THE COLORIMETRIC DETERMINATION OF
NIOBIUM WITH THIOCYANATE

by

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INTRODUCTION

A. METHODS FOR THE DETERMINATION OF NIOBIUM

Gravimetric Methods.

Up to now the most accurate and widely used methods
for the determination of niobium have been gravimetric.
Probably the most prominent researcher in the gravimetric
field has been Schoeller (30), who with his students made
extensive gravimetric studies of the analytical chemistry
of niobium and tantalum. In a recent paper Waterkamp (32,
pp.5-8) reviewed several different methods for the gravi-
metric separation of niobium and tantalum from steel and
some methods for the gravimetric separation of niobium from
tantalum. Gravimetric methods for niobium suffer from
three distinct disadvantages. First, determination in the
presence of tantalum, which is usually present with niobium,
is very difficult owing to the chemical similarity of the
two elements. Second, the procedures are tedious and time
consuming, and third, gravimetric methods are inadequate
for very small amounts of niobium.

Very recently a technique using octachloropropane
as a reagent for chlorinating earth oxide mixtures was
described (17, p.683). As a direct consequence of this, a
distillation separation of tin and titanium from niobium,

tantalum, and zirconium was effected, leaving those latter
elements spectroscopically free in only one chemical
operation. This provides a method of separation of
niobium, tantalum and zirconium from tin and titanium.

Volumetric Methods.

The fact that niobium can be reduced from the
pentavalent to the trivalent state with amalgamated zinc,
and then oxidized back to the pentavalent form with per-
manganate has formed the basis of a volumetric method for
niobium. Tantalum is not reduced under these conditions.
Studies with this method have been made by Cunningham
(5, p.233) and more recently by Knowles and Lundell (22,
p.405). Although capable of yielding accurate results, the
reduction and the oxidation steps are often not stoichio-
metric, thus causing large errors in some cases. The life
of the zinc reductor is very short, leading to costly and
time-consuming replacements of the amalgamated zinc.

Colorimetric Methods.

The best known colorimetric method for niobium is
based on the yellow color of perniobic acid formed when
pentavalent niobium in concentrated sulfuric acid solution
is treated with hydrogen peroxide. This method first
reported by Klinger and Koch (21, p.179) and Thanheiser
(31, p.260) was adapted by Geld and Carrol (11, pp.1098-
1101) for the determination of niobium in high temperature
alloys. In this method the solution containing up to

30 milligrams of pentavalent niobium was treated with 150
ml. of sulfuric acid (97 per cent) and evaporated until
fumes of sulfuric acid appeared, and the evaporation was
continued with continuous strong fuming (250°C. or higher)
until a volume of 125 ml. was reached. The beaker was
covered with a watch glass, and the solution was allowed
to cool at room temperature for 0.5 hour, and then was
transferred to a dry 200-ml. volumetric flask, rinsing
the beaker with sulfuric acid (97 per cent). One hundred
ml. of this master solution was transferred to a dry
100-ml. volumetric flask, 0.10 ml. of 30 per cent c.p.
hydrogen peroxide was added and the solution was mixed
well and left standing for ten minutes at room temperature.
Using a 420-mμ filter, the color intensity of the test
solution was compared against a portion of the same master
solution containing no hydrogen peroxide. The niobium
content was found by reference to a graph prepared from
similarly processed National Bureau of Standards steels
and by application of corrections for the interference due
to tungsten and titanium. To correct for the interference
of tungsten 0.43 mg. of niobium was deducted for each
25 mg. of tungsten in the sample.

To correct for the interference of titanium 1.38
mg. of niobium was deducted for each 10 mg. of titanium
present in the 100-ml. aliquot for niobium. The titanium
present was determined as follows. Ten ml. of the master

solution was diluted to 100 ml. with distilled water, 0.5 ml. of 30 per cent c.p. hydrogen peroxide was added and the solution mixed. The test solution of the sample was compared against the reagent blank solution in the photo-electric colorimeter using a 420-mu filter. The weight of titanium in a 100-ml. aliquot of the master solution was found by reference to a graph based upon known titanium solutions.

The two chief disadvantages of this colorimetric method are the inconvenience of working with concentrated sulfuric acid as a solvent and the lack of sensitivity of the method, as several milligrams of niobium are needed for sufficient color development.

Niobium can be reduced to the trivalent state by various metals such as zinc and tin in acid solution. In this way a brown color is obtained which can be made the basis of a colorimetric method, (28, p.213). This method has been used only for rough visual comparisons. Other reagents for niobium are pyrogallol and quinalizarin (28, p.213). No thorough study of the uses of these reagents for the quantitative colorimetric determination of niobium has been made.

B. THIOCYANATE METHODS FOR METALS

Since thiocyanate complexes are the basis of many
important colorimetric and spectrophotometric methods for
several metals, a brief review of these methods will be
given as a background for the work on the determination
of niobium.

Iron.

The oldest and best known of these thiocyanate
methods is the one for iron based on the red ferric thio-
cyanate complex, which has been the subject of numerous
investigations.

Woods and Mellon (33, p.551) made a critical
spectrophotometric study of this colored system. They
preferred the use of ammonium thiocyanate as the color
forming reagent and nitric acid as the solvent with Beer's
law being obeyed through the pH range 1.2 to 1.5. The
sensitivity and stability of the color was greatly
increased by using a 60 per cent acetone solution.

Peters and French (26, p.607) made a study of the
effect of variables such as hydrochloric acid concentra-
tion, thiocyanate concentration, iron concentration, acids
and anions, salts, and foreign ions on the ferric thio-
cyanate color. Ether extraction of the complex was also
studied. They found that the most favorable acidity was

0.01 N, larger and smaller amounts of acid giving less color. Increasing the thiocyanate overcame the effect of higher concentrations of hydrochloric acid to lessen color intensity. Also at higher concentrations of thiocyanate less acid was needed to develop the same color intensity. Increasing the thiocyanate progressively increased the colored substance with no indication of reaching a maximum.

By use of a filter type photometer with two color filters Brown (4, p.228) used thiocyanate for the colorimetric estimation of 0.07 to 0.5 mg. of iron in the presence of variable amounts of cobalt up to 90 mg.

More recently Kitson (20, p.664) determined simultaneously iron with cobalt and copper using thiocyanate as the reagent, utilizing the fact that the three complexes absorb most strongly at three widely different wave lengths.

From ion migration studies and molecular weight determinations Schlesinger and Van Valkenburgh (29, p.1216) arrived at the structure $Fe(CNS)_6^{---}$ for the ferric thiocyanate complex. However, Bent and French (3, pp. 568-572), Gould and Vosburgh (12, p.1631), Edmonds and Birnbaum (7, p.1472), and Harvey and Manning (14, p.4492), all using spectrophotometric methods concluded that the structure was $FeCNS^{++}$.

Cobalt.

The blue color formed with thiocyanate and divalent
cobalt in solutions containing organic solvents has also
been widely studied as a colorimetric method for cobalt.
Young and Hall (34, p.264) extracted the color with an
amyl alcohol-ether mixture and then analyzed this solution
colorimetrically. Their method proved satisfactory for
0.01 to 4.0 per cent cobalt although Beer's law was not
obeyed. Putsche and Malooly (27, p.236) applied the blue
cobalt-thiocyanate color to the determination of cobalt
in stainless steel. The steel was obtained in a slightly
acid medium and a single zinc oxide separation was made
to remove iron and other interfering elements. An
aliquot portion of the solution was reduced with sulfurous
acid, and a strong sodium thiocyanate solution was added.
After dilution to a definite volume, a measured amount of
acetone was added, and the intensity of the blue complex,
$Na_2Co(SCN)_4$ was measured by means of a photoelectric
colorimeter. The method had the added advantage that the
solution obeyed Beer's law.

Babko and Drako (2, p.1809) made an extensive study
of cobalt thiocyanate complexes in solution and confirmed
by spectrophotometric measurements and transference
determinations the formation of the blue $Co(CNS)_4^-$ ion.
In a recent paper Katzin and Gebert (19, p.5662) reported
the following on the cobalt thiocyanate complex. In very

dilute solution in acetone, cobalt (II) yields trithio-
cyanate and tetrathiocyanate complexes. In dilute solution
in isopropyl or t-butyl alcohol, only dithiocyanate and
trithiocyanate complexes are found. The extinction
coefficient of the tetrathiocyanate complex is about twice
that of the trithiocyanate complex. In relatively
concentrated solution in acetone, an unstable complex
involving a single thiocyanate group can be identified.

Copper.

Kitson (20, p.664) determined cobalt simultaneously
with copper and iron by forming the thiocyanate complexes
of all three metals together in one solution and measuring
the absorbancies at three different wave lengths. This
was the first paper that proposed the cupric thiocyanate
complex as a basis for the determination of copper. The
cupric thiocyanate complex, like the cobalt complex,
develops only in solutions containing organic solvents
such as acetone. It is probably due to a complex ion,
and is readily reduced, being so unstable that a holding
oxidant must be used to make accurate color measurements.

Molybdenum.

Molybdenum forms an orange-colored complex with
thiocyanate and stannous chloride in strong acid solution.
This serves as a basis for a rapid colorimetric determina-
tion of molybdenum. Hoffman and Lundell (18, p.497) give
a procedure for the colorimetric determination of

molybdenum in substances containing rhenium, which also forms a complex with thiocyanate. In their method a dilute hydrochloric acid solution is shaken with mercury, potassium thiocyanate, and ethyl ether, but only molybdenum is reduced to the form which produces an ether-soluble colored compound with thiocyanate. The color of the ether extract serves for the determination of molybdenum. Addition of stannous chloride to the acid solution remaining after the molybdenum has been extracted produces a yellow to yellowish-red ether-soluble compound which serves for the determination of rhenium. Hiskey and Meloche (16, p.1565) made a study of the nature of the thiocyanate complex of molybdenum. From their investigations they concluded that the molybdenum is present in the complex in the pentavalent state and that the ratio of thiocyanate to molybdenum is three to one. Ellis and Olson (8, p.328) reported that the use of acetone as a reducing agent increased the sensitivity and eliminated the rapid fading of the color complex encountered when other reducing agents were used.

Rhenium.

Rhenium is known to form a colored complex with thiocyanate which is the basis of a colorimetric determination of that metal. Hiskey and Meloche (14, p.652) describe a method for the quantitative determination of 5-microgram amounts of rhenium in the presence of

millionfold excesses of molybdenum which combines a
modified distillation and modified colorimetric technique.
Melaven and Whetsel (23, p.1209) reported a method for the
quantitative colorimetric determination of rhenium with
thiocyanate, but their method is not recommended for
samples containing more than 1 mg. of molybdenum. Malouf
and White (24, p.497) have very recently presented a
colorimetric method using thiocyanate for small amounts of
rhenium in the presence of large amounts of molybdenum.
The molybdenum is separated from rhenium as a metalorganic
compound, formed with ethyl xanthate, and extracted from
dilute acid solution with an organic solvent mixture. The
rhenium is then determined with stannous chloride and
sodium thiocyanate, with ether extraction.

Uranium.

Currah and Beamish (6, p.609) have developed a
colorimetric determination of uranium with thiocyanate.
The determination is based on the estimation of the color
produced with thiocyanate and a hydrochloric acid solution
containing uranyl ion and stannous chloride.

Tungsten.

If thiocyanate and stannous chloride in hydrochloric
acid are added to a tungstate solution containing sodium
hydroxide, a yellow color slowly forms in the acid
solution on standing. A method for the determination of
tungsten in low grade tungsten ores based on this reaction

has been worked out by Grimaldi and North (13, p.652).
Aliquot portions were adjusted to deal with quantities of
tungsten ranging from 0.04 to 0.40 mg. of tungsten
trioxide. The maximum permissable concentrations of
possible interfering ions were determined and a graphical
method of correcting for the usually slight interference
of molybdenum was developed. Geld and Carrol (11, p.1098)
determined tungsten in high temperature alloys containing
niobium using the stannous chloride-thiocyanate reaction.
Niobium did not interfere because the solution was about
6 N in sulfuric acid. Freund, Wright, and Brookshier (10)
have recently made a study of the variables involved in
the stannous chloride-thiocyanate method for the colori-
metric determination of tungsten. Freund and Dreisbach
(9) have recently concluded that only pentavalent tungsten
is involved in this stannous chloride-thiocyanate method.

C. THE USE OF THIOCYANATE FOR THE COLORIMETRIC DETERMINATION OF NIOBIUM

Since pentavalent tungsten forms a complex with
stannous chloride and thiocyanate, work was started to
attempt to form a similar complex with niobium. A search
of the Chemical Abstracts revealed no such reaction for
niobium. The 1949 Chemical Abstracts were not available
as they were at the bindery. After preliminary work had
been begun on the niobium thiocyanate complex, a search of

the 1949 Chemical Abstracts revealed a paper by Russian
chemists (1, p.30) reporting that pentavalent niobium
forms a yellow-colored complex with potassium thiocyanate
and hydrochloric acid. This complex is extractable with
various immiscible organic solvents, and a colorimetric
method was devised by them in which the niobium thio-
cyanate is extracted with ether and compared with standards.
Curves obtained by plotting per cent transmission of the
ether solutions against wave length were given for two
different niobium concentrations in the wave length range
of 400 to 700 mμ. The curves show a drop in per cent
transmission as the 400 mμ mark is neared, but they were
not carried far enough into the ultraviolet region to
produce minima. Curves are shown which show the variation
of extinction with hydrochloric acid and potassium thio-
cyanate concentration. A standard plot is shown in which
extinction is plotted against mg. niobium pentoxide per
10 ml. of ether solution. Color measurements for this
curve were apparently made with a photoelectric colorimeter
type of instrument using a filter with maximum transmission
at 500 mμ. Their experimental directions for a niobium
analysis was as follows. Mix the sample with 0.5 to 2.0
g. of potassium pyrosulfate, and fuse at 600-700°C. If
the fusion reaction is incomplete, add a few drops of
concentrated sulfuric acid and fuse again. Cool, dissolve
in 10-20 ml. of hot 15 per cent tartaric acid solution,

transfer into a 25 to 100-ml. (depending on size of sample) volumetric flask, and add water to the mark. Transfer (pipet) an aliquot containing 0.008-0.2 mg. of niobium pentoxide to a ground-glass stoppered cylinder, add 5 ml. of 20 per cent potassium thiocyanate, 3 ml. of 15 per cent stannous chloride, and 5 ml. of hydrochloric acid. Mix after each addition. To this solution add 10 ml. of ether and shake well. In the presence of niobium, the ether layer will be yellow. If more than 0.1 mg. of niobium is present, the yellow color appears even before the addition of ether. The maximum intensity of color appears after 30-40 minutes and remains for several hours. After some time the intensity of color will increase owing to decomposition of thiocyanic acid. Measure the color intensity by comparing with standards. Interfering substances listed were molybdenum, tungsten, uranium, vanadium, iron, chromium, cobalt, copper, gold, platinum, oxalate, fluoride, sulfate, phosphate, and arsenate. Oxalate interfered most; sulfate, phosphate and arsenate caused discoloration when present in considerable excess. Tantalum apparently gave no interference up to 100:1 ratios of tantalum pentoxide to niobium pentoxide, but results of these analyses were only given to one or two significant figures.

Lauw-Zecka and Hume (23) have recently developed a spectrophotometric method for niobium based on extraction

of the niobium thiocyanate complex with diethyl ether.
They also report no interference from tantalum.

This thesis presents a study of the factors
influencing the formation of the niobium thiocyanate com-
plex, thereby improving both the reliability and applica-
bility of the method. The major part of the work deals
with the use of homogeneous systems, eliminating the ether
extraction. A study is made of the variables involved in
the use of homogeneous systems, and optimum solution
conditions for the determination are selected. Extraction
of the complex with an immiscible solvent provides a
convenient means of separation and concentration of niobium
and its retention under certain circumstances may be
desirable. A method for extraction of the complex with an
immiscible solvent is given in this work and a comparison
of the two procedures is made. The effects of certain
interfering ions are studied. A procedure is given for the
colorimetric determination of niobium in stainless steel.

APPARATUS AND SOLUTIONS

Beckman Model DU Spectrophotometer.

All spectrophotometric measurements were made with a Beckman Model DU Spectrophotometer. Matched 1.00 centimeter Corex cells were used for all absorbancy measurements. When aqueous systems were used, the instrument was set at 0.000 absorbancy with distilled water in the null cell. In using isopropyl ether solutions pure isopropyl ether was used in the null cell.

Standard Niobium Solution.

A standard solution was prepared containing 0.0355 mg. of niobium per ml. by fusing 0.0508 grams of pure niobium pentoxide obtained from A. D. MacKay, 198 Broadway, New York 7, with 1-2 grams of potassium bisulfate, dissolving in 75 ml. of hot 0.5 M tartaric acid, and diluting to 1.000 liter with distilled water.

Two Molar Stannous Chloride.

The solution was made by dissolving 113 grams of c.p. stannous chloride dihydrate in concentrated hydrochloric acid and making up to 250 ml. with concentrated hydrochloric acid.

Three Molar Potassium Thiocyanate.

The solution was prepared by dissolving 292 grams of c.p. potassium thiocyanate in distilled water and diluting to 1 liter with distilled water.

Standard Titanium Solution.

A standard solution was prepared containing 0.0596 mg. titanium per ml. by fusing 0.0995 gram of titanium dioxide with 2 grams of potassium bisulfate, dissolving in 75 ml. of hot 0.5 M tartaric acid, and diluting to 1.000 liter with distilled water.

Standard Tantalum Solution.

A standard solution was made containing 0.0819 mg. of tantalum per ml. by fusing 0.1000 gram of tantalum pentoxide with 5 grams of potassium bisulfate, dissolving in 75 ml. of hot 0.5 M tartaric acid, and diluting to 1.000 liter with distilled water.

Standard Tantalum-Niobium Solutions.

The solutions were prepared by mixing an accurately weighed amount of tantalum pentoxide with 0.1008 gram of niobium pentoxide, fusing the mixture with 10 grams of potassium bisulfate, dissolving in 150 ml. of hot 0.5 M tartaric acid, and diluting to 2.000 liters with distilled water.

Magnesium Chloride Solution (4.71 M).

The solution was prepared by dissolving 454 grams of c.p. magnesium chloride hexahydrate in 181 ml. of distilled water. Analysis by titration of a diluted aliquot with standard silver nitrate gave 9.42 moles of chloride per liter or 4.71 moles of magnesium chloride per liter.

NATURE OF COLOR REACTION IN A HOMOGENEOUS SYSTEM

A pale yellow color is formed when 5 ml. of the
niobium standard solution (0.0355 mg. niobium per ml.) is
mixed with 5 ml. of concentrated hydrochloric acid, 1 ml.
of 2 M stannous chloride and 5 ml. of 3 M potassium thio-
cyanate. The stannous chloride serves to reduce traces of
iron, thereby preventing the interference due to the
ferric thiocyanate complex. Dilution with water bleaches
the color completely. Consequently aqueous systems as
such offer little hope for the development of a sensitive
colorimetric method.

The preferential solubility of the niobium thio-
cyanate complex in ether, with its resulting increase in
color intensity, suggests the use of aqueous systems
containing various organic solvents miscible with water.
Those studied were acetone, dioxane, methyl cellosolve,
ethyl alcohol, methyl alcohol, and i-propyl alcohol. The
experimental procedure for this investigation was as
follows. Exactly two ml. of standard niobium solution,
10.00 ml. of concentrated hydrochloric acid, 1.00 ml. of
2 M stannous chloride, 10.00 ml. of organic solvent,
10.00 ml. of 3 M potassium thiocyanate were pipetted into
a 50-ml. volumetric flask. The solution was made up to
50.00 ml. with distilled water and well mixed. Absorbancy
readings were taken at 385 mμ.

TABLE I

EFFECT ON NIOBIUM THIOCYANATE COMPLEX ABSORBANCY OF THE ADDITION OF CERTAIN MISCIBLE ORGANIC SOLVENTS

Solvent	Absorbancy
acetone	0.344
dioxane	0.230
methyl cellosolve	0.141
water	0.072
i-propyl alcohol	0.066
ethyl alcohol	0.048
methyl alcohol	0.041

The solvents are listed in Table I. Many resulted in increased absorbancy ($\log_{10} I_o/I$) over that obtained in a water system, but acetone and dioxane offer the greatest promise.

Several common mineral acids such as hydrochloric, perchloric, phosphoric, and sulfuric were tried as the source of the free acid. With the high salt concentrations in the acetone-water systems both perchloric and phosphoric acid caused precipitation, and the complex was bleached by sulfuric acid. Hence hydrochloric acid was used in the subsequent experimental work.

EFFECT OF VARIABLES ON THE NIOBIUM
THIOCYANATE COMPLEX ABSORBANCY

Effect of hydrochloric acid concentration on absorbancy.

In an effort to obtain an optimum hydrochloric acid concentration, a study was made of the effect of acidity on the formation of the niobium thiocyanate complex. The experimental procedure was as follows. Varying amounts of concentrated hydrochloric acid from 0.00 ml. to 25.00 ml. were pipetted into a series of 50.00 ml. volumetric flasks. Two M stannous chloride (1.00 ml.), 2.00 ml. of standard niobium solution, 10.00 ml. of acetone, and 10.00 ml. of 3 M potassium thiocyanate were then added. Each sample was diluted to the mark with water, thoroughly mixed, and placed in a thermostat at 20.0°C. For each different concentration of hydrochloric acid used, a blank containing no niobium was prepared in the same manner. Absorbancy readings on all solutions were taken fifteen minutes after color development. The time of standing and the temperature were held constant in order to minimize the value of the blank. The blank effect, which was studied in some detail, is caused by polymerization of thiocyanic acid and has a high absorbancy maximum at 345 mμ. When certain reagents as acetone are added to the mixture in the flask, a large quantity of heat is liberated and the mixture becomes quite warm. If the solution containing thiocyanic acid is allowed to stand

warm for some time, the polymerization reaction proceeds much faster, and the absorbancy due to this reaction overlaps the absorbancy due to the niobium thiocyanate complex at 385 mμ. This effect will increase with temperature and time. In this study absorbancies were determined at 385 mμ, the wave length of maximum absorption of the complex. Water was placed in the null cell, and the absorbancy due to the niobium thiocyanate was obtained by subtracting the absorbancy of the blank from the value for the total absorbancy of the solution. The data are shown in Table II and plotted in Figure 1. The addition of more than 15 ml. of concentrated hydrochloric acid caused salting out of the potassium thiocyanate. Moreover high acidity causes increasing blanks due to polymerization of thiocyanic acid. Hence 10 ml. of concentrated hydrochloric is used as a compromise.

TABLE II

EFFECT OF HYDROCHLORIC ACID CONCENTRATION ON ABSORBANCY

Volume of conc. hydrochloric acid in ml.	Total Absorbancy of solution	Absorbancy of blank	Absorbancy of niobium thiocyanate
0.00	0.028	0.023	0.005
2.00	0.041	0.021	0.020
5.00	0.106	0.023	0.083
7.00	0.141	0.017	0.124
10.00	0.341	0.029	0.313
12.00	0.380	0.023	0.357
15.00	0.408	0.026	0.382
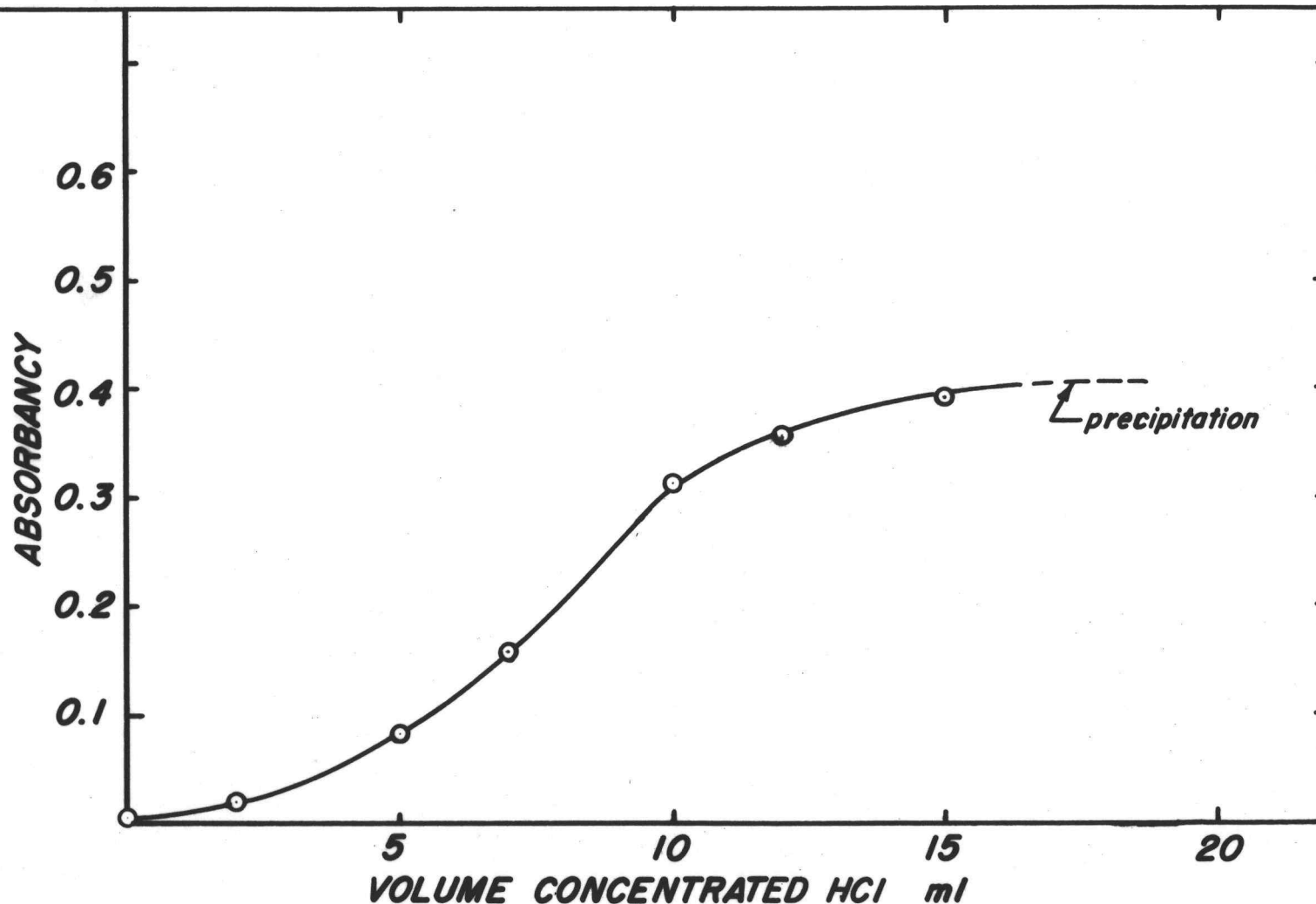
FIGURE 1. EFFECT OF HYDROCHLORIC ACID CONCENTRATION ON ABSORBANCY

Effect of chloride ion concentration on absorbancy.

Because of the increase in absorbancy of the niobium thiocyanate complex with increasing hydrochloric acid concentration it was decided to attempt to find out whether this change was caused by free acid, by chloride ion, or by both. In preliminary experiments it was determined that in order to produce a significant color development a moderate amount of hydrochloric acid had to be added to the solution. When this amount was present, however, an increase of chloride ion concentration (accomplished by adding chloride in the form of a neutral soluble salt) caused an increase in absorbancy. A quantitative study of the effect of chloride ion on the absorbancy of the niobium thiocyanate complex was made using the same procedure as the hydrochloric acid study, except that 5.00 ml. of standard niobium solution, 5.00 ml. of acetone, and a constant value of 1.27 moles per liter of free acid, together with varying amounts of 4.71 M magnesium chloride solution (9.42 molar in chloride) were used. These results shown in Table III are plotted in Figure 2. From these results it is thus concluded that both free acid and chloride ion play an essential role in the formation of the niobium thiocyanate complex.

TABLE III

EFFECT OF CHLORIDE ION CONCENTRATION ON ABSORBANCY

Chloride ion concentration in moles per liter	Total absorbancy of solution	Absorbancy of blank	Absorbancy of niobium thiocyanate complex
1.34	0.069	0.018	0.051
1.72	0.097	0.020	0.077
2.28	0.160	0.021	0.139
2.66	0.214	0.023	0.191
3.22	0.359	0.023	0.336
3.58	0.499	0.038	0.461
4.13	0.663	0.049	0.614

FIGURE 2. EFFECT OF CHLORIDE ION CONCENTRATION ON ABSORBANCY
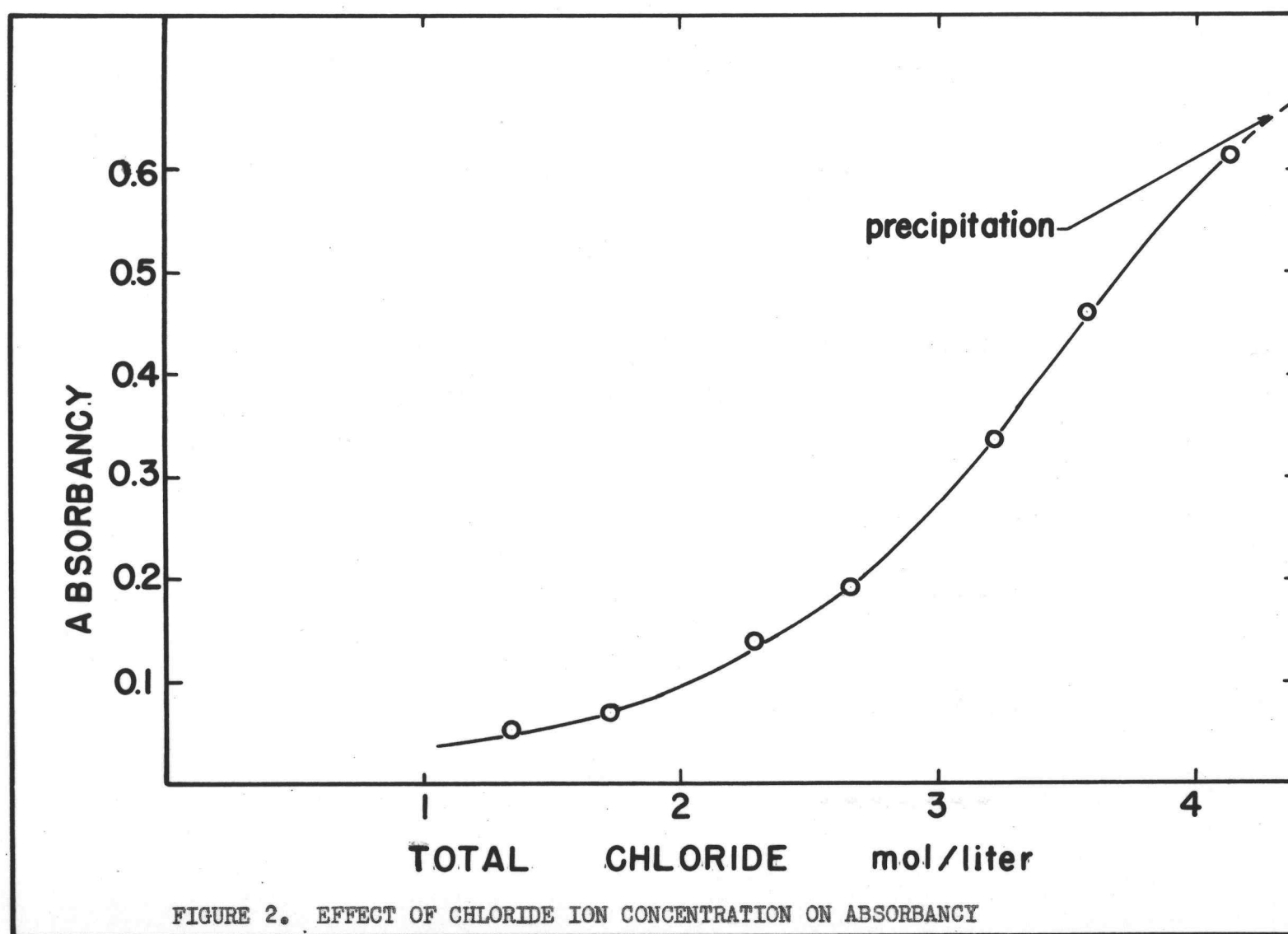
Effect of potassium thiocyanate concentration on absorbancy.

A study was made of the effect of thiocyanate concentration on the formation of the complex with the hope than an optimum thiocyanate concentration could be ascertained. The experimental procedure was identical with the hydrochloric acid study except that the hydrochloric acid content was fixed at 10.00 ml. and the amounts of 3 M potassium thiocyanate ranged from zero to 25.00 ml. Precipitation occurred when amounts of potassium thiocyanate greater than 15.00 ml. were added. These data shown in Table IV are plotted in Figure 3. As in the case of hydrochloric acid a compromise between opposing effects is necessary. The salting out combined with the increased blank tends to offset the advantage due to an increase in the amount of niobium complex formed. Ten ml. of 3 M potassium thiocyanate is used for subsequent work.

TABLE IV

EFFECT OF POTASSIUM THIOCYANATE
CONCENTRATION ON ABSORBANCY

Volume of 3 M potassium thiocyanate in ml.	Total absorbancy of solution	Absorbancy of blank	Absorbancy of niobium thiocyanate complex
0.00	0.030	0.025	0.005
1.00	0.028	0.028	0.000
2.00	0.042	0.024	0.018
3.00	0.073	0.022	0.051
4.00	0.111	0.028	0.083
5.00	0.162	0.025	0.137
7.00	0.244	0.027	0.217
10.00	0.344	0.028	0.316
12.00	0.393	0.020	0.373
15.00	0.452	0.013	0.439
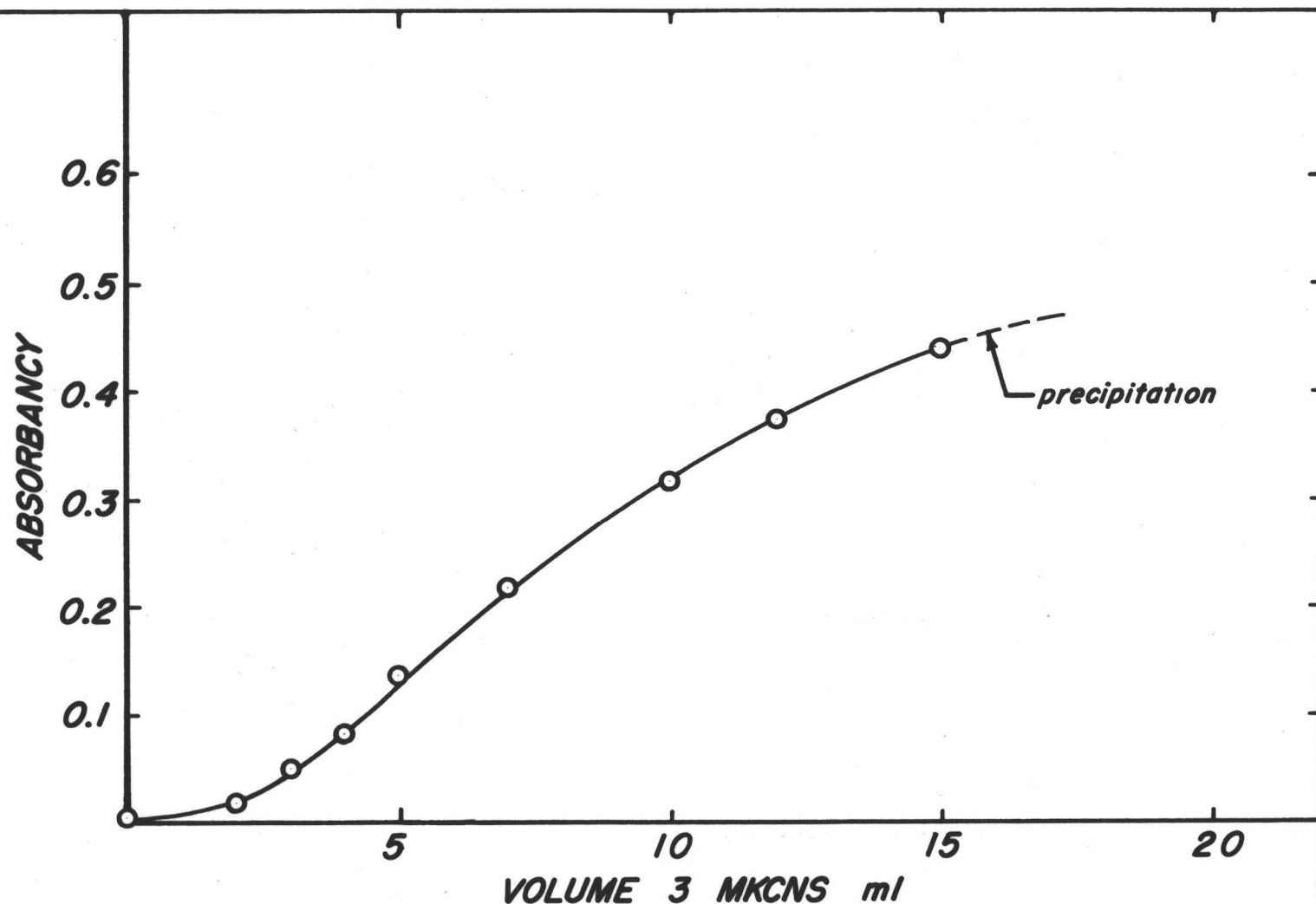
FIGURE 3. EFFECT OF POTASSIUM THIOCYANATE CONCENTRATION ON ABSORBANCY

Effect of acetone and dioxane concentration on absorbancy.

Because of the increase in absorbancy of the
complex with additions of acetone or dioxane, studies were
made of the effect of the concentration of each on the
absorbancy of the niobium thiocyanate. The experimental
procedure for these two studies was the same as in the
hydrochloric acid investigation except that the amounts of
hydrochloric acid and 3 M potassium thiocyanate were fixed
at 10.00 ml. each. In the acetone study, and also the
dioxane study, the amounts of organic solvent added varied
from 0.00 to 25.00 ml. In both cases precipitation
occurred with the addition of 20.00 or more ml. of organic
solvent. The data for these experiments are shown in
Tables V and VI. Curves showing the variation of
absorbancy with concentration of organic solvent are
plotted in Figure 4. An optimum amount of 10.00 ml. of
each solvent was chosen, acetone being the solvent chosen
for future work, because of its more powerful color inten-
sifying properties.

TABLE V

EFFECT OF ACETONE CONCENTRATION ON ABSORBANCY

Volume of acetone in ml.	Total absorbancy of solution	Absorbancy of blank	Absorbancy of niobium thiocyanate complex
0.00	0.041	0.006	0.035
5.00	0.103	0.018	0.085
7.00	0.191	0.020	0.171
8.00	0.250	0.020	0.230
10.00	0.339	0.021	0.318
12.00	0.447	0.020	0.427
15.00	0.500	0.020	0.480
20.00	0.561	0.013	0.548

TABLE VI

EFFECT OF DIOXANE CONCENTRATION ON ABSORBANCY

Volume of dioxane in ml.	Total absorbancy of solution	Absorbancy of blank	Absorbancy of niobium thiocyanate complex
0.00	0.047	0.008	0.039
5.00	0.104	0.008	0.096
10.00	0.230	0.013	0.217
15.00	0.350	0.012	0.338
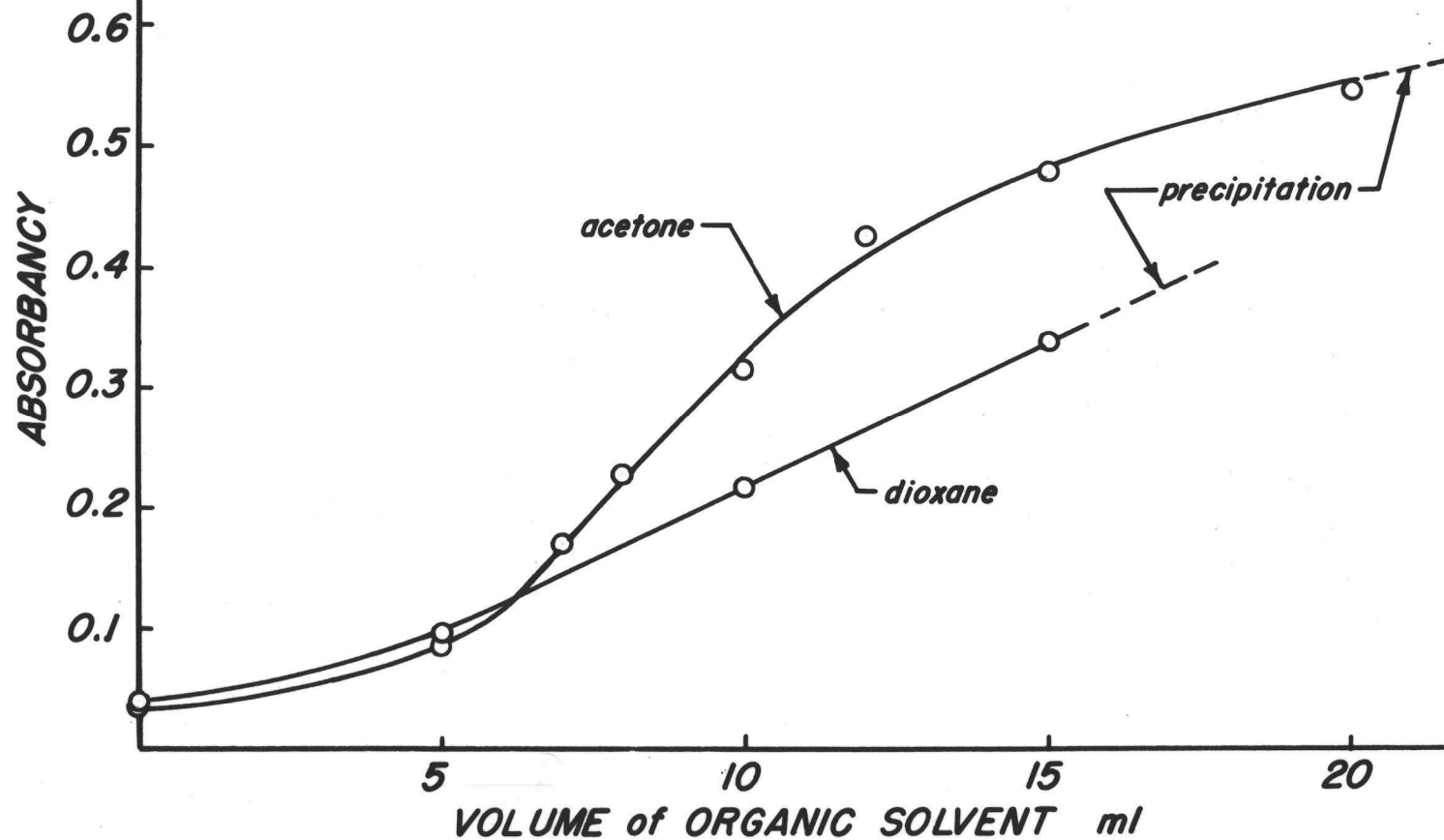
FIGURE 4. EFFECT OF ACETONE AND DIOXANE CONCENTRATIONS ON ABSORBANCY

30

THE ABSORPTION CURVE OF NIOBIUM THIOCYANATE
IN AQUEOUS ACETONE SOLUTION

After the selection of optimum concentration of
solution variables an absorption curve was prepared for
niobium thiocyanate according to the following procedure.
Exactly ten ml. of concentrated hydrochloric acid, 1.00
ml. of 2 M stannous chloride, 2.00 ml. of standard niobium
solution (0.0710 mg. niobium), 10.00 ml. of acetone, and
10.00 ml. of 3 M potassium thiocyanate were pipetted into
a 50.00 ml. volumetric flask. The solution was diluted to
the mark with water, thoroughly mixed, and placed in the
thermostat at 20.0°C. for approximately ten minutes. A
blank solution containing the same amounts of reagents
excluding niobium was prepared simultaneously. The
absorbancy of each solution at various wave lengths was
measured with respect to water. The absorbancy of the
complex was obtained by subtracting the absorbancy value
for the blank from the total absorbancy of the solution.
Absorbancy data are shown in Table VII, and the absorption
curve is shown in Figure 5. The curve shows a broad
absorption peak at a wave length of 385 mμ. This broad
peak permits the use of wider slit widths than could other-
wise be used if the peak were sharper.

TABLE VII

VARIATION OF ABSORBANCY OF NIOBIUM
THIOCYANATE WITH WAVE LENGTH

Wave length in mu	Total absorbancy of solution	Absorbancy of blank	Absorbancy of niobium thiocyanate complex
345	0.243	0.115	0.128
355	0.220	0.050	0.170
360	0.243	0.034	0.209
365	0.276	0.027	0.249
370	0.311	0.021	0.290
375	0.345	0.018	0.327
380	0.362	0.016	0.346
385	0.373	0.015	0.358
390	0.365	0.014	0.351
395	0.353	0.012	0.341
400	0.325	0.011	0.314
410	0.244	0.004	0.240
420	0.177	0.000	0.177
430	0.132	0.000	0.132
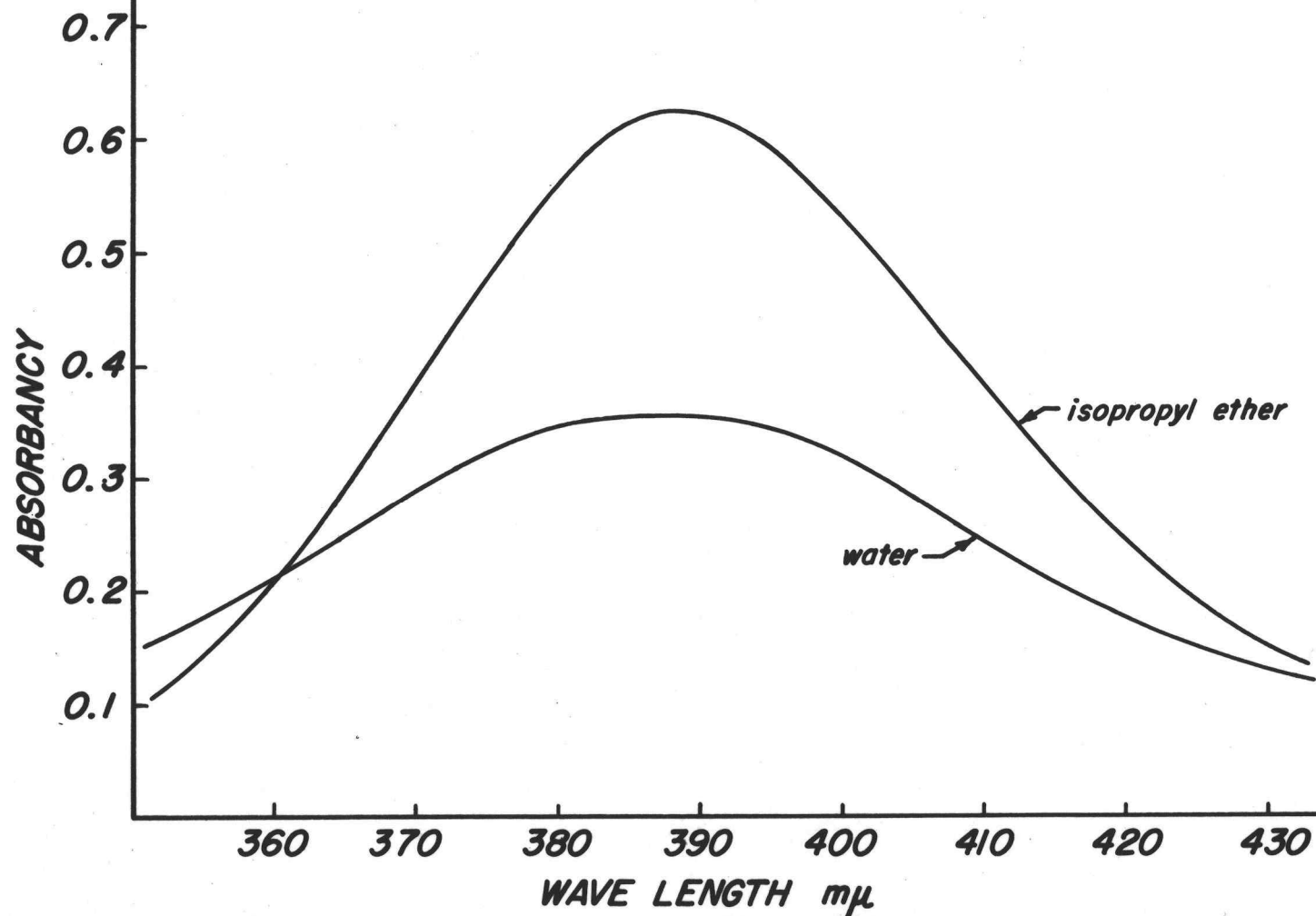
FIGURE 5. ABSORPTION CURVES OF NIOBIUM THIOCYANATE

STANDARD CURVES FOR THE DETERMINATION OF NIOBIUM

With the establishment of suitable experimental conditions, a standard curve for niobium could be prepared. The experimental procedure for the first standard curve was the same as for the absorption curve except that varying amounts of standard niobium solution were used. The data are shown in Table VIII. The plot of absorbancy at 385 mµ versus niobium concentration in Figure 6 shows an obeyance of the Beer-Bouguer law up to niobium concentrations of 2.84 µg. of niobium per ml. The absorbancy index is 240 at 385 mµ when the concentration is expressed in mg. niobium per ml. and the optical path in centimeters.

In later work it was found that the sensitivity and also the range of concentrations in which Beer's law is obeyed were increased by adding the standard niobium solution to the other reagents already mixed together in the flask, and then diluting to the mark with water. Data resulting from this modified procedure are shown in Table IX, and plotted in Figure 7. Beer's law is thus obeyed up to concentrations of 3.52 µg. niobium per ml. The absorbancy index is 251, an improvement over the first method.

TABLE VIII

VARIATION OF ABSORBANCY WITH NIOBIUM CONCENTRATION
ORIGINAL METHOD

Niobium concentration in μg. per ml.	Total absorbancy of solution	Absorbancy of niobium thiocyanate complex*
0.355	0.112	0.090
0.710	0.200	0.178
1.065	0.286	0.264
1.420	0.369	0.347
1.775	0.449	0.427
2.130	0.509	0.487
2.840	0.681	0.659

*Total absorbancy of solution - 0.022 (absorbancy of blank)

TABLE IX

VARIATION OF ABSORBANCY WITH NIOBIUM CONCENTRATION
NEW PROCEDURE

Niobium solution added last.

Niobium concentration in μg. per ml.	Total absorbancy of solution	Absorbancy of niobium thiocyanate complex*
0.706	0.180	0.177
1.412	0.357	0.354
2.118	0.532	0.529
2.824	0.695	0.692
3.530	0.878	0.875

*Total absorbancy of solution - 0.003 (absorbancy of blank)
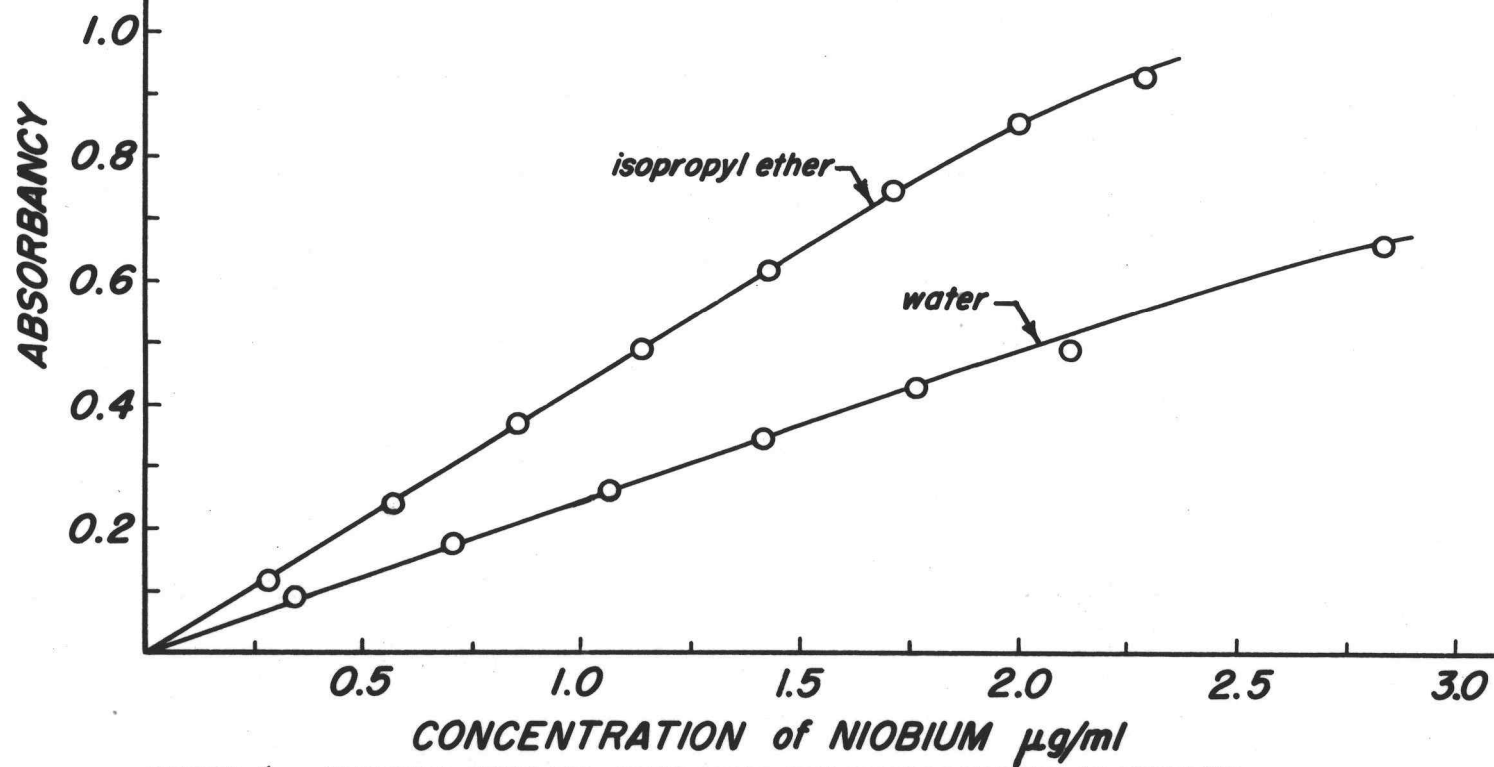
FIGURE 6. ORIGINAL STANDARD CURVES FOR THE DETERMINATION OF NIOBIUM

Figure 7

STANDARD CURVE FOR THE DETERMINATION
OF NIOBIUM, MODIFIED PROCEDURE
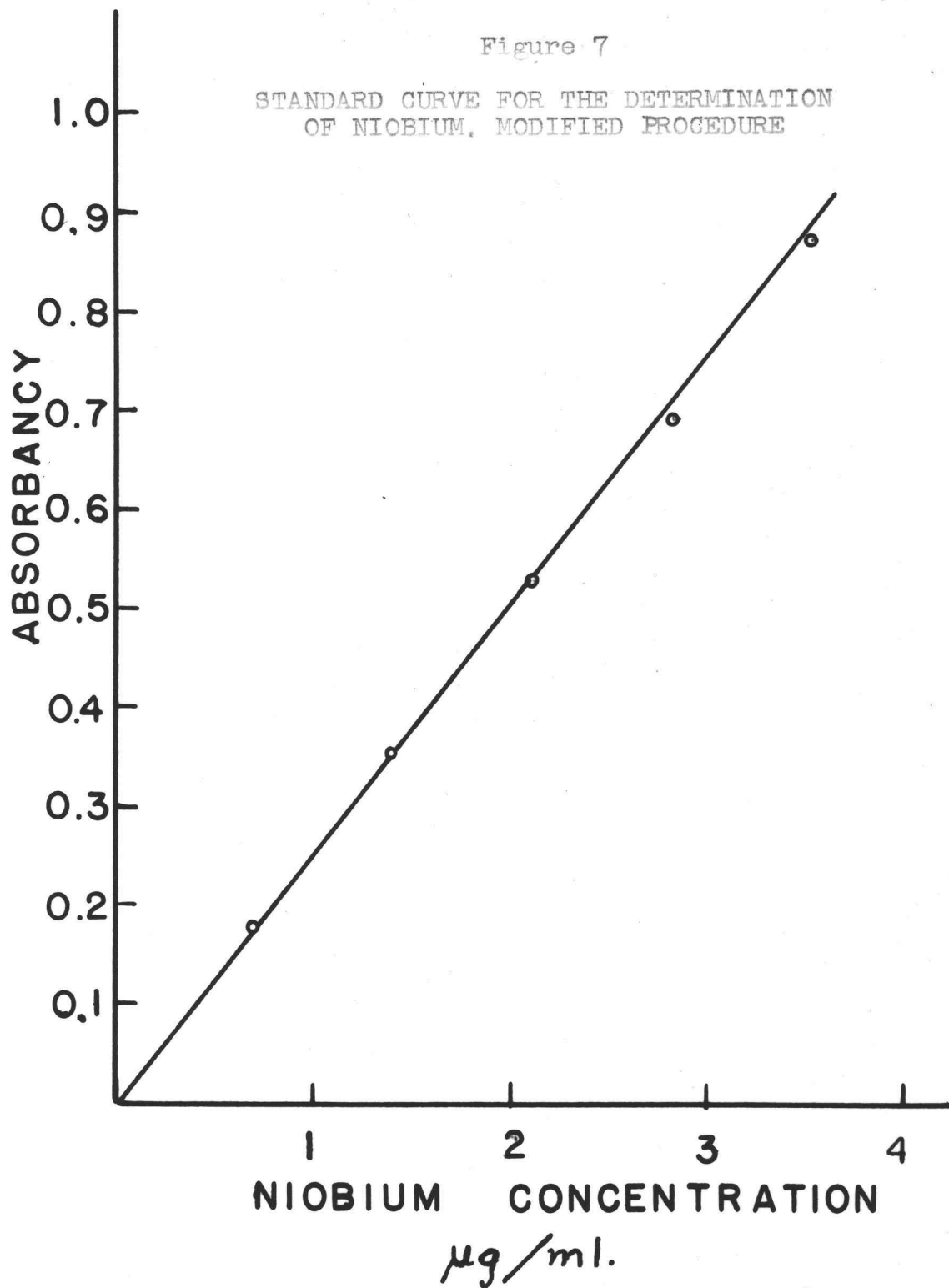
EXTRACTION OF THE NIOBIUM THIOCYANATE COMPLEX
WITH AN IMMISCIBLE SOLVENT

Anticipating the application of this thiocyanate method to colored solutions, it was decided to study solvent extraction of the niobium thiocyanate complex. Ether has been used as the solvent (1, p.30;23), but it suffers disadvantages because of its high volatility and the high mutual solubility between water and ether. In preliminary experiments benzene and carbon tetrachloride failed to extract the yellow color; n-butyl acetate extracted the yellow color, but the yellow butyl acetate layer was turbid; and isopropyl ether, ethyl acetate, and methyl ethyl ketone appeared to completely extract the yellow color from the water layer. Isopropyl ether was selected for subsequent studies because of the low mutual solubilities between the water and ether layers.

An absorption curve and also a standard curve showing variation of absorbancy with niobium concentrations were determined for the isopropyl ether extracts. The procedure was as follows. Exactly ten ml. of concentrated hydrochloric acid, 1.00 ml. of 2 M stannous chloride, the requisite amount of diluted standard niobium solution, 10.00 ml. of 3 M potassium thiocyanate, and enough distilled water to make a total volume of 30.00 ml. were pipetted into a 125 ml. separatory funnel and were well mixed. The separatory funnel was then placed in the

thermostat at 20.0°C. for 10 minutes. The solution was then extracted with first 10, then 5 ml. of isopropyl ether. The isopropyl ether extracts were transferred to a 25-ml. volumetric flask and diluted to the mark with isopropyl ether, the absorbancy of a blank containing no niobium being subtracted from the total absorbancy to obtain the values plotted in the graphs. Data for the absorption curve of a concentration of 1.42 μg. niobium per ml. are shown in Table X, and the curve, shown in Figure 5, has a sharper maximum than the corresponding curve for the aqueous solution. Data showing variation of absorbancy at 385 mμ of the isopropyl ether solution with niobium concentration are given in Table XI. The graph of these data in Figure 6 shows that the Beer-Bouguer law is followed up to 2 μg. niobium per ml., and the absorbancy index is 425 when the concentration is expressed in mg. per ml. and the optical path is in centimeters.

Extraction of the niobium thiocyanate complex with isopropyl ether is a convenient method for the separation, concentration and determination of very small amounts of niobium. It has even a higher sensitivity than the method using a homogeneous system.

TABLE X

VARIATION OF ABSORBANCY OF NIOBIUM THIOCYANATE IN
ISOPROPYL ETHER SOLUTION WITH WAVE LENGTH

Wave length in millimicrons	Total absorbancy of solution	Absorbancy of blank	Absorbancy of niobium thiocyanate complex
350	0.379	0.287	0.092
360	0.338	0.121	0.217
370	0.451	0.065	0.386
380	0.605	0.046	0.559
385	0.658	0.043	0.615
390	0.658	0.035	0.623
400	0.554	0.028	0.526
410	0.389	0.015	0.374
420	0.251	0.012	0.239
430	0.160	0.010	0.150

TABLE XI

DATA FOR STANDARD CURVE OF NIOBIUM WHEN NIOBIUM
THIOCYANATE COMPLEX IS EXTRACTED WITH ISOPROPYL ETHER

Concentration of niobium in ug. per ml.	Total absorbancy of solution	Absorbancy of niobium thiocyanate complex*
0.284	0.155	0.112
0.568	0.281	0.238
0.852	0.409	0.366
1.14	0.529	0.486
1.42	0.658	0.615
1.71	0.789	0.746
1.99	0.895	0.852
2.27	0.970	0.927

*Total absorbancy of solution − 0.043 (absorbancy of blank)

ANALYSIS OF STAINLESS STEEL OF KNOWN NIOBIUM CONTENT

In order to test the accuracy of the method, an analysis was made of a sample of Bureau of Standards No. 123-a stainless steel containing 0.75 per cent niobium. The following experimental procedure was used. A sample of the steel containing approximately 4 mg. of niobium (about 0.5 gram) was accurately weighed out into a 400-ml beaker and dissolved by heating with 25 ml. of a mixture containing 1 volume of concentrated hydrochloric acid, 1 volume of concentrated nitric acid, and 2 volumes of distilled water. After the sample was dissolved, 20 ml. of 70 per cent perchloric acid was added, and the mixture was heated until perchloric acid fumes appeared, and gently refluxed for 20-30 minutes. The mixture was cooled, and the perchlorates that had precipitated out were dissolved by adding 25 ml. of distilled water. Then 25 ml. of saturated sulfurous acid and a small quantity of filter paper pulp were added, and the solution was diluted to 150 ml. with distilled water. The solution was heated with stirring, boiled gently for 10-15 minutes with stirring, and placed on a steam bath for 30 minutes. The solution was then filtered through a No. 40 Whatman filter paper, and the paper was washed thoroughly with 2 per cent hydrochloric acid, the filtrate being discarded. The paper

and precipitate were transferred to a platinum crucible,
charred, and ignited at a dull red heat in the Tirril
burner flame. After cooling, silica was removed by
evaporation with hydrofluoric and sulfuric acids, and the
residue in the curcible was ignited to the oxides. After
cooling, the residue was fused with 3 grams of potassium
bisulfate, cooled, and then dissolved in 40 ml. of hot
0.5 M tartaric acid. The tartrate solution was cooled and
quantitatively transferred to a 500-ml. volumetric flask
and diluted to the mark with distilled water. An aliquot
of this solution was used for the analysis. In a 50-ml.
volumetric flask were placed 10.00 ml. of concentrated
hydrochloric acid, 1.00 ml. of 2 M stannous chloride, and
10.00 ml. of acetone. After cooling in the thermostat at
20.0°C., 10.00 ml. of 3 M potassium thiocyanate, and a
5.00 to 15.00 ml. aliquot of the niobium-tartrate solution
were added. The solution was diluted to the mark with
distilled water, well mixed, and placed in a thermostat at
20.0°C. A reagent blank containing no niobium was simul-
taneously prepared. Fifteen minutes later the absorbancies
of the niobium solution and the blank were measured with
respect to water and the concentration of niobium in the
solution was read off from the standard curve shown in
Figure 7. From this value the percentage of niobium in
the steel sample was readily calculated. The average value
obtained was 0.715 per cent niobium. This amounts to a

relative error of 4.7 per cent.

TABLE XII

RESULTS OF STAINLESS STEEL ANALYSIS

Weight of sample (g.)	Final Vol. (ml.)	Ali- quot (ml.)	Total absor- bancy of solu- tion	Absor- bancy of niobium thiocy- anate*	μg. Nb per ml.	Per cent Nb
0.5030	500	10.00	0.364	0.361	1.45	0.721
0.5030	500	5.00	0.182	0.179	0.710	0.706
1.0100	1000	10.00	0.360	0.357	1.43	0.708
1.0100	1000	5.00	0.182	0.179	0.720	0.713
0.5497	500	15.00	0.588	0.585	2.34	0.711
0.5497	500	10.00	0.400	0.397	1.59	0.724
0.5497	500	5.00	0.202	0.199	0.790	0.720

*Total absorbancy of solution - 0.003 (absorbancy of blank)

INTERFERENCES

Because of their frequent presence in the solution used for niobium analysis, the effects of sulfate, titanium, and tantalum on the aqueous color system were studied. The effect of sulfate ion was studied by adding different specified amounts of sulfate in the form of sulfuric acid to each reaction solution containing the same amounts of reagents as in the absorption curve determination and then measuring the absorbancy of each solution. The results are shown in Table XIII. They show that a concentration of sulfate greater than 0.014 M will cause a relative error greater than 3 per cent in the determination. Thus the sulfate ion concentration should be kept below this value.

TABLE XIII

EFFECT OF SULFATE ON COLOR DEVELOPMENT

Concentration of sulfate in moles per liter	Total Absorbancy of solution	Absorbancy of niobium thiocyanate complex*
0.0000	0.348	0.336
0.0072	0.348	0.336
0.0144	0.336	0.324
0.036	0.313	0.301
0.072	0.298	0.286
0.108	0.286	0.274
0.144	0.271	0.259
0.216	0.249	0.237
0.36	0.224	0.212
0.72	0.207	0.195
1.08	0.201	0.189

*Total absorbancy of solution - 0.012 (absorbancy of blank)

It was noticed that the presence of titanium in the reaction solution caused a slight increase in absorbancy. This effect was studied by adding different specified amounts of standard titanium solution to each reaction solution flask before the same amounts of reagents as were used in the absorption curve determination were added. The absorbancy of each solution was read and the results are shown in Table XIV. The results show that a concentration of 6 μg. of titanium per ml. causes a relative error of 3 per cent in the absorbancy reading of niobium thiocyanate solutions containing 1.41 μg. niobium per ml. Thus the

method is not accurate if the titanium-niobium weight ratio is greater than 4.

TABLE XIV

EFFECT OF TITANIUM ON COLOR DEVELOPMENT

Concentration of niobium in μg. per ml.	Concentration of titanium in μg. per ml.	Weight Ti / Weight Nb	Total absorbancy of solution	Absorbancy of niobium thiocyanate complex*
1.41	0.00	0.00	0.342	0.324
1.41	3.58	2.53	0.348	0.330
1.41	5.96	4.22	0.352	0.334
1.41	11.92	8.44	0.371	0.353
1.41	17.9	12.66	0.374	0.356

*Total absorbancy of solution - 0.018 (absorbancy of blank)

In the ether extraction method of Alimarin and Podval'naya (1, p.40) tantalum was reported not to interfere. Using the homogeneous method it was found that tantalum gives no absorbancy under the same conditions as those under which the niobium thiocyanate complex is formed. It was therefore originally assumed that tantalum would not interfere in this determination. However when tantalum was present in the solution with niobium during color development, a bleaching effect of the niobium thiocyanate color was observed. The effect seemed very erratic as solutions containing the same amounts of tantalum and niobium gave

varying absorbancy readings. In general the effect increased with increasing tantalum concentrations. When the tantalum was added after the niobium thiocyanate was formed, no bleaching of the color was observed.

Finally a satisfactory procedure was developed by which the tantalum interference could be studied. A series of three standard niobium-tantalum solutions were made up, all containing the same amount of niobium but different amounts of tantalum. The niobium thiocyanate complex was formed as follows. To each of three 50.00 ml. volumetric flasks were added 10.00 ml. of concentrated hydrochloric acid, 1.00 ml. of 2 M stannous chloride, 10.00 ml. of acetone with cooling, 10.00 ml. of 3 M potassium thiocyanate and a requisite amount of one of the standard niobium-tantalum solutions. The solution was diluted to the mark with distilled water and placed in the thermostat at 20.0°C. A blank solution was also made up with the same amount of reagents excluding niobium and tantalum. The absorbancy of each solution was determined 15 minutes after color development. The results of this study are shown in Table XV. They show that a tantalum-niobium ratio of greater than 0.5 will cause a relative error in absorbancy reading greater than 3 per cent.

TABLE XV

EFFECT OF TANTALUM ON ABSORBANCY OF NIOBIUM
THIOCYANATE COMPLEX USING AQUEOUS SYSTEM

Concentration of niobium in μg. per ml.	Concentration of tantalum in μg. per ml.	Weight Ta / Weight Nb	Total absorbancy	Absorbancy of niobium thiocyanate complex*
1.41	0.00	0.00	0.357	0.354
1.41	0.71	0.50	0.344	0.341
1.41	1.41	1.00	0.335	0.332
2.11	0.00	0.00	0.532	0.529
2.11	1.06	0.50	0.520	0.517
2.11	2.11	1.00	0.503	0.500

*Total absorbancy - absorbancy of blank (0.003)

In the hope that the use of the isopropyl ether extraction method might minimize or eliminate this interference from tantalum, a study was made of the effect of the presence of tantalum on the color using the extraction method. The procedure was identical with that of the standard curve for the isopropyl ether extraction method except that various amounts of standard tantalum solution were added to a fixed amount of standard niobium solution, and the absorbancy readings of the different solutions were compared. The results are shown in Table XVI. They show that tantalum-niobium ratios of greater than 1.2 will cause relative errors in absorbancy readings greater than 3 per cent. Thus the extraction method lessens the

interface of tantalum but does not eliminate it.

TABLE XVI

EFFECT OF TANTALUM ON THE ABSORBANCY OF
THE NIOBIUM THIOCYANATE COMPLEX USING
ISOPROPYL ETHER EXTRACTION

Concentration of niobium in µg. per ml.	Concentration of tantalum in µg. per ml.	Weight Ta Weight Nb	Total absorbancy	Absorbancy of niobium thiocyanate complex*
0.56	0.00	0.00	0.274	0.231
0.56	0.33	0.60	0.271	0.228
0.56	0.66	1.20	0.266	0.223
0.56	3.3	6.0	0.228	0.185

*Total absorbancy - absorbancy of blank (0.003)

SUGGESTIONS FOR FUTURE WORK

In the future it is planned to continue with the
study of the niobium thiocyanate complex in cooperation
with Lauw-Zecha and Hume of Massachusetts Institute of
Technology. They are currently making a spectrophoto-
metric study of the niobium thiocyanate method using
diethyl ether extractions exclusively. Work at Oregon
State College will be done primarily on the homogeneous
niobium thiocyanate method. It has been found that niobium
pentoxide can be dissolved in concentrated hydrochloric
acid. Studies will be made attempting to use this method
of solution for the colorimetric determination of niobium
with thiocyanate.

An attempt will be made to improve the working range
of the method.

A thorough investigation of the effect of interfering
ions is planned. Included in this will be a study of the
effects of molybdenum, tungsten, cobalt, stannous tin,
uranium, rhenium, titanium, copper, gold, platinum, vanad-
ium, chromium, oxalate, fluoride, sulfate, phosphate and
arsenate. The amount of each necessary to cause a rela-
tive error of more than 3 per cent in absorbancy readings
will be determined. Since both Alimarin and Podval'naya
(1, p.40) and Lauw-Zecha and Hume (23) report no interfer-
ences from tantalum, using ether extraction, further stud-
ies of the effect of tantalum on the complex will be made.

SUMMARY

A colorimetric method for the determination of small amounts of niobium based on the yellow thiocyanate complex has been presented.

The study of the effects of free acid, chloride, potassium thiocyanate, and acetone on color development has been made, and optimum concentrations of potassium thiocyanate, hydrochloric acid, and acetone have been determined.

The absorption curve for the complex in aqueous solution was determined; the maximum absorbancy occurs at 385 mμ. The Beer-Bouguer Law is followed in the concentration range of 0 to 3.5 μg. niobium per ml. The absorbancy index is 251 when the concentration is expressed in mg. niobium per ml. and the optical path in centimeters.

A method based on the extraction of the complex with isopropyl ether has been studied. Using this method the maximum absorbancy occurs at 385 mμ, but the peak is much sharper than with aqueous systems. The Beer-Bouguer Law is followed in the concentration range of 0 to 2 μg. niobium per ml. Since the absorbancy index is 425, the extraction method is more sensitive than the method using aqueous systems.

A procedure for the colorimetric determination of niobium in stainless steel has been described.

The effects of certain interfering ions on the color development have been studied.

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