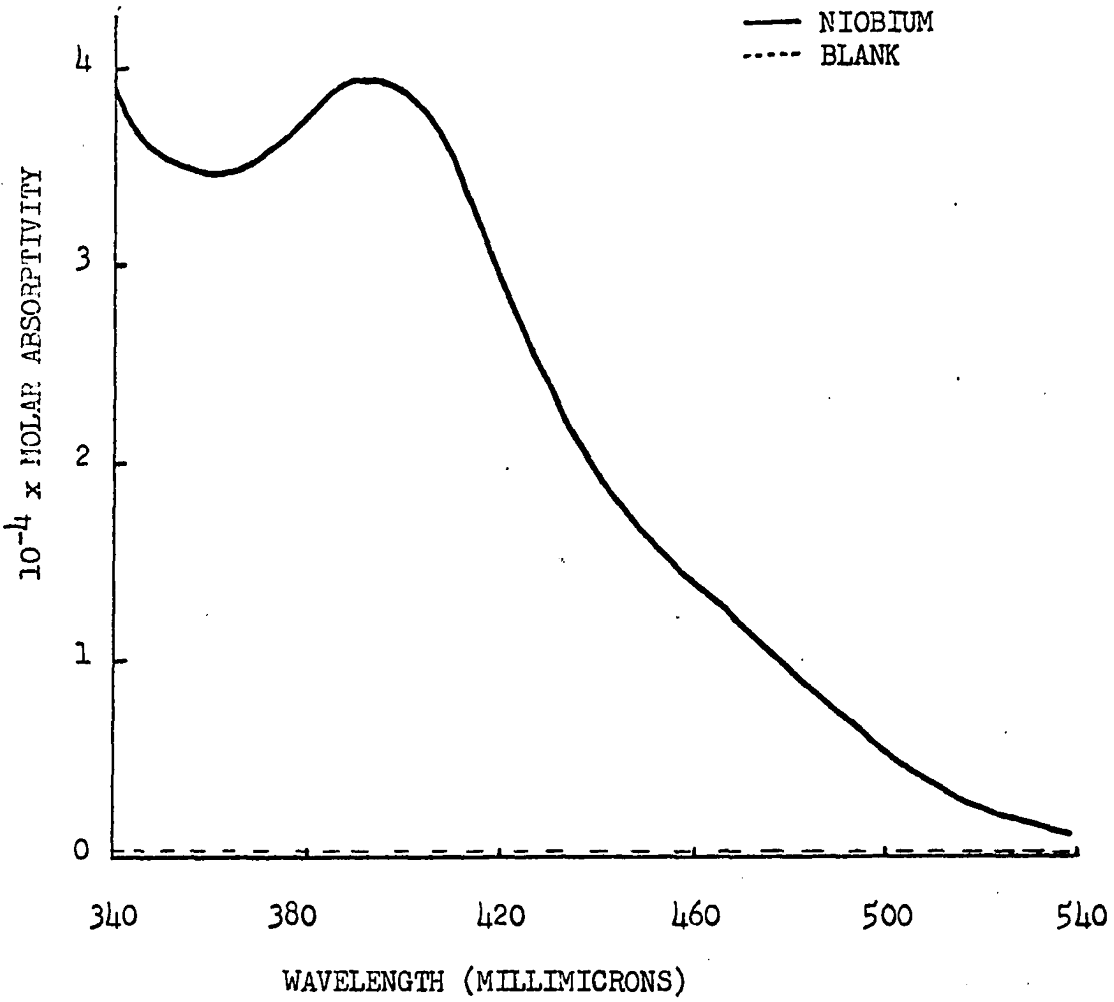


FIGURE 6

extracted. The TPAC is quantitatively extracted from the solutions, so the ion-pair precipitates which formed on the addition of TPAC disappear with the extraction, but little, if any, of the metals is extracted. In the absence of niobium, the final isolating step is seen to be the spectral measurement of absorbance, for although Sn (II) is extracted, its chloroform solutions are transparent at 406 mμ, where the tungsten absorbs and is measured.

The interference of niobium is eliminated by another complexation step after extraction. The $CHCl_3$ layer is shaken with an aqueous solution saturated with $NH_4F \cdot HF$. This causes formation of the NbF_6^- ion which is colorless. The tungsten remains in the $CHCl_3$, but the anion undergoes some sort of modification (Section 3A - Results & Discussion) and the maximum absorbance occurs at 402 mμ rather than 406 mμ. The niobium thiocyanate extract is yellow with a shoulder at 385 mμ and thus interferes considerably if it is not masked. The spectrum of the niobium extract is shown in Figure 6.

The severest test for freedom from interference from a conglomerate of metals is the analysis of alloys containing many and various metals. The next section describes the results of the analysis of a number of tungsten bearing alloys.

5. Alloy Analysis

The empirical process described in Section 11 - Experimental has been applied to fifteen tungsten bearing alloys of widely varying composition and tungsten content. The alloys contain some or all of the metals Co, Ni, Cr, Mo, Nb, Ta, V, Mn, and Fe in addition to W. The results of these analyses are listed in Table 6 along with the elemental

TABLE 6

RESULTS OF STEEL ANALYSES

Sample	% W Rep't	% W Found	Diff	Standard Deviation	Number of Samples	Sample Description and Percent Composition
NBS 50a	18.25	18.22	-0.03	±0.25	5	STEEL: (Cr)(3.5);V(1.0):Mn(0.4);C(0.6)
NBS 50b	18.05	18.16	+0.11	±0.04	4	STEEL: Cr(4.1);(V(1.0);Mo(0.4);C(0.7)
NBS123b	0.18	0.176	+0.004	±0.002	4	STEEL: Nb(.75);Ta(.2);Mo(.2);V(.05)
NBS132	6.29	6.26	-0.03	±0.05	5	STEEL: Cr(4.1);V(1.6);Mo(7.1);(Cu .15)
NBS 132a	6.20	6.19	-0.01	±0.07	7	STEEL: Cr(4.2);V(1.9);Mo(4.5);Mn(.3)
NBS 134	1.82	1.90	+0.08	±0.02	4	STEEL: Cr(3.7);V(1.1); Mo(8.7);C(0.8)
NBS 153	1.58	1.61	+0.03	±0.02	6	STEEL: Cr(4.1);Co(8.5);Mo(8.4);V(2.)
NBS 155	0.517	0.501	-0.016	±0.02	3	STEEL: Cr(0.5);Mn(1.24);Ni(.1);C(.9)
NBS 167	4.50	4.52	+0.02	±0.03	5	HRA: Ni(20);Co(41);Cr(20);Mo(4);Nb(3) Ta(1);Fe(3.4)
NBS 168	3.95	3.99	+0.04	±0.01	4	HRA: same as above
SS 2	4.33	4.35	+0.02	±0.08	5	STEEL: Cr, V
SS 4	17.77	17.20	-0.57	±0.03	4	STEEL: Cr, V
SS 10	2.85	2.99	+0.14	±0.01	6	STEEL: Cr, V.
SS 11	14,58	14.8	+0.2	±0.2	4	STEEL: Cr, V
SS 23	14.8	15.3	+0.5	±0.3	3	STEEL: Cr, V

composition of the alloys. The table is divided into two sections -- one listing results for National Bureau of Standards (NBS) samples and the other listing results for student steel samples. In the NBS analyses, only two determinations gave results which fell outside the reported range (Samples 50a and 155). Sample 134 differed the greatest from the reported value, but no range was reported for this sample. It is believed that the standard deviations for samples 50a and 153 could be reduced to values comparable to those of the other steels if more care is taken in running the analyses; however, a large number of determinations would be necessary before a significant reduction in the standard deviation could be made. Analysis of these samples shows comparatively low precision because the samples were the first studied, and the best technique was developed after their analysis. Carrying out a large number of determinations on these two samples seemed unwarranted.

The major time factor in alloy analysis is sample dissolution. Some nitric acid is required in the dissolution of almost all steels in order to oxidize the carbon, but because of the interference of nitrogen oxides as mentioned previously, it is desirable to keep the addition of HNO_3 at a minimum. A high ratio of HNO_3 to HCl also makes precipitation of tungstic acid possible. Therefore, as much of the steel as possible is dissolved in hot concentrated HCl. When the dissolution rate has slowed down considerably or stopped or when large amounts of carbon are present, concentrated HNO_3 is added dropwise to complete the dissolution. If a considerable amount of HNO_3 has been added, tungstic acid may precipitate when the solution is cooled. For this reason, it is best to transfer the hot solution directly to a volumetric flask, dilute almost to the full volume, and allow the solution to cool before final dilution. It is not necessary to evaporate the solutions to dryness to remove nitrates, for nitrates do not interfere (since they are not extracted into $CHCl_3$, while the oxides are). Furthermore, evaporation invariably causes tungstic oxide to precipitate, and the oxide is often difficult to redissolve. It is normally sufficient to boil the solution for about five minutes to remove all the nitrogen oxides, but if some are still present after dilution, they may be removed by a pre-extraction as described above. It is a good idea to check each solution for the presence of nitrogen oxides by shaking a small portion with $CHCl_3$. A brownish tint to the $CHCl_3$ indicates the presence of the oxides.

Some steels (particularly high-vanadium steels) leave a brownish-red scum (probably V_2O_5) after all the metal has dissolved. These samples always require a pre-extraction with chloroform, and often a filtration step is required to remove a silky white precipitate which remains after the pre-extraction.

Two Co-Ni-Cr base heat resisting alloys were analyzed. For these alloys, an excess of HNO_3 results in a rapid reaction but causes the eventual precipitation of niobic and tungstic acids which are very difficult to redissolve. With these alloys, it is best to be patient and use the method described in Section 11, N & O - Experimental for dissolution of the samples. The procedure is lengthy but is simple and sure.

When niobium is present, it must be masked with fluoride as described in the previous section. The fluoride wash used for this masking is best prepared immediately before the masking step by saturating about 10 ml. of H_2O with ammonium bifluoride. The wash solution is cold, which is desirable, because of the heat required to dissolve the fluoride. A little solid $NH_4F \cdot HF$ may be present with no ill effects. It is best to shake the $CHCl_3$ extract with the fluoride wash for about two minutes, or until the second yellow color appears to be fully formed. The absorbance of the final yellow solution should be measured at the absorption maximum which falls close to 402 mμ.

6. Study of Composition of Precipitate and Extract

A. Variational Analyses

The determination of the composition of the tungsten complex involved in the precipitation and extraction of tungsten has proved to be quite a formidable problem. Because of the instability of the tungsten-thiocyanate complex ion, a large excess of thiocyanate is always present when the complex is formed. Apparently tetraphenylarsonium thiocyanate has much the same solubility characteristics as the ion-pair of tetraphenylarsonium and the tungsten complex. Thus, we have not succeeded in obtaining a pure precipitate of the ion-pair by direct precipitation. Various methods of preparing the yellow salt were attempted as described in Section 13 A-Experimental. Subsequent analyses as discussed below, gave indefinite, uninterpretible results.

Since the salt proved difficult to isolate, it was decided to use some kind of concentration variational scheme to determine the stoichiometry associated with the extraction. It was felt that this kind of analysis would be more informative than direct precipitation analysis for it would furnish specific information about the extracted species rather than the precipitated species. This may be an important consideration as it is possible that a different species is precipitated than is extracted.

The same analytical technique was utilized to determine both the thiocyanate-tungsten ratio and tetraphenylarsonium to tungsten ratio in the extracted ion-pair. This analysis does not reveal the entire composition of the compound; however, it does tell the charge on the tungsten anion (since the cation charge is +1) and the number of thiocyanates in the anion. It does not tell the remaining components of the anion nor even the number of ligands bound to the tungsten.

To determine the molar stoichiometric ratio of tetraphenylarsonium to tungsten in the extracted species, a series of extractions of tungsten is made at a high and constant concentration of thiocyanate and HCl but a low and variable quantity of TPAC. Thus TPAC is the limiting reagent in each of the extractions.

A stoichiometric chemical equation is set up as follows:

$$1.)\quad n\,(C_6H_5)_4As^+ + WX_z^{-n} \rightleftharpoons \left\{\left[(C_6H_5)_4As\right]_n WX_z\right\}_{aq}$$

For convenience let $\left[\left[(C_6H_5)_4As\right]_n WX_z\right] = \left[W\right]$ and $\left[(C_6H_5)_4As^+\right] = \left[T\right]$.

For the formation of the aqueous ion-pair then,

$$2.)\quad \frac{\left[W\right]_{aq}}{\left[T\right]^n \left[WX_z^{-n}\right]} = K$$

Since all forms of tetraphenylarsonium are extracted quantitatively into the chloroform with one equilibration, the relative equilibrium compositions of the species involved in reaction 1) are not altered by the extraction. This is so if the extraction process is rapid compared to the complex formation so that all the species are extracted in the form in which they are present at the time of extraction. It is best to think of the extraction process simply as a tool which reaches in and picks out the already formed ion-pair complexes. Thus $[W]_{aq}$ is replaced by $[W]_{org}$ in equation 2) to give

$$3.) \qquad K_2 = \frac{[W]_{org}}{[T]^n \, [WX_z^{-n}]}$$

It will be noted that $[W]_{org} + [WX_z^{-n}]_{aq} = [W]_{total}$, i.e., the total tungsten concentration taken is the sum of the concentrations of tungsten in the respective layers. Also $[T]_{total} = [T]_{free} + n[W]_{org}$, since there are n tetraphenylarsonium radicals in each molecule of the tungsten ion-pair.

Equation 3) thus becomes

$$K_2 = \frac{[W]_{org}}{\left\{[T]_{total} - n[W]_{org}\right\}^n \cdot \left\{[W]_{total} - [W]_{org}\right\}}$$

or

$$4.) \qquad \frac{[W]_{org}}{([W]_{total} - [W]_{org})} = K_2 \left\{[T]_{total} - n[W]_{org}\right\}^n$$

The absorbance at 406 mμ is proportional to $[W]_{org}$.

Thus $[W]_{org} = A/a$, and for complete extraction $[W]_{org} = A_o/a$.

Equation 4.) now becomes

$$5.) \qquad \frac{A/a}{\left(\frac{A_o}{a} - \frac{A}{a}\right)} = K_2 \left\{[T]_{total} - n\,[W]_{org}\right\}^n = \frac{A}{A_o - A},$$

and taking logarithms of both sides, we have

PLOT FOR DETERMINING STOICHIOMETRIC
MOLAR RATIO OF TPA TO TUNGSTEN

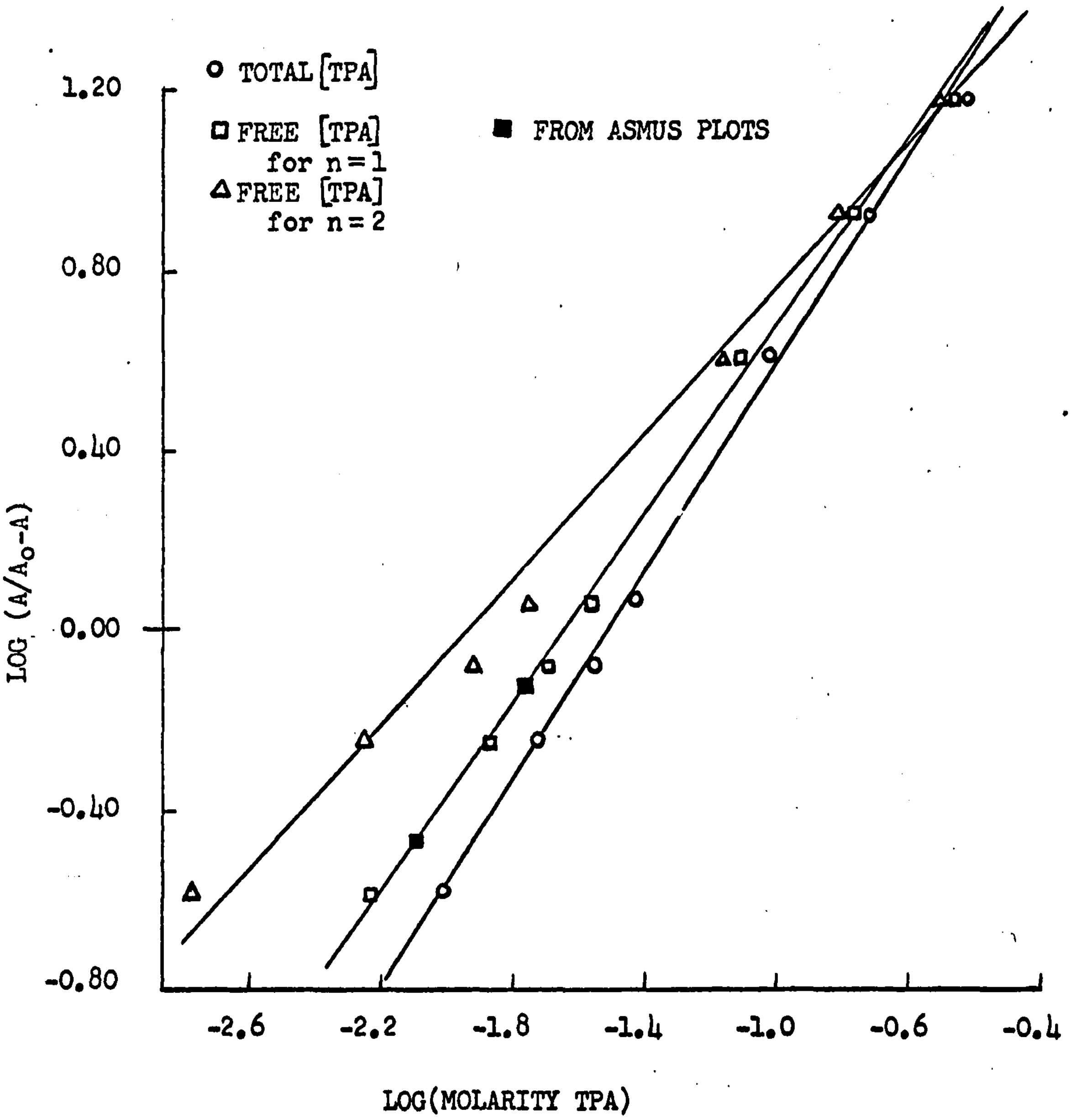


FIGURE 7

$$6.)\qquad \log\left(\frac{A}{A_o - A}\right) = \log K_2 + n \log\left(\left[T\right]_{total} - n\left[W\right]_{org}\right)$$

A plot of $\log\left(\frac{A}{A_o - A}\right)$ vs. $\log\left(\left[T\right]_{total} - n\left[W\right]_{org}\right)$ should, according to equation 6.), yield a straight line of slope n. Of course, n is not known, so it is impossible to compute $\left[T\right]_{total} - n\left[W\right]_{org}$. However, $\left[W\right]_{org}$ is normally small compared to $\left[T\right]_{total}$ and can be ignored for a first approximation. Thus a plot of log $(A/A_o - A)$ vs. log $\left[T\right]_{total}$ yields a straight line whose slope, n', is a fairly good approximation to n. The integer closest to n' is thus used to calculate $\left[T\right]_{total} - n\left[W\right]_{org}$ and a new plot is made of log $(A/A_o - A)$ vs. log $(\left[T\right]_{total} - n \left[W\right]_{org})$.

The slope of this new plot, n' ', should yield a more accurate value of the stoichiometric ratio. As seen in Figure 7 this was the case. n' was calculated as 1.15 and n'' as 1.02. Thus n was taken as 1. Assuming $n = 2$ in equation 6.), the data were more scattered and the slope was 0.86. Had 2 been the correct value for n, substitution for n by 2 in equation 6.) should have caused the slope to come closer to 2 rather than farther from two as was the case. In fact, equation 6.) shows that any acceptable (positive) value of n will cause the slope, n'', to be less than the slope n'. The greater the value of n, the greater the decrease in the value of the slope of the corrected plot over the value of the slope of the rough plot. Thus any value of n greater than 1 moves the slope lower and lower below one as well as increasing the scatter in the points. Using $\frac{1}{2}$ as the value of n, the slope is not decreased as much as it is for $n = 1$, and since the slope $n'' = 1.02$

EXTRACTION EFFICIENCY AS A FUNCTION OF TETRAPHENYLARSONIUM ION CONCENTRATION

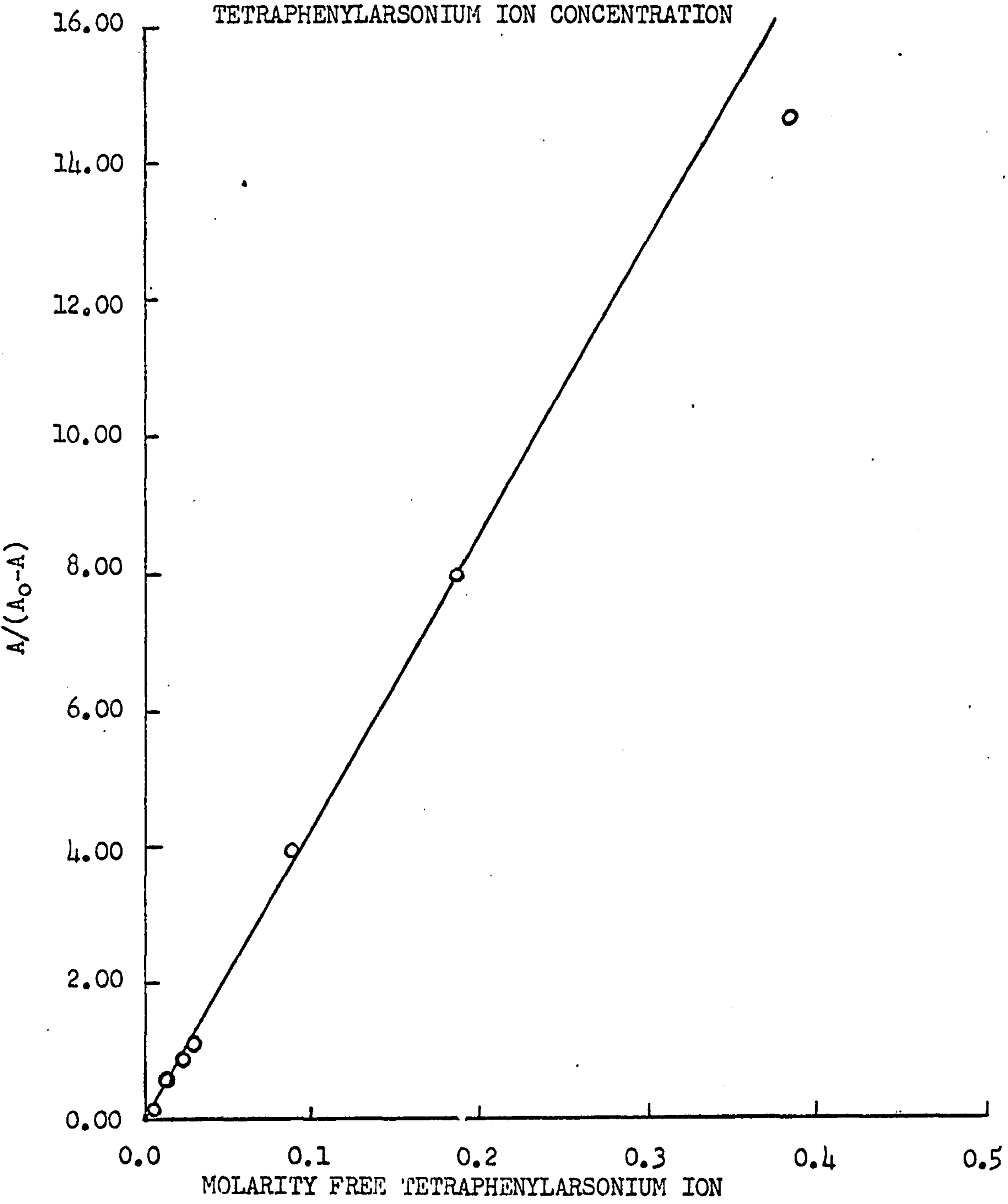


FIGURE 8

for n = 1, it is unlikely that $\frac{1}{2}$ is the proper value of n. With these arguments, it is evident that the results of the analysis indicate a value of 1 for n. All slopes were calculated by least squares analysis of the data.

For the experimental work, seven points were calculated from tetraphenylarsonium concentrations ranging from 10 μmolar to 400 μmolar and tungsten concentration of 20 μmolar. The data and calculations are presented in Table 7. For the high tetraphenylarsonium concentration term, the uncertainty is quite high, for the denominator of $A/A_0 - A$ is close to zero and an uncertainty of ± 0.002 in each absorbance reading gives a corresponding uncertainty of approximately 20% in the value of $(A/A_0 - A)$ and an even larger uncertainty in the logarithm.

Since n = 1, it is seen that a plot of $A/A_0 - A$ vs. $([T]_{total} - [W]_{org})$ should be linear. Figure 8 verifies this, although the scatter is great. Again the point with highest absorbance is highly uncertain.

A quite similar treatment was carried out for thiocyanate and tungsten. A stock solution of thiocyanate was prepared, and a variable volume of this stock solution was added to a constant quantity of reduced tungsten. Because of the precipitation of tetraphenylarsonium thiocyanate, only a ten-fold excess of TPAC was used, but this amount of TPAC maintained the TPAC concentration at an essentially constant value from one extraction to the next. The thiocyanate concentration ranged from about a five to a seventy-five fold excess, so the total added thiocyanate concentration, $[SCN]_t$, was essentially equal to the free thiocyanate concentration, $[SCN]_f$. As is seen below, this makes it possible to use the volume of thiocyanate added as the independent variable rather than the free thiocyanate concentration.

TABLE 7

DATA FOR VARIATIONAL ANALYSIS OF TPA - TUNGSTEN RATIO

$(TPA)_{tot}$	A	A/A_o-A	$(TPA)_{free}$			$(TPA)_{free}^{-n}$			1/A
			$n = 1$	$n = 2$	$n = \frac{1}{2}$	$n = 1$	$n = 2$	$n = \frac{1}{2}$	
0.010	0.061	0.260	0.00586	0.00173	0.008	170.5	345,000	11.2	16.40
0.020	0.106	0.562	0.0128	0.00600	0.0166	78.0	27,800	7.75	9.45
0.030	0.133	0.821	0.0210	0.0120	0.0256	47.6	6,950	6.25	7.51
0.040	0.157	1.138	0.0294	0.0187	0.0348	34.0	2,850	5.35	6.36
0.100	0.235	3.920	0.0841	0.0692	0.0922	11.9	209	3.28	4.26
0.200	0.262	7.940	0.1822	0.1645	0.1913	5.49	37.0	2.28	3.82
0.400	0.276	14.515	0.3813	0.3626	0.3908	2.62	27.6	1.60	3.64
*	0.125*	0.736*	0.0166*			60.0*			8.00*
*	0.071*	0.317*	0.00715*			140*			14.10*

(TPA) = millimolar concentration of tetraphenylarsonium ion

A = Absorbance

$A_o = 0.295$

* Points taken from Asmus plot for n = 1

The reaction may be represented by:

$$7.)\quad n\,SCN^- + (C_6H_5)_4As^+ + WX_z^- \rightleftharpoons [W]_{aq} + nX^-$$

The equilibrium expression for this reaction is

$$8.)\quad K_1 = \frac{[W]_{aq}[X^-]^n}{[SCN]_f^n\,[T]\,[WX_z^-]}$$

where $[W]_{aq}$ and $[T]$ have the same meanings as before. X^- is Cl^- and this concentration is large and constant between runs. As explained above, $[T]$ is also constant, so

$$9.)\quad \frac{[W]_{aq}}{[SCN]_f^n\,[WX_z^-]} = K_2$$

Assuming again that the chloroform extraction merely acts as an analysis tool, and using $[W]_{aq} = [W]_{org} = A/a$, we have

$$[WX_z^-] = [W]\text{ total} - [W]_{aq} = (A_o - A)/a$$ and equation 9.)

becomes

$$10.)\quad A/A_o - A = K_2\,[SCN^-]_f^n\ .$$

But $[SCN^-]_f = [SCN^-]_{total}$, so the total thiocyanate concentration is proportional to the volume aliquot of stock thiocyanate added. i.e.,

$$11.)\quad [SCN^-]_t = \frac{M_{KSCN}}{V_{total}} \times V_{KSCN} = k\,V_{KSCN}$$

substituting equation 11.) into 10.) gives

$$12.)\quad A/A_o - A = K_3\,V_{KSCN}$$

with $K_3 = k\,K_2$. Taking logarithms,

$\log(A/A_o - A) = \log K_3 + n \log V_{SCN}$, so that a plot of $\log(A/A_o - A)$ versus $\log V_{SCN}$ should have a slope of n. Note that it is not necessary to know the value of k, so the absolute thiocyanate

PLOT FOR DETERMINING STOICHIOMETRIC MOLAR RATIO OF THIOCYANATE TO TUNGSTEN

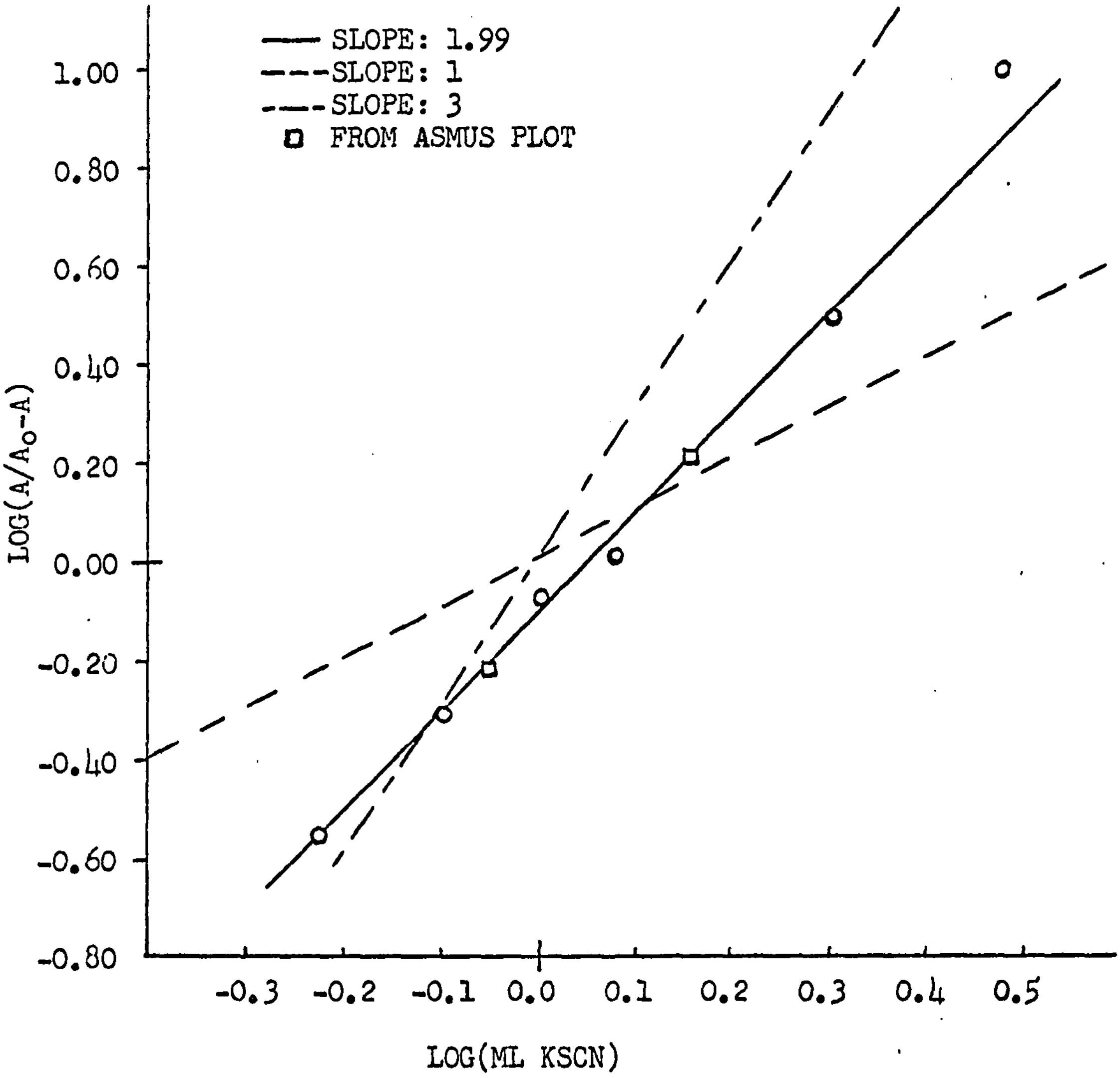


FIGURE 9

concentration need not be known.

For this plot, no refinement is required as it was in the TPAC variation, for the difference between the total thiocyanate concentration and the free thiocyanate concentration is always small in comparison to the total thiocyanate concentrations.

The data are tabulated in Table 8 and illustrated in Figure 9. The slope of the line by least squares analysis is 1.99 indicating an n value of two (2). Lines of slope one and three are also drawn in for comparison.

To check the data for both the TPA and thiocyanate variation experiments, the data were plotted according to the method of Asmus (19). Asmus showed that for a series of solutions of complex ions with a constant total concentration of metal ions, the absorbance due to the complex, A, was related to the volume, V, of ligand solution added from a stock solution of ligand and to the stoichiometric ratio, n, by

$$13.)\qquad \frac{1}{A} = b + \frac{c}{V^n} ,$$

(b and c constant) if the total volume was kept constant and if the complex was sufficiently weak that V was proportional to the free ligand concentration (i.e., the total ligand concentration was a good approximation to the free ligand concentration). The equation is valid for stronger complexes if put in the form

$$14.)\qquad \frac{1}{A} = b + \frac{d}{\left[X\right]^n_{free}} ,$$

where $\left[X\right]_{free}$ is the concentration of unbound ligand. b, c, and d are constants whose values depend on the absorptivity, concentrations of

TABLE 8

DATA FOR VARIATIONAL ANALYSIS OF THIOCYANATE - TUNGSTEN RATIO

V	A	A/A_o-A	LOG V	LOG (A/A_o-A)	1/A	V^{-n}		
						n = 1	n = 2	n = 3
0.60	0.128	0.277	-0.222	-0.557	7.81	1.66	2.76	4.59
0.80	0.196	0.498	-0.097	-0.302	5.10	1.25	1.56	1.95
1.00	0.268	0.833	0.000	-0.079	3.74	1.00	1.00	1.00
1.20	0.300	1.033	0.079	0.016	3.33	0.833	0.69	0.516
2.00	0.448	3.158	0.301	0.499	2.23	0.500	0.25	0.125
3.00	0.535	9.72	0.477	0.987	1.87	0.333	0.11	0.037
1.47*	0.364*	1.61*	0.168*	0.207*	2.75*		0.46*	
0.89*	0.222*	0.603*	-0.049*	-0.220*	4.50*		1.25*	

V = Volume of KSCN solution added (in milliliters)

A_o= 0.590

* Points taken from Asmus plot for n = 2.

ASMUS PLOT FOR DETERMINING THE

TETRAPHENYLARSONIUM-TUNGSTEN STOICHIOMETRY

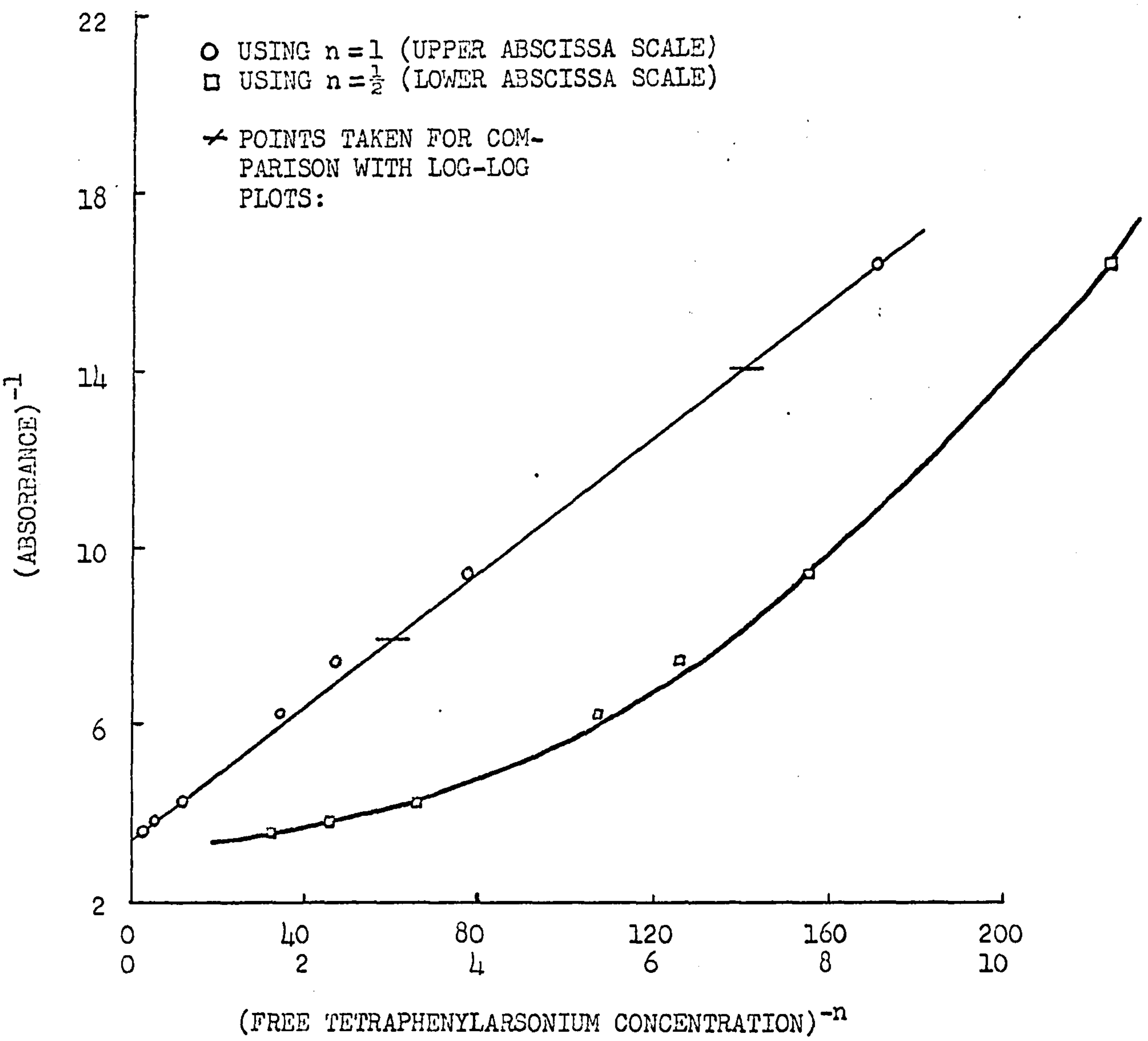


FIGURE 10

ASMUS PLOT FOR THIOCYANATE VARIATION

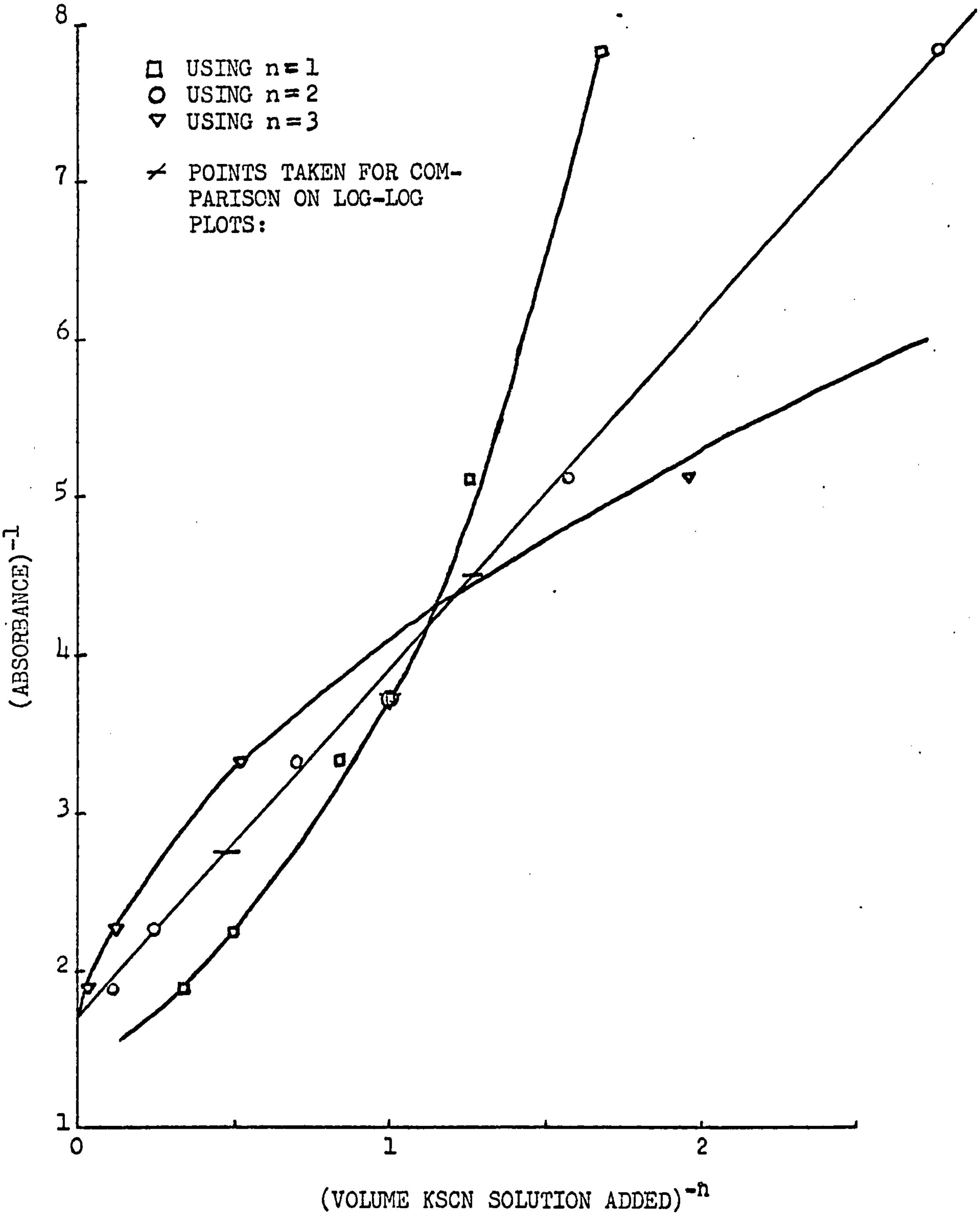


FIGURE 11

stock solutions, and volumes used. It is evident from equation 13.) that a plot of 1/A vs. $1/V^n$ for weak complexes yields a linear relationship if - and only if - n is the stoichiometric ratio of ligand to metal. Other values of n give curved plots. Thus, to evaluate n, one plots 1/A vs. $1/V^n$ for various values of n. The plot which is linear yields the corresponding value of n as the stoichiometric ratio. Likewise, a plot of 1/A vs. $1/\left[X\right]^n_{free}$ for stronger complexes yields a straight line only for the proper value of n.

The thiocyanate data were plotted according to equation 13.) and the TPA data according to equation 14.). The scatter for the Asmus plots was greater than that for the log-log plots. While the n = 2 plot for the thiocyanate and the n = 1 plot for the TPA were most nearly linear of the n values plotted, they alone would have given highly uncertain values of n. However, the two kinds of plot, the log-log and the Asmus type, agreed well with each other. Correlation between the two plots was checked in two ways. First, it was qualitatively noticed that points deviating from linearity on the log-log plots also deviated from smooth lines for all the values of n used to construct the Asmus plots. Secondly, smooth curves were drawn for the various n values of the Asmus plots. From these smooth curves, corresponding values of A and V or of A and $\left[X\right]_{free}$ were obtained. These values were used to calculate values of the corresponding log-log type and were plotted on the log-log graphs. The synthetic points from the Asmus curve fell very close to the least squares log-log lines for both the TPA and thiocyanate data. Figures 10 and 11 show the Asmus plots.

B. Preparation of Solid Compounds

Section 13 - Experimental describes the procedures used in preparing samples of the salt of tetraphenylarsonium and the tungsten-thiocyanate complex. The first method attempted was a direct precipitation of a large amount of reduced tungsten in the same manner as those samples prepared in the extraction process. The precipitated compound was filtered, washed with water, and air dried. This sample contained a large amount of excess tetraphenylarsonium thiocyanate. To help reduce the amount of tetraphenylarsonium thiocyanate impurity, the precipitation was carried out in a mixture of ethanol and HCl, since the thiocyanate salt of TPA is more soluble in ethanolic solutions than is the tungsten compound. The separated precipitate was then washed with water, ethanol, and a mixture of water and ethanol. Analysis of this compound by x-ray emission gave a molar ratio of arsenic to tungsten of 2.25 to 1. Thus it appears that excess tetraphenylarsonium thiocyanate was still present. Repeated washings with ethanol continued to remove the thiocyanate, but the composition of the compound remained about the same., probably due to the decomposition of the compound to give tetraphenylarsonium thiocyanate. If this is so, it is impossible to purify the compound by ethanol or water washes.

A large amount of the green crystals which precipitate from $CHCl_3$ solution following an extraction of the tungsten complex was prepared by scaling up the extraction process as described in Section 13 B - Experimental. While the crystalline appearance of this material is always the same, the composition varies depending on the conditions. The arsenic to tungsten molar ratio in the compound obtained by extraction from

SPECTRUM OF TETRAPHENYLARSONIUM CHLORIDE

IN CHLOROFORM

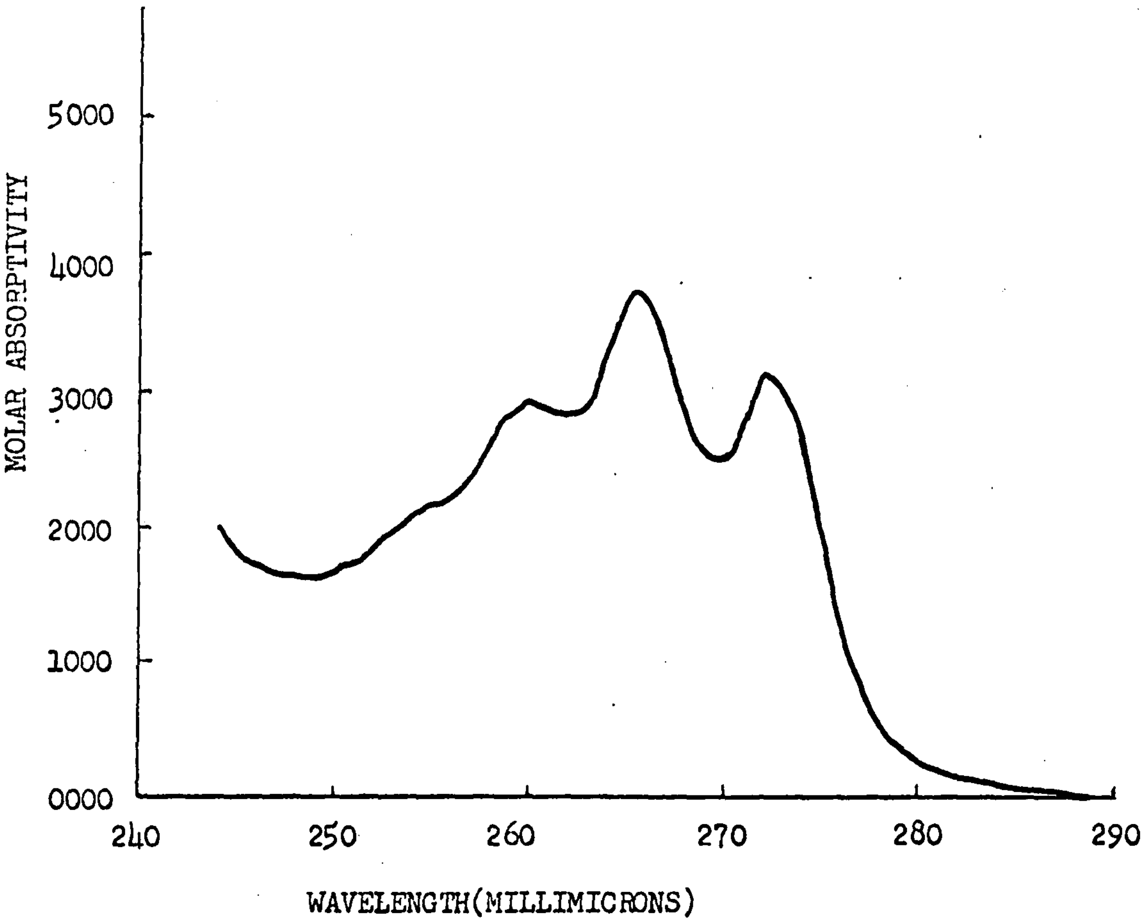


FIGURE 12

BEER'S LAW PLOT FOR TPAC IN $CHCl_3$ AT 265 mμ

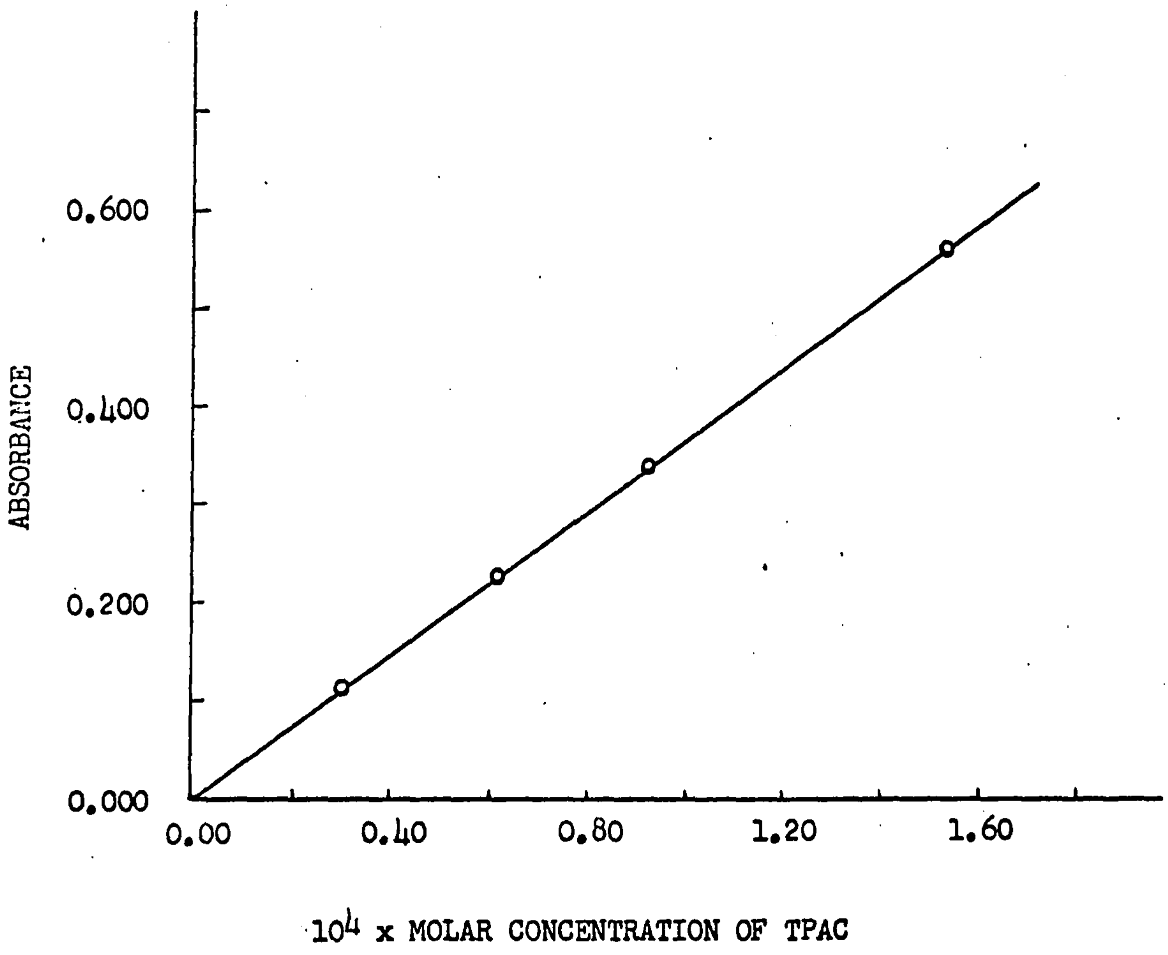


FIGURE 13

low HCl concentration was about 7 to 1. When the compound was prepared by backwashing a chloroform extract with distilled water, however, the arsenic to tungsten molar ratio was 2.5 to 1. Thus it is likely that these crystals are mixtures of two or more tetraphenylarsonium compounds and may be double salts of tetraphenylarsonium thiocyanate and a tungsten salt.

C. Spectrophotometric and Gravimetric Analysis of Solids

Section 13 C - Experimental describes the procedures used for analysis of arsenic and tungsten in the various prepared solids. Direct spectrophotometric analysis by dissolving the sample in chloroform or acetone was not possible because the solids were not soluble in chloroform and the acetone solutions were not sufficiently stable.

Nitric acid treatment of the samples completely decomposes them without affecting the tetraphenylarsonium ion. Tungstic acid precipitates. The tetraphenylarsonium ion can then be extracted into chloroform as the chloride to separate it from the nitrates which are present in the aqueous phase. The nitrates absorb very strongly in the ultraviolet. The TPA maximum at 265 $m\mu$ (Figure 12) is a convenient peak for analysis. The molar absorptivity at 265 $m\mu$ is 3645 $M^{-1}cm^{-1}$ using $CHCl_3$ as a solvent. (Figure 13).

The tungsten is recovered by evaporating most of the HNO_3 leaving a wet precipitate containing the tungstic acid. The tungstic acid is then easily dissolved in 1 to 6 M strong base and diluted to a suitable volume with concentrated HCl making sure the final HCl concentration is greater than 10 M. The tungsten solution is then analyzed by the method described in this paper.

An attempt at gravimetric analysis of the tungsten by filtering the precipitated tungstic acid and igniting the precipitate under the full heat of the Meker burner was unsuccessful, for the ignitate continued to lose weight with each ignition. The ignitate was originally yellow and then turned green.

D. X-ray Analysis of As/W Ratio

An x-ray emission spectroscopic procedure for determining the arsenic to tungsten molar ratio was developed. The samples were suspended on thin glass plates by melting parafin, adding the solid sample, and allowing it to settle evenly through the parafin onto the glass plate before the parafin had resolidified. The samples were irradiated with Cr radiation. The intensities of the arsenic $K\alpha$ line (1.1774A) and the tungsten $L\beta_1$ (1.2792 A) and $L\alpha_1$ (1.4734 A) lines were measured with a scintillation counter and read off an automatic read out device. A calibration curve was made by plotting the ratios of intensities of arsenic emission to tungsten emission versus arsenic to tungsten molar ratio for the standard samples. The ratio of intensities of arsenic emission to tungsten emission for the unknown was then located on the standard plot, and the corresponding molar ratio of the sample was computed.

X-ray emission analyses normally require quite careful control of conditions. For the analysis of the absolute quantity of material in a sample, the thickness of the sample and thickness of the references must be identical, and the intensity of the radiation must be constant. The composition of the reference and sample compounds must be similar, and the irradiated surfaces of the references and sample must be identical in form. However, when the ratio of two elements is determined, most of this care is unnecessary, for when the ratio of intensities is measured, each constituent serves as an internal reference for the other. The necessary conditions are that the distribution of the two constituents be even throughout the sample and that the intensity of irradiation of each constituent be affected in the same way by variation in sample size, sample thickness, surface irregularities, and incident beam intensity.

The calibration curve obtained was linear up to a molar ratio of three arsenics per tungsten before showing a positive deviation. Mixtures of $Na_2WO_4 \cdot 2H_2O$ and TPAC•HCl were used as the references. These compounds were analyzed chemically and found to be 99.5 and 99.8 percent pure, respectively. The two compounds were weighed separately and mixed to give samples having molar ratios of $\frac{1}{2}$, 1, 2, 3, and 4, of arsenic to tungsten. As_2O_3 was also used as the arsenic reference and was found to give a satisfactory calibration curve. The two compounds of the reference must be mixed thoroughly with a mortar and pestle to give a uniform sample.

7. Preliminary Study of Niobium Extraction Using TPAC

Experimentation showed that treatment of a niobium (V) thiocyanate solution in concentrated HCl with TPAC yielded a yellow, chloroform soluble precipitate. The absorption spectrum of a chloroform extract of this compound has a relative maximum as a shoulder at 385 mμ on the long wavelength side of a very strong band which continues increasing into the ultraviolet. The shoulder-peak is not interfered with by a blank absorption, so it is suited for use in spectrophotometric analysis. The spectrum is displayed in Figure 6, page 62.

An attempt was made to determine a Beer's law line for the absorbance of the extract at 385 mμ. While the extraction was apparently quantitative at high acid concentrations (7 to 10 M), a satisfactory Beer's law line was not obtained. However, it is believed that suitable conditions for a reproducible, quantitative extraction can be determined. It was noticed that the color of the extracts was not always the same, indicating that more than one extractable species may be formed.

The extractions were performed in the same manner as used in the tungsten determination without the reduction step. Variables which may be studied to improve the extraction are time of complex formation, temperature, and reagent concentrations.

If a suitable spectrophotometric analysis of niobium can be obtained from the above procedure, the analysis of niobium in the presence of many other metals should be possible. If iron or molybdenum is present in a niobium sample and tungsten is absent, treatment with stannous chloride should reduce the iron or molybdenum to oxidation states which do not interfere. Niobium (V) is not reduced by stannous chloride. In the presence of tungsten and the absence of such species as iron (III) and molybdenum (VI), specific analysis of the niobium could be achieved without a reduction step. Another aliquot of such a sample could be analyzed for tungsten by the method described in this paper. Use of a selective reductant to reduce iron and molybdenum and yet not affect tungsten would allow an analysis of niobium essentially free from interferences.

8. Summary

The analytical procedure developed for tungsten fulfills all the requirements for a good analytical method: it is specific for tungsten if niobium is masked by fluoride; it is sensitive, allowing analysis of tungsten in concentrations of 10^{-4} M; and the extracted species is stable for at least 24 hours. The major disadvantage is the interference of oxidizing agents such as nitrogen oxides, and care must be taken to exclude all such substances.

Variational analysis has shown the stoichiometry associated with the extraction to involve two thiocyanate ions and one tetraphenylarsonium ion per tungsten; however, a solid of constant composition could not be isolated.

The oxidation number of the tungsten in the extracted species is probably five, but no chemical verification of this was achieved.

A similar analytical procedure for niobium is apparently possible, and further work for its development is recommended.

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