THE ANALYTICAL CHEMISTRY OF α-BENZOIN OXIME COMPLEXES OF MOLYBDENUM, TUNGSTEN, CHROMIUM, AND VANADIUM

By

Henry John Hoenes, Jr.

A THESIS

Submitted to the School for Advanced Graduate Studies
of Michigan State University of Agriculture and
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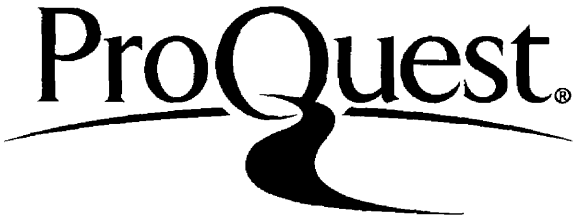

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AN ABSTRACT

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ABSTRACT

The α-benzoin oxime complexes of vanadium, molybdenum, and tungsten have been thoroughly studied. An attempt to do the same with chromium was unsuccessful due to preferential reduction of chromium (VI) by the reagent.

The molybdenum complex has been determined to be bis(α-benzoinoximato)dioxomolybdenum (VI), $MoO_2(C_{14}H_{12}O_2N)_2$. For tungsten, it is bis(α-benzoinoximato)dioxotungsten (VI), $WO_2(C_{14}H_{12}O_2N)_2$. Vanadium has been found to form two different complexes, a white precipitate and a dark yellow precipitate. The white form has been determined to be α-benzoinoximatodioxovanadium (V), $VO_2(C_{14}H_{12}O_2N)$. The yellow form, containing one α-benzoin oxindine molecule per vanadium, is the result of complex formation with some highly polymerized vanadium species. The formation of all these complexes has been correlated with literature data concerning the species of these metals in acid solution.

The proper conditions for maximum complex formations have been determined. For molybdenum, quantitative precipitation occurs in 5 to 20% mineral acid solution. For tungsten and vanadium quantitative precipitation was found to be impossible. Maximum precipitation of tungsten was found to require not only mineral acid but also a mole ratio of fluoride to tungsten ion from 7:1 to 10:1. For vanadium, the yellow species forms more completely at the isoelectric point of pH 2.2.

The white species forms very slowly from solutions at the isoelectric point, or of greater acidity.

As a result of these studies, a number of factors concerning the use of α-benzoin oxime as an analytical reagent for these elements have been determined.

Molybdenum may be quantitatively precipitated by α-benzoin oxime from acid solution. When the precipitation is done properly the complex may be dried and weighed and the molybdenum calculated as 16.51% of the complex. It was found impossible to obtain quantitative precipitation of tungsten in the same manner, even when conditions were rigidly adjusted. A quantitative precipitation of vanadium was also found to be impossible. This is because the yellow species is not stable but undergoes conversion to the white form, and the length of time required for complete precipitation of the white form results in precipitation of excess reagent.

On the basis of the studies completed, the newly proposed extraction procedure for molybdenum (1) has been revised. This revision has resulted in making the method specific for molybdenum. It may now be employed even in the presence of tungsten.

The extreme insolubility of the tungsten complex and the fact that it does not extract as a colloidal precipitate as does molybdenum has made the development of a new extraction procedure for tungsten impossible.

As a final result of these studies, an extraction procedure for the determination of vanadium has been developed. This method is quite specific and can be employed for vanadium solutions containing from 5 to 80 micrograms per ml. It involves extraction of the vanadium complex into chloroform from an aqueous solution at pH 2.2. Measurement is made by developing the color of the 8-quinolinol complex of vanadium directly in the presence of the α-benzoin oxime. The only interferences found to give difficulty in this method were antimony and bismuth, and to a slight extent, the uranyl ion.

LITERATURE CITED

(1) Goldstein, G., Manning, D. L., and Menis, O., Anal. Chem. 30, 539-42 (1958).

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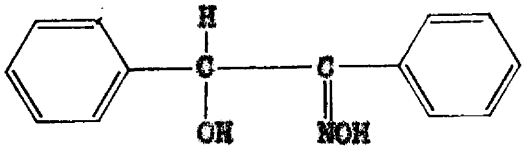
I. INTRODUCTION

A. Historical

1. Summary of α-benzoin oxime procedures. The reagent, α-benzoin oxime, has been used for quantitative determinations since 1923 when Feigl (6) first reported a quantitative procedure for the precipitation of copper from an ammoniacal solution. Later when Knowles (17) was checking the interferences in the copper determination he discovered that molybdenum could be quantitatively precipitated from a mineral acid solution with α-benzoin oxime. Later work (30) proved successful for the simultaneous precipitation of tungsten and molybdenum using the procedure devised by Knowles.

The structure of α-benzoin-oxime is as follows:



Its molecular weight is 227.3 and it melts at 149-51° C. It is soluble in acetone, alcohol and ether, but insoluble in water.

Knowles (17) method for molybdenum involves precipitation of the complex from an acid solution followed by ignition to molybdenum trioxide in a muffle furnace at 500-525° C. Hydrochloric, nitric, or sulfuric acid may be used and the recommended acidity is 5% by volume, although up to 20% acid is permissible. A two to five times excess of reagent, on the basis of a postulated complex of three α-benzoin oxime

molecules per molybdenum, is required in this method. Also the presence of a slight excess of bromine and precipitation from a cold solution are necessary to prevent reduction of molybdenum by the reagent.

Knowles checked a wide variety of elements for interference, including silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, tin, selenium, silicon, tungsten, tantalum, niobium, cerium, uranium, rhenium, nickel, cobalt, manganese, zinc and the six platinum metals. He found that of these only tungsten, palladium (II), chromium (VI), vanadium (V) and tantalum form precipitates with α-benzoin oxime in mineral acid solutions. Of these, only tungsten and palladium gave precipitates which were "seemingly quantitative." Precipitation of chromium and vanadium could be eliminated completely by reduction of the elements before addition of the reagent. He reported the precipitate of tantalum to be that of the hydrated acid rather than a compound with the reagent. Niobium and silicon were also found to contaminate the molybdenum precipitate through formation of insoluble hydrated acids.

Yagoda and Fales (30) adopted the original method for the quantitative precipitation of combined molybdenum and tungsten. They redissolved the precipitate and separated the molybdenum and tungsten by means of hydrogen sulfide. Due to the fact that ignition to the trioxide resulted in precipitates of small weight, especially for low concentrations, they redissolved the tungsten trioxide and molybdenum trioxide and converted to thallous tungstate and thallous molybdate for weighing. It is interesting to note in their results that

determinations on pure sodium tungstate in all cases gave a negative error. However, this was not true for steel samples from which both molybdenum and tungsten were precipitated.

Taylor-Austin (29) has shown that the molybdenum precipitation is incomplete in the presence of tartrate and that acetone may be successfully substituted for ethanol as the α-benzoin oxime solvent proposed in Knowles' method.

Cravens et al. (4) used the method for the determination of molybdenum in tungsten bearing steels. Following the combined precipitation, the molybdenum is determined by the formation of thiomolybdate in alkaline solution. This is decomposed to the sulfide with dilute acid and ignited to the oxide.

In the method of Sterling and Spuhr (27) the molybdenum-α-benzoin oxime complex is dissolved in ammonium hydroxide and hydrogen peroxide. The molybdenum is then precipitated as lead molybdate from a lead acetate buffer mixture.

Nicholls and Rodgers (23) used Knowles' precipitation method for the determination of molybdenum in plant materials. They analyzed samples containing as little as 0.0005% molybdenum by precipitating the α-benzoin oxime complex, dissolving the precipitate and determining molybdenum polarographically.

A good review of these modifications as well as Knowles' original method may be found in Flagg's Organic Reagents (9). Also, several methods for molybdenum and tungsten all involving a separation of

molybdenum and tungsten from the bulk of the solution according to the method of Knowles may be found in Analytical Chemistry of the Manhattan Project (15).

More recently, this author (12) has shown that, contrary to Knowles' originally postulated 3:1 α-benzoin oxime to molybdenum complex, the compound contains 16.51% molybdenum. On this basis the complex has been postulated as $MoO_2(C_{14}H_{12}O_2N)_2$, which contains 16.51% molybdenum. In addition to this, if the precipitation is carried out to avoid precipitation of excess reagent with the complex, and it is washed free of all excess reagent, the complex can be dried at 105° C. and weighed. Calculating the molybdenum as 16.51% of the complex gave good results for a number of N.B.S. steel samples. In this method acetone is employed as the solvent to give a greater solubility of the reagent. Also the excess reagent is held to a 30% excess on the basis of two α-benzoin oxime molecules per molybdenum. This eliminates the necessity of adding bromine and keeping the solution cold; however, as in Knowles' original work, any chromium (VI) or vanadium (V) are first reduced with sulfur dioxide or ferrous ammonium sulfate. The method cannot be applied to tungsten-bearing steels.

In addition to its use as a precipitating reagent for molybdenum and tungsten, α-benzoin oxime has been used more recently in extraction procedures for these elements. The first was a procedure devised by Jeffrey (14) for the determination of microgram quantities of molybdenum and tungsten in ore samples. The ore is fused with alkali hydroxide and the silica precipitated and dehydrated with hydrochloric

acid, and finally removed by evaporation with hydrofluoric acid. The remaining residue is then refused, dissolved and transferred to a separatory funnel, where it is made 1.5N in HCl. α-Benzoin oxime in ethanol is then added to precipitate the molybdenum and tungsten complexes which are extracted with four 5 ml. portions of chloroform. The final determination involves a simultaneous photometric method employing the complexes formed with toluene-3:4-dithiol.

Goldstein, Manning and Memis (10) developed a spectrophotometric method for molybdenum involving the extraction from acid solution into a 0.1% α-benzoin oxime solution in chloroform. The absorption measured is that developed by an aliquot of extract with a 0.1% quercetin solution in ethanol. Good results were obtained in the range of 0.5 to 5.0 mg. of molybdenum. The only interferences reported were tungsten (VI) and vanadium (V), and the authors made no attempt to eliminate these interferences as they are not commonly associated with the samples which they test.

Considering the few elements which are reported to form complexes with α-benzoin oxime in mineral acid solutions, it is interesting to note that, with the exception of palladium (II), they all belong to groups VB and VIB of the periodic table. These are the same elements whose chemistry in acid solution is so poorly characterized due to the formation of isopoly and heteropoly acids and salts.

On the basis of the postulated formula of $MoO_2(C_{14}H_{12}O_2N)_2$ for the molybdenum complex it would appear that the complexes of the other

group VB and VIB metals will also be compounds of oxygenated cationic species. Palladium again is an exception and does not belong in this group, the composition of its complex already having been established as $Pd(C_{14}H_{12}O_2N)_2$ (25).

The probability that these compounds are formed through oxygenated cations of these metals is further indicated by the complexes which these metals form with 8-quinolinol. Hiericker and Treadwell (24) have determined the best method for precipitation of these elements as 8-quinolinolates using controlled pH precipitations. They report the composition of these complexes to be $WO_2(C_9H_6ON)_2$, $MoO_2(C_9H_6ON)_2$, and $V_2O_3(C_9H_6ON)_4$. While the acidity for these precipitations is much less than for the formation of the α-benzoin oxime complexes, they are still all precipitated from acid media.

2. Brief survey of postulated vanadium, molybdenum, and tungsten species in acid media. According to Jonassen and Kirschner in Bailar's Chemistry of the Coordination Compounds (1) poly-acids are those which contain more than one acid anhydride molecule per acid anion. If they contain one kind of acid anhydride they are isopoly acids, if more than one, heteropoly acids. The elements capable of this type of condensation are vanadium, niobium, tantalum, chromium, molybdenum, tungsten and uranium.

a. Isopoly acids. The above elements have been shown to form a series of poly-acids in the crystalline state, the 6- and 12-poly acids. A great deal of work has been done on them, and their structure and

composition have been fairly well-established. However, the solid state of these poly acids is of no importance in the present work and can therefore be ignored at this time.

Of importance to this work is the aggregation or degradation phenomena occurring in solution, and these are unfortunately very poorly understood.

One of the best collections of data and theories concerning this problem is found in Huckel's Structural Chemistry of Inorganic Compounds (13). Unfortunately, there has been a great deal of work done since the publication of this book which has not been collected and evaluated on the basis of work done by others. Because the majority of recent publications deals only with the phenomena observed with one element, it will be of more value to consider the data for vanadium, molybdenum and tungsten separately.

The results of studies of vanadium in acid solutions were summarized earlier by Huckel (13) as follows. Several aggregations observed in the alkaline pH region lead to the postulation of mono-, di-, and tetra-vanadic acid above pH 7. From pH 7 to 2.2, a penta-vanadic acid is postulated which forms slowly from tetra-vanadic acid upon acidification. This pentavanadic acid is not stable beyond the isoelectric point which is attained at a pH 2.2. Further acidification, however, does not lead to further aggregation, but rather to a degradation to VO_2^+ or VO^{+++}. These variations are accompanied by color changes, the pentavanadic acid being a deep orange, and the simple or hydrated cation being pale yellow in color.

Later works by Hazel, McNabb, and Santini (11) gave evidence that in the region below pH 7, the species is really a decavanadic acid, $V_{10}O_{27}^{-4}$ rather than pentavanadic acid as previously postulated. They also believed that in the region of the isoelectric point, pH 2.2, there is a formation of a linear polymer which is in equilibrium with low molecular weight decavanadic acid. This polymer is in turn converted to VO_2^+ by cleavage caused by further acidification. This could be represented as

$$V_{10}O_{27}^{-4} \rightleftharpoons (VO_2^+)_q(OH^-)_p \rightleftharpoons VO_2^+ \text{ (where } q > 10).$$

The species postulated by Ducret (5) for this low acid region do not correspond to those postulated by most other workers. However, it is interesting to note that he shows the conversion to VO_2^+ at the isoelectric point is not sharp, but that an equilibrium process is involved, and the acidity must be increased to a pH of 1.5 for the majority of the vanadium to be present as VO_2^+.

Morachevski and Belyaeva (20) state that the transitions which occur upon acidifying a vanadate solution occur in a series of steps. As $[V]:[H^+]$ approaches 1:1 the following reactions take place,

$$HVO_3 \rightleftharpoons H^+ + VO_3^- \quad \text{and} \quad HVO_3 \rightleftharpoons OH^- + VO_2^+$$

$$\text{to give} \quad 2HVO_3 \rightleftharpoons H_2O + VO_2VO_3.$$

When the excess of H^+ over V is 100-fold:

$$VO_2VO_3 + 2HCl \rightleftharpoons 2VO_2Cl + H_2O$$

And at very high H^+ concentrations:

$$VO_2Cl + 2\ HCl \rightleftharpoons VOCl_3 + H_2O$$

These authors contend that at the isoelectric point the salt $VO_2VO_3 \cdot nH_2O$ is formed, and that all polyvanadium acids are association products of these salt molecules. This theory was a result of a spectrophotometric study of aqueous vanadium solutions and was perhaps not thorough enough to establish the complexity of aqueous, acid vanadium solutions.

Rossotti and Rossotti (26) published a paper dealing with equilibrium studies of isopolyvanadates in acidic media which contains an excellent review of previous work. On the basis of spectrophotometric and potentiometric measurements they assigned the following equilibria to the isopolyvanadate system in the range from pH -0.5 to 6.5:

$$10VO_2^+, aq. + 8H_2O \rightleftharpoons H_2V_{10}O_{28}^{-4}, aq. + 14H^+$$
$$H_2V_{10}O_{28}^{-4}, aq. \rightleftharpoons HV_{10}O_{28}^{-5}, aq. + H^+$$
$$HV_{10}O_{28}^{-5}, aq. \rightleftharpoons V_{10}O_{28}^{-6}, aq. + H^+$$

They found VO_2^+, aq. to be the sole species in solution from pH -0.5 to 1.3, $H_2V_{10}O_{28}^{-4}$ is the predominant species in the pH range from 2.5 to 3.5, $HV_{10}O_{28}^{-5}$ from 4 to 5.5, and $V_{10}O_{28}^{-6}$ from 6 to 7. The $H_2V_{10}O_{28}^{-4}$ corresponds to the $V_{10}O_{27}^{-4}$ which had been suggested by Hazel, McNabb, and Santini (11) as well as others reported in the review.

For molybdenum and tungsten, although the situation does not seem quite as complex, it is probably no better understood. According to Huckel's (13) book, molybdenum exists as the simple molybdate ion in alkaline solution. Between pH 7 and 5, aggregation occurs which from diffusion studies appears to yield a hexamolybdate ion. No further aggregation is encountered until a pH of 1.75 is reached when a species corresponding to dodecamolybdate is observed from pH 1.5 to 1. The isoelectric point is reached at pH 0.9 where the solution becomes unstable and precipitates molybdenum trioxide. Beyond this pH, there is a degradation of the polymerized species as the acidification is further increased.

Linquist (19) postulated the presence of polynuclear complexes such as (MoO_m^{2m+}) sheets in more strongly acid solutions, that is, in more acid solutions than the pH 0.9 at which the isoelectric point occurs. By applying results of spectra of compounds containing Mo:Cl ratios of 1:2, 1:3 and 1:4 in ether, Neumann and Cook (21) attempted to show the species present in hydrochloric acid solutions. Their results indicated that the most important species is that containing two chlorines per molybdenum. The maximum for this species occurs at 6 M.HCl. At greater acidities a species containing three chlorines becomes more important. Chauveau (3) also found evidence to indicate the presence of MoO_2Cl_2 in hydrochloric acid solutions. In addition to this, the presence of the MoO_2^{+2} cation had been indicated in acid media much earlier when Nicholls, Saenger and Wardlaw (22) showed the presence of MoO_2SO_4 in sulfuric acid solutions.

The situation with tungsten is quite similar to that for molybdenum, according to Huckel (13). Tungsten exists in the form of the $WO_4^{=}$ ion in the basic region, and evidence of polymerization begins around pH 8. From pH 6 to 1.5, the hexatungstate ion exists in solution. The isoelectric point occurs at pH 1 for tungsten. However, there is no evidence given to indicate degradation of the polymer beyond the isoelectric point as in the case of molybdenum. Another quite obvious difference in acidification of tungstate solutions lies in the fact that beyond the isoelectric point hydrated tungstic acid precipitates from solution. Tungstic acid, H_2WO_4 is a yellow amorphous material which is formed when a hot tungstate solution is acidified with hydrochloric acid. Upon acidification of a cold solution, the white dihydrate, $H_2WO_4 \cdot H_2O$ is formed (18).

A more recent study of the species existing in acidified tungstate solutions has been carried out by Bettinger and Tyree (2). This work simply verifies the polymerization occurring, but cites the fact that there is evidence of an intermediate predominant species occurring between the monomer and hexamer. Their results are very compatible with existing theories of the complex tungsten species.

b. Heteropoly acids. As stated before, beyond the isoelectric point for tungsten, hydrated tungstic acid precipitates from solution. However, if phosphate ion is present, this phenomenon is not observed. The reason for this is that tungsten as well as the other group V and VI metals form heteropoly as well as isopoly acids, as previously mentioned.

A wide variety of elements such as phosphorus, silicon, boron, iodine, selenium, and arsenic are capable of assuming the role of central atom for heteropoly acid formation. The phospho-heteropoly acids are probably most important because they were the first discovered and have been more extensively studied. Therefore, the following brief discussion will be confined to the phospho-heteropoly acids, although this is only one small portion of the entire picture.

As with the isopoly acids, the solid heteropoly acids are much more clearly understood. They are quite easily prepared by crystallization of salts from acid media. The acids are not stable in alkaline media due to hydrolysis. Heteropoly acids having a wide variety of composition ratios have thus been obtained, but the limiting ratio for molybdenum and tungsten has been found to be 12 per one central atom. That is, the limiting phospho-tungstic acid is $P_2O_5 \cdot 24WO_3 \cdot 63H_2O$ (13). For tungsten, salts having a tungsten to phosphorus ratio of 12:1, 11:1, 21:2, 10:1, 9:1, 17:2, and 8:1 are known (18).

X-ray analysis has been fairly successful in establishing the structure for the limiting acids for heteropoly compounds, but there is still a great deal to be done on those containing fewer MoO_3 or WO_3 groups, and even less is known about the heteropoly acids in solution. A very recent paper by Kerker, Lee, and Chou (16) describes the determination of molecular weights of two phosphotungstic acids in a series of solvents by light scattering techniques. Their measurements in a number of organic solvents show the molecular weight of 12-phosphotungstic acid corresponds to the monomer, $H_3PW_{12}O_{40}$, while that of

9-phosphotungstic acid corresponds to the dimer, $H_6P_2W_{18}O_{62}$. Unfortunately, attempts in aqueous solutions were futile since the method depends upon the solute being a nearly ideal non-electrolyte, and phosphotungstic acids are actually strong electrolytes in aqueous media.

Formation of heteropoly acids of tungsten is not the only method for preventing the precipitation of tungstic acid from an acidified solution. The presence of fluoride ion causes formation of a complex ion, $(WO_2F_4)^{=}$ (1) which is quite different from phosphotungstates, but as effective for keeping tungsten in acid solution. Molybdenum, vanadium, chromium, niobium and tantalum also form oxygenated fluoride complexes of this type. In fact Feigl (8) has published a paper showing that by the addition of fluoride practically all colorimetric and gravimetric reactions of molybdenum, tungsten, and vanadium can be eliminated. However, the complete absence of any experimental data, concentration values, and acidity values, as well as reported non-interference of fluoride by other authors, greatly decreases the value of the published work.

A discussion of the poly acids of chromium has been omitted here because results obtained in the experimental portion have made such a discussion unimportant with respect to the data being presented.

B. Statement of Problem

α-Benzoin oxime has been in use as an analytical reagent for a number of years, in fact, since Feigl (6) first published his method for the determination of copper. It has been employed very widely since 1932 when Knowles (17) described its use in the determination of molybdenum, and since 1938 when Yagoda and Fales (30) reported the simultaneous precipitation of molybdenum and tungsten by this reagent.

However, it was only recently that this author (12) discovered the original suggestion by Knowles of a three to one complex was in error and that the complex is actually two α-benzoin oxime molecules per molybdenum. It was also shown at the same time that the reported instability of the complex was incorrect, and that by removal of excess reagent the complex could be dried at 105° C. and weighed.

During this same period of time, no suggestion had been made as to the composition of the tungsten-α-benzoin oxime complex. In fact it had not even been established whether a complex is formed or if excess reagent is simply carrying down the hydrated tungstic acid. Since precipitation conditions are suitable for formation of hydrated tungstic acid this could occur.

In addition to this Knowles stated that complexes of chromium (VI) and vanadium (V) were observed to form in mineral acid solution, yet no further work had been done on these complexes. In fact, except for the use of α-benzoin oxime to extract molybdenum and tungsten for

determination by other colorimetric methods (14,10), nothing had been done with this reagent except minor modifications of Knowles original method.

From the long list of elements which fail to form complexes with α-benzoin oxime in mineral acid solution it is apparent that with the exception of palladium, this reagent forms complexes exclusively with groups VB and VIB metals. It appeared from a survey of the literature that a study of these metal complexes is non-existent, and thus, due to the specificity of these reactions, that a valuable reagent was being ignored.

With this in mind, it seemed desirable to conduct a study of the complexes of α-benzoin oxime with the more common group V and VI metals, that is, vanadium, chromium, molybdenum, and tungsten. One of the major items to be determined was the composition of the complexes formed, or at least the α-benzoin oxime to metal ratio. In addition to this it was desired to determine the conditions for complex formation, and under what conditions, if any, the formations were quantitative. Also the effect of interfering ions needed to be studied, if new analytical methods, or modifications of older methods were to be developed. The main purpose of this work was thus to gain as complete a picture as possible of the reactions of α-benzoin oxime with vanadium, chromium, molybdenum, and tungsten. The main experimental techniques employed for this purpose were precipitation and extraction methods.

II. REAGENTS, APPARATUS, AND EXPERIMENTAL METHODS

A. Reagents and Apparatus Used

The following is a list of the reagents used in this work.

Aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, Mallinckrodt Analytical Reagent.

α-Benzoin oxime, $C_{14}H_{13}O_2N$, Paragon Testing Laboratories. When high purity of reagent was desired this material was recrystallized twice from ethanol.

Bismuth chloride, $BiCl_3 \cdot H_2O$, Mallinckrodt Analytical Reagent.

Chloroform, $HCCl_3$, Merck Reagent grade.

Ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, "Baker's Analyzed" Reagent.

Ferric chloride, $FeCl_3 \cdot 6H_2O$, reagent grade from General Chemical Division of Allied Chem. and Dye Corp.

8-Quinolinol, C_9H_7ON, Merck Reagent grade.

Potassium chromate, K_2CrO_4, Mallinckrodt Analytical Reagent.

Potassium fluoride, $KF \cdot 2H_2O$, "Baker's Analyzed" Reagent.

Potassium phosphate, monobasic, KH_2PO_4, Mallinckrodt Analytical Reagent.

Quercetin, $C_{15}H_{10}O_7 \cdot 2H_2O$, student preparation, M.p. 195° C.

Sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$, "Baker's Analyzed" Reagent.

Sodium tungstate, $Na_2WO_4 \cdot 2H_2O$, Mallinckrodt Analytical Reagent.

Sodium vanadate, $NaVO_3 \cdot 4H_2O$, Fisher Scientific Co., Eimer and Amend, C. P. Grade.

Uranium acetate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, "Baker's Analyzed" Reagent.

In addition to the above, distilled water and C. P. grade ethanol and acetone were employed in making all other solutions.

Apparatus used in these experiments included the following:

Beckman model H2 glass electrode pH meter.

Beckman model DU spectrophotometer.

Beckman model DK2 automatic recording spectrophotometer.

Burrell Technical Supply Company model B6 automatic shaker which was modified to give a more vigorous agitation for extraction work. This was accomplished by attaching the clamps to either end of one foot lengths of pipe which were in turn fastened perpendicularly to the rocker arm of the shaker.

B. General Experimental Methods

Several procedures were used extensively during the course of this investigation, and therefore, in order to avoid repetition later, they are described here in detail.

1. Precipitation procedures. The precipitation reactions were studied for these elements using the following procedure. Solution containing the desired amount of the element being studied was pipeted, by means of a calibrated pipet, into a 150-250 ml. beaker. The acidity of the solution was adjusted to the desired value and any additional materials were added. The desired amount of α-benzoin oxime dissolved in 50% acetone, or in a few instances, 50% ethanol, was then added drop-wise from a buret. The solutions were stirred during the addition of reagent. After the precipitates had been allowed to stand for the desired length of time, they were filtered with suction on previously weighed 30 ml., medium porosity sointered glass crucibles. The precipitates were washed with varying wash solutions, but in each case extreme care was used in washing down the sides of the crucible. The precipitates were then dried to constant weight at 105° C.

For the determination of the per cent by weight of the metals in the complexes the following procedure was used. A portion of the complex was placed in a silica crucible and dried to constant weight in a 105° C. oven. It was then ignited to the corresponding oxide in a muffle furnace at 500-550° C. From the weight of the oxide it was possible to calculate the weight of metal and thus the per cent metal in the α-benzoin oxime complex.

2. Extraction procedures. All of the extraction work done involved the simplest type of extraction. The solutions to be extracted were pipeted into 60 ml. separatory funnels. In most cases any additional materials were added in solution directly to the contents of the separatory funnel. In cases where strict acidity control was not required, the acidification was carried out by direct addition of the acid to the separatory funnel. Where controlled pH was important, the pH of the solution was adjusted using a pH meter before samples were pipeted into the separatory funnels.

Extractions were carried out using solutions of α-benzoin oxime in chloroform having the desired reagent concentrations. In all cases, the amount of chloroform solution used for extraction was carefully controlled by adding the reagent from a buret. Extraction was carried out by shaking the separatory funnels on the modified Burrell shaker previously described. This allowed a more careful control of extraction conditions than shaking by hand, when such control was desired. It also made it possible to run a larger number of samples in a shorter period of time.

When the chloroform layer was drawn off with extreme care, it was found that the minute portions of aqueous solution which escaped from the separatory funnel adhered to the glass stem of the funnel. Therefore, this caused no difficulty in the procedure. Of course it was necessary to leave a small amount of the chloroform layer in the separatory funnel with each extraction until the final one. If this was not done, the aqueous solution trapped in the stopcock orifice was forced out with the following chloroform extraction.

The extracts were drawn off and combined in volumetric flasks of the desired volume, along with a final pure chloroform extract which was used in most experiments. In all cases, a colorimetric procedure was used to determine the metal extracted. This was done either by diluting the combined extracts to volume and measuring the color formed with an aliquot, or by developing the color directly in the combined extracts.

Difficulties, which will be mentioned later, made it impossible to get any data to substantiate the α-benzoin oxime to metal ratios by the method of continuous variations. Therefore, the following method was used with considerable success. A series of solutions of varying concentrations of the metal being studied was prepared. A certain volume, for example, ten ml. of these solutions was extracted with a certain volume of α-benzoin oxime solution in chloroform of known concentration. The α-benzoin oxime solution was made up so that, on the basis of the postulated complex ratio, there would be an excess of α-benzoin oxime for the lower metal ion concentrations and a

deficiency for those of higher concentrations. That is, for a postulated one to one complex the metal ion concentrations could vary from 1×10^{-3} M. to 3×10^{-3} M., and for extraction with an equal volume of α-benzoin oxime solution, its concentration would be 2×10^{-3} M.

By determining the amount of metal extracted spectrophotometrically, a plot of the absorbance versus metal:α-benzoin oxime ratio resulted in a curve with a sharp break at the metal-α-benzoin oxime ratio of the compound.

Other specific procedures which were used, but not extensively, will be described when applicable during the discussion of the experimental work.

III. MOLYBDENUM

Since earlier work on molybdenum actually gave rise to this study, molybdenum has been selected as the starting point for the discussion of these complexes.

A. Results of Gravimetric Work

A brief report of earlier work by this author (12) is included here as a starting point for a discussion of the experimental work conducted more recently. Although the α-benzoin oxime complex was originally reported as unstable when heated, it was found that when all excess reagent was removed, the complex could be dried to constant weight at 105° C. and weighed. Using the method earlier described in the experimental procedure section, the complex was found to contain 16.51% molybdenum. This gives a much more favorable gravimetric factor than ignition to the trioxide which contains 66.65% molybdenum. On the basis of these results the complex of molybdenum with α-benzoin oxime was postulated as bis(α-benzoinoximato)dioxomolybdenum (VI). This postulated complex contains 16.51% molybdenum, the value determined experimentally.

It was also shown that the large excess of reagent used in the original method was not necessary. In fact a 10% excess of α-benzoin oxime was all that was required for quantitative precipitation of molybdenum from a solution 5 to 20% acid by volume. This made possible the complete removal of excess reagent, which was necessary to obtain the complex in a stable weighing form.

The quantitative precipitation was shown to be successful in the presence of iron (III), chromium (VI), and vanadium (V) when the chromium (VI) and vanadium (V) were first reduced with sulfurous acid or ferrous ammonium sulfate.

On this basis a method for the determination of molybdenum in non-tungsten steels was developed. The samples were dissolved in 1:5 sulfuric acid, followed by the addition of sufficient nitric acid to oxidize the carbon and molybdenum present. Sufficient sulfurous acid or ferrous ammonium sulfate was added to reduce any chromium (VI) or vanadium (V). The molybdenum was then precipitated by the drop-wise addition of a 30 to 40% excess of the α-benzoin oxime in 50% acetone. The precipitates were immediately filtered on sintered glass crucibles, washed with two 5 ml. portions of 50% acetone, and dried to constant weight in a 105° C. oven. The molybdenum was calculated as 16.51% of the complex.

The method was applied with considerable success to seven non-tungsten steels from the National Bureau of Standards.

In this original work, the complex was postulated as $MoO_2(C_{14}H_{12}O_2N)_2$ on the basis of the per cent molybdenum determined. However, additional evidence to support this postulation was desired.

Literature data indicate that the MoO_2^{++} cation is the major species in solution only when the acidity is increased beyond the isoelectric point at pH 0.9. On this basis it appears quite logical that in 5 to 20% acid solution the MoO_2^{++} ion will be the species involved in complex

formation. To further substantiate this point, the following experiment was run.

A series of solutions containing an equivalent amount of molybdenum were adjusted to varying acidities with hydrochloric acid using a pH meter. Sufficient α-benzoin oxime in 50% acetone was then added to each drop-wise from a buret.

In solutions of pH 2.5-7 there was no precipitate formed. At pH 2.5, a slight cloudiness was observed in the solution and at 1.75 a much cloudier solution resulted. At pH 1 a considerable amount of flocculent white precipitate was formed. At pH values below one a large amount of heavy white flocculent precipitate was formed. These results indicate even more strongly that it is the MoO_2^{++} cation which enters into complex formation, since very little precipitate is formed at pH values above the isoelectric point.

To further substantiate the proposed formula of the molybdenum complex, additional evidence of the formation of a two to one complex was required. Although the complex itself is colorless, the possibility of determining the complex ratio by the method of continuous variations, through absorption in the ultra-violet was considered.

The solubility of both α-benzoin oxime and the molybdenum complex in water is almost negligible. In addition to this, an acid solution is required for the formation of the complex. A solvent system was required which could be made 5% in hydrochloric acid while still maintaining a sufficient solubility of molybdenum ion, α-benzoin oxime,

and complex. A 1:1 acetone-water system meets the above requirements, but, due to the acetone cut off in the ultra-violet, could not be used. Therefore a 1:1 ethanol-water system was selected in spite of the decreased solubility of the complex.

Using a 1:1 ethanol-water system containing 5% hydrochloric acid as the solvent, the following solutions were made up: (1) 1×10^{-4} M. molybdate, (2) saturated solution of pure molybdenum-α-benzoin oxime complex, (3) 0.5×10^{-4} M. molybdate and 0.5×10^{-4} M. α-benzoin oxime. Spectra of these solutions were run on the Beckman DK-2 Spectrophotometer using the described solvent as a reference. In each case one absorption peak was observed with a maximum at 250-252 millimicrons. Anticipating future work, a similar series were run for the tungsten-α-benzoin oxime complex with the same results. Since no noticeable differences were observed in the ultra-violet spectra for the reagent and the complexes, a method of continuous variations experiment could not be devised.

B. Extraction Methods to Substantiate Mo:α-Benzoin Oxime Ratio

At this point, another method to establish the complex ratio was carried out. This method was based upon the procedure involving spectrophotometric measurement of the quercetin-molybdenum complex devised by Goldstein, Manning and Menis (10). The general method used subsequently in this work has been described in the procedures section.

1. Extraction from 5% acid. A series of molybdenum solutions varying in concentration from 0.2×10^{-3} M. to 1.8×10^{-3} M. were made

up by dilutions with 5% HCl from a 1 x 10^{-2} M. sodium molybdate in 5% HCl solution. Ten ml. of each of these solutions were pipeted into 60 ml. separatory funnels. Twenty ml. of a 1.0 x 10^{-3} M. α-benzoin oxime in chloroform solution was pipeted into each of the separatory funnels. The separatory funnels were then shaken on the automatic shaker for 15 minutes and the layers allowed to separate. The chloroform layer was carefully drawn off into 50 ml. volumetric flasks and the aqueous layer was then extracted with a ten ml. portion of chloroform. This was combined with the extracts in the 50 ml. volumetric flasks, which were diluted to volume with chloroform. Two ml. aliquots of these solutions were pipeted into 25 ml. volumetric flasks containing ten ml. of 95% ethanol and three ml. of a 0.1% quercetin solution in ethanol. The solutions were then diluted to volume and the absorbance measured at 420 mμ, absorption maximum for the molybdenum-quercetin complex. The absorbance was then plotted versus the molybdenum:α-benzoin oxime ratio for each solution in Figure 1. The data are recorded in the Appendix.

A definite break is observed in the curve where 0.95 x 10^{-2} millimole of molybdenum has been extracted with 2 x 10^{-2} millimole of α-benzoin oxime. The fact that the break comes at slightly less than 1.0 x 10^{-2} millimole is to be expected since extraction of solutions in the absence of excess reagent is not complete.

This extraction procedure along with the per cent molybdenum determination substantiates the postulated two to one complex. Also the fact that this complex forms completely only in the acidity region

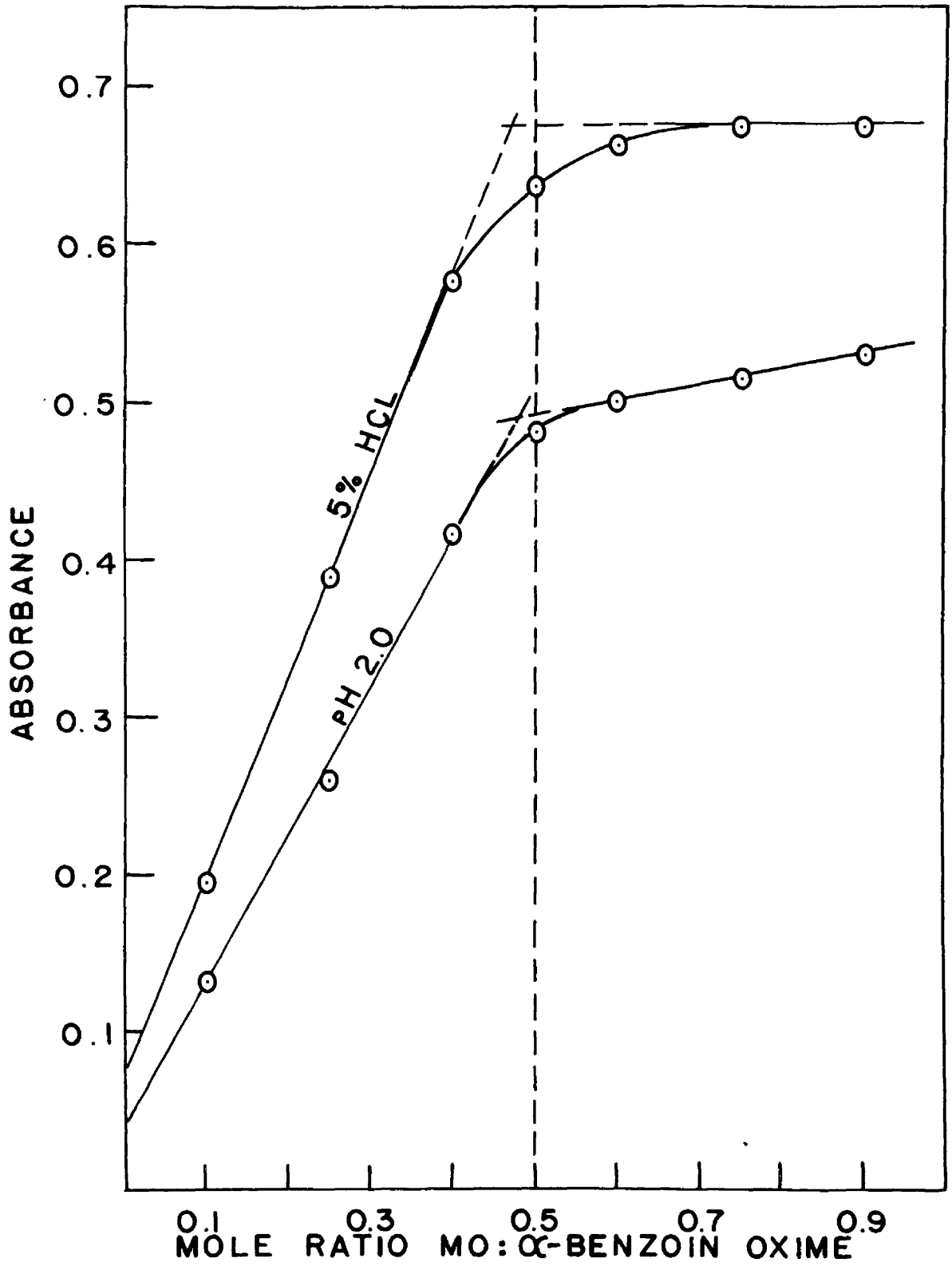


Figure 1. Determination of Molybdenum: α-Benzoin Oxime Ratio by Extraction Procedure.

where MoO_2^{++} is the reported species in solution, as well as the per cent molybdenum in the complex, definitely indicate that the complex is $MoO_2(C_{14}H_{12}O_2N)_2$.

2. Extraction at pH 2.0. The one other possibility that it appeared desirable to check was the possible formation of a different complex in less acid media. Even though the precipitate formed in less acid media appeared to be the same flocculent white material. To do this, the exact extraction procedure as reported above was employed. The only factor varied was the acidity of the molybdenum solutions which this time were adjusted to a pH of 2 with hydrochloric acid rather than using 5% HCl solutions. These results are also plotted in Figure 1, and the data recorded in the Appendix.

In this case as before, a sharp break occurs showing the complex contains two α-benzoin oxime molecules per molybdenum. The fact that the extraction is much less at pH 2 as shown by a comparison of the two plots is also in accord with theoretical predictions. The conversion to MoO_2^{++} ion is not complete until the acidity has been increased well beyond the isoelectric point at pH 0.9. Therefore complete extraction of molybdenum as $MoO_2(C_{14}H_{12}O_2N)_2$ would not be expected at pH 2 because the equilibrium processes for the isopoly acid conversions appear to be slow. This is quite clearly indicated by a comparison of the two plots.

C. Revision of Molybdenum Extraction Procedure

The success of the gravimetric method for the determination of molybdenum indicated that a better extraction procedure than that of Jeffrey (14) for small amounts of molybdenum could be worked out. Jeffrey's method involves the precipitation of the complexes of molybdenum and tungsten followed by extraction into chloroform. The solvent is then evaporated off and the complexes dissolved with concentrated sulfuric acid to obtain solutions to be extracted as complexes of toluene-3:4-dithiol. In addition to the involved procedure, only microgram quantities can be determined by this method.

However, while the present investigation was being conducted the extraction method of Goldstein, Manning and Menis (10) was published. This method which has been referred to earlier can be very successfully applied to samples containing 0.05 to 5.0 mg. of molybdenum. Although the method is good, the authors reported serious interference was caused by the presence of tungsten and vanadium. They made no attempt to correct for this since for their purposes this was not important. The greatly increased applicability of this method if these interferences could be eliminated seemed an appropriate part of the study which was being conducted. Since a thorough investigation of these complexes was being conducted a large amount of data was available for this purpose.

Several factors which will be discussed in more detail in the tungsten and vanadium sections made the elimination of these interferences appear possible. These factors are the very small solubility of the

tungsten-α-benzoin oxime complex in chloroform, the apparent stability of phosphotungstic acid, and the fact that vanadium (IV) does not form an α-benzoin oxime complex.

The method proposed by Goldstein, Manning and Menis involves three extractions of the molybdenum containing solutions with 15 ml. portions of 0.1% α-benzoin oxime solution in chloroform. This is followed by a final extraction with 20 ml. of chloroform.

The extracts are combined in a 100 ml. volumetric flask and diluted to volume with chloroform. A one ml. aliquot is then pipeted into a 25 ml. volumetric flask containing ten ml. of ethanol and three ml. of a 0.1% quercetin solution in ethanol. This is diluted to volume with chloroform and the absorbance measured at 420 millimicrons against a quercetin blank. The amount of molybdenum is then determined from a prepared calibration curve. For solutions containing less than 0.5 mg. of molybdenum, 5.0 cm. cells are used for absorbance measurements on the spectrophotometer. It is also of interest that for samples containing more than 0.5 mg. of molybdenum, the combined chloroform extracts have a cloudy appearance. This is due to the fact that the molybdenum complex has a very limited solubility, but is still extracted into the chloroform layer. If these solutions are allowed to stand, the precipitates can be seen to coagulate into a white flocculent precipitate. For this reason it is very important that they be thoroughly shaken before the one ml. aliquot is removed for color development.

The first attempt to eliminate the interference of tungsten involved a decrease in the volume of chloroform used for the extraction

of molybdenum. However, attempts to develop a calibration curve under these conditions gave very poor results. Therefore, the exact extraction procedure was found to be necessary.

At this point a calibration curve was prepared for the range from 0.5 to 1.50 mg. of molybdenum. Only two modifications of the exact literature procedure were incorporated. The first involved dilution of the combined chloroform extracts to 100 ml. with ethanol rather than chloroform. This gave a much greater solubility of the complex and thus more assurance of a homogeneous system for removal of the aliquot. In addition, since a lower molybdenum range was being studied, two ml. aliquots of the extracts were used for color development with quercetin. Very good results were observed in the preparation of the calibration curve.

The proposed method for the elimination of the interferences, tungsten and vanadium, involved the reduction of vanadium with ferrous ammonium sulfate, and complexing the tungsten as phosphotungstate prior to molybdenum extraction. This was based on two phenomena. Vanadium can be eliminated as an interference in the gravimetric method by prior reduction. And, as will be discussed later, the formation of the tungsten α-benzoin oxime complex is greatly hindered by the presence of phosphate. Also the original method has shown phosphate not to interfere in the molybdenum extraction.

A series of samples containing one mg. of molybdenum were run. To these were added either vanadium (V) or tungsten (VI) or both as interferences. To the samples containing vanadium (V), excess ferrous

ammonium sulfate was added before extraction, to those containing tungsten, excess monobasic potassium phosphate. For combined interferences, both reagents were added in excess. The molybdenum value was determined from the previously prepared calibration curve. The results of these experiments are listed in Table I.

The results listed in Table I clearly show that the method of Goldstein, Manning, and Menis has been revised so that it can now be applied even to samples containing a moderate amount of vanadium and tungsten. This means an extremely rapid method for the determination of molybdenum in a wide variety of samples is available.

It is of interest to note that a larger excess of ferrous ion is required for the reduction of vanadium. This would tend to indicate that heteropoly acid formation in the presence of molybdenum or tungsten may make the vanadium (V) less accessible to reduction. It is also interesting that with phosphate present, where phospho molybdates, tungstates, and vanadates should be formed, the vanadium is easily reduced with a smaller excess of ferrous ion. Also there exists a slight negative error where phosphate and vanadium but no tungsten are present. This may involve a formation of a slight amount of vanado-phosphomolybdate in which either the vanadium is not reduced or the heteropoly acid is formed with vanadium (IV). The presence of tungsten which forms a more stable vanado phosphotungstate eliminates this effect.

It is therefore possible to remove the interference caused by vanadium by the addition of ferrous ammonium sulfate in excess.

TABLE I

ELIMINATION OF INTERFERENCE OF VANADIUM AND TUNGSTEN IN MOLYBDENUM EXTRACTION PROCEDURE

Interference, Mg.		Inhibitor, Mg.		Molybdenum, Mg.		
W (VI)	V (V)	$PO_4^{=}$	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	Present	Found	Difference
				1.00	0.98	-0.02
					1.00	.00
					0.99	-0.01
1.0					1.45	+0.45
	1.0				1.15	+0.15
1.0		2.5			0.99	-0.01
1.0		2.5			0.99	-0.01
2.0		2.5			0.99	-0.01
	1.0		50		1.05	+0.05
	1.0		50		1.06	+0.06
	1.0		50		1.05	+0.05
	2.0		100		1.04	+0.04
	1.0		100		1.00	0.00
	1.0		100		1.00	0.00
	1.0	2.5			0.95	-0.05
	1.0	2.5	100		0.95	-0.05
1.0	1.0	2.5	50		1.00	0.00
1.0	1.0	2.5	50		0.99	-0.01
2.0	2.0	5.0	100		1.01	+0.01

Tungsten interference can be eliminated by the addition of excess phosphate. This can be accomplished simultaneously in the presence of both elements, or individually when only one is present.

IV. TUNGSTEN

On the basis of the reported data in the literature concerning the determination of tungsten using α-benzoin oxime, no difficulties in the experimental work were anticipated. Since no dissimilarities between molybdenum and tungsten were reported, the possibilities of repeating the molybdenum work on tungsten with no major problems seemed possible. However, this was far from true. Dissimilarities were more numerous than similarities.

A. Solution Problems

The first troublesome factor, which had been anticipated, was the problem of maintaining acidified solutions of sodium tungstate without precipitation of hydrated tungstic acid. As can be seen from species studies on acidified tungstate solutions, no evidence has been presented for the formation of a WO_2^{++} cation beyond the isoelectric point. Whether or not this occurs has not been definitely established, as it may be this cationic species which unites with a hydrated tungsten anionic species to form the hydrated tungstic acid which precipitates. At any rate, precipitation occurs beyond the isoelectric point, and has been observed in solutions less acid than pH 1 after long periods of time.

Tungsten may be maintained in acid solution by the addition of phosphate or other ions which form heteropoly acids with tungsten, since the heteropoly acids are very soluble in aqueous media. Tungsten may also be complexed with tartrate, citrate or fluoride.

The formation of the fluoride complex has been quite extensively used for preventing precipitation of tungstic acid. In addition, the fluoride complex is reported to be $WO_2F_4^{=}$, which gives some evidence for the existence of the WO_2^{++} ion.

The acid used for acidifying tungsten solutions is also important. If, for example, a 1×10^{-2} M. sodium tungstate solution is acidified with 6N·HCl, there is an immediate formation of hydrated tungstic acid. However, if 6N·H_2SO_4 is used, there is no evidence of precipitation for fifteen to twenty minutes.

With respect to the addition of phosphate or fluoride to keep tungsten in acid solution, the following facts were observed. With the addition of a slight excess of phosphate over the amount required for the formation of the limiting 12-phosphotungstic acid, no difficulty was encountered with precipitation of tungstic acid for any of the solutions used in this experimental work. When a solution 2×10^{-2} M. in tungstate and 1×10^{-1} M. in fluoride was made 5% in sulfuric acid, no immediate precipitation occurred. However, after standing for fifteen to twenty minutes, the yellow β-tungstic acid, H_2WO_4, began to precipitate from the solution. This solution contained a 20% excess of fluoride on the basis of a $(WO_2F_4)^{=}$ complex. When the fluoride ion concentration was doubled, this was not observed in the same time period, but standing over-night gave the same results.

This is just a brief description of solubility problems and the effect of complexing reagents. Further discussion is included as the factors apply to specific cases in the α-benzoin oxime procedures.

B. Extraction Experiments

On the basis of the success achieved in establishing the ratio of the molybdenum complex by means of extraction into chloroform, similar results were predicted for tungsten. Jeffrey (14) had reported no dissimilarities in his procedure for the extraction of microgram quantities of molybdenum and tungsten α-benzoin oxime complexes into chloroform.

Since the toluene-3:4-dithiol method is rather involved, and also used for very small quantities of tungsten, it was hoped that a different method for tungsten could be devised. After the publication of the quercetin procedure for molybdenum, and the reported interference of tungsten, the possibility of using the same procedure for tungsten was considered.

With this purpose in mind the spectra of the tungsten-α-benzoin oxime complex was determined using the Beckman DK-2, and is shown in Figure 2. For this purpose chloroform was employed as the solvent and quercetin in chloroform was used as the reference. Comparing these results with the reported spectrum for molybdenum it may be seen that both exhibit the same absorption maxima, the only difference being a slight displacement. For molybdenum the peak occurs at 420 mμ, for tungsten at 425 mμ. In addition, the absorbance shown by tungsten with a broad peak occurring from 370-380 mμ is not reported for molybdenum.

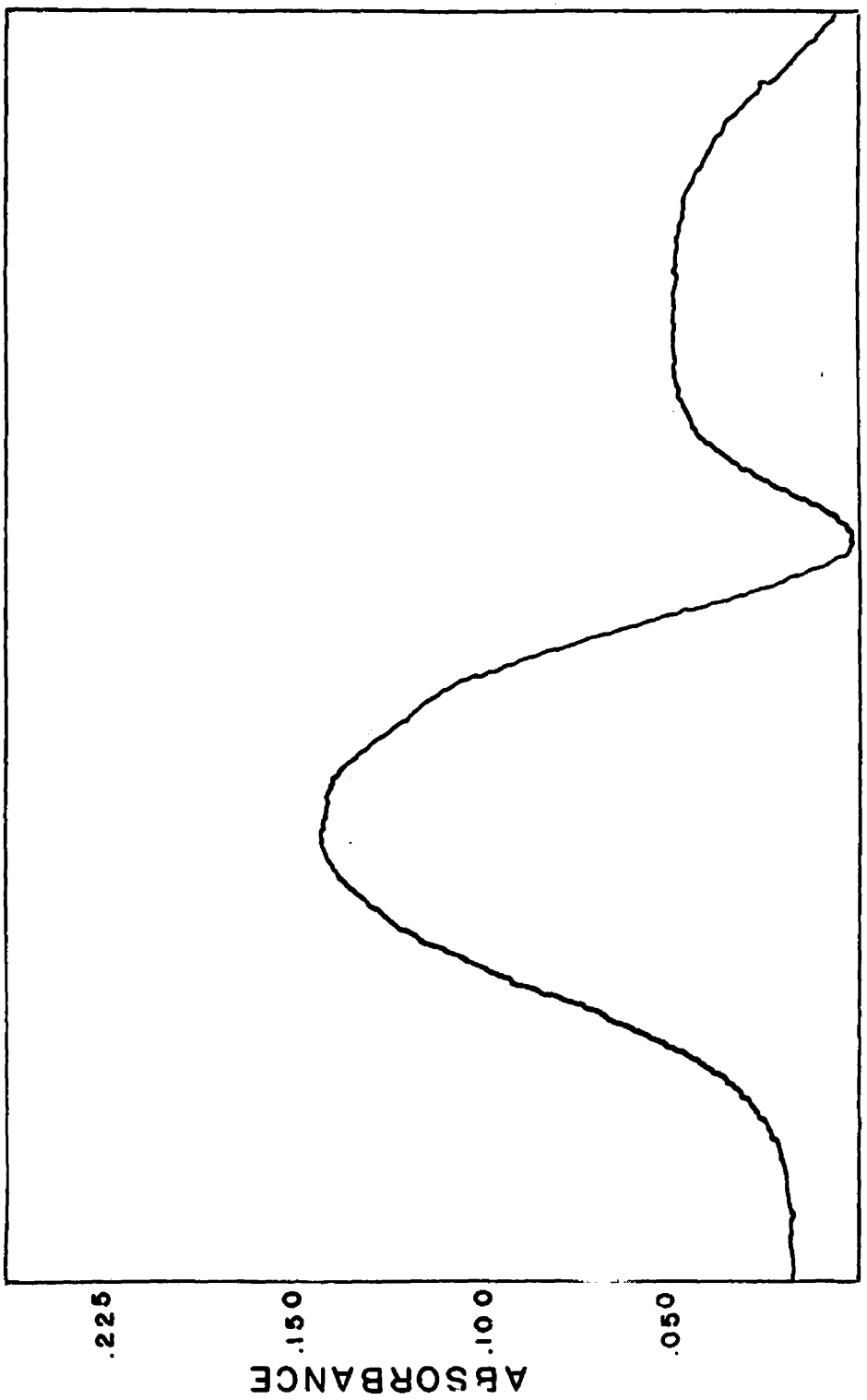


Figure 2. Absorption Spectrum of Tungsten-Quercetin Complex Versus Quercetin.

This suggested two experimental possibilities. The first being the determination of the complex ratio using the same method as that for molybdenum. The second, a simultaneous, differential method for molybdenum and tungsten by measurement of the color developed by the quercetin complex at 420 and 375 mμ.

The same extraction procedure as reported in the procedural section, and for molybdenum, was used in an attempt to establish the tungsten-α-benzoin oxime complex ratio. A series of solutions having a tungsten concentration from 0.2×10^{-3} to 2.0×10^{-3} M. were prepared, each containing an equimolar amount of tungsten and phosphate ion. The acidities were then adjusted to contain 4% sulfuric acid by addition of the concentrated reagent. The phosphate was added before acidification to prevent precipitation of tungstic acid. Ten ml. portions of these solutions were extracted with 20 ml. portions of 1×10^{-3} M. α-benzoin oxime in chloroform, followed by extraction with ten ml. portions of chloroform. The extracts were combined in 50 ml. volumetric flasks and diluted to volume with chloroform. Three ml. aliquots were used for color development with quercetin which was done exactly as for molybdenum. When the absorbance was measured at 425 mμ it was found that for the entire series of solutions the absorbance varied only between .010 and .012. This variation is within the variation of the instrument, and thus insignificant. In fact, the very slight amount of absorbance showed the amount of tungsten present to be almost negligible.

During the extraction procedure, there was no evidence of a formation of cloudy white precipitate in the chloroform layer as in the case of molybdenum. At the time this suggested three possibilities: (1) that the tungsten complex is more soluble than that of molybdenum, (2) that the tungsten complex is not very soluble in chloroform and does not extract as a colloidal precipitate as does molybdenum, or (3) that the presence of phosphate almost completely eliminates the complex formation.

On the basis of the above results with quercetin on the extracts, greater solubility of the tungsten complex is not the explanation. This meant that either the tungsten complex is not extractable into chloroform to any extent, or the presence of phosphate prevents the formation of the complex.

To check on the latter, the exact procedure was followed with the exception that no phosphate was added. It was found at these low concentrations that if each sample was acidified and extracted with chloroform immediately no precipitation of tungstic acid occurred. This allowed the omission of the phosphate. In this case, the absorbance measurements varied from .063 to .073, here, again, within experimental error. These results proved that while the extraction of tungsten is quite obviously reduced by the presence of phosphate, the major factor appears to be the very slight solubility of the tungsten-α-benzoin oxime complex. In fact, ignition of a portion of the white material which collected at the interface of the two liquids showed the presence of tungsten. Although some white material is observed to form at the

interface during a molybdenum extraction, this is simply excess reagent, and does not contain molybdenum.

These results indicated that a more successful procedure might be possible by decreasing the concentration of tungsten and α-benzoin oxime by a factor of ten. This would of course decrease the concentration of the tungsten in solution and thus the method was modified as follows.

A series of solutions containing 0.2×10^{-4} to 2.0×10^{-4} M. tungstate were prepared. Ten ml. of each of these solutions were first extracted with 20 ml. of 1.0×10^{-4} M. α-benzoin oxime in chloroform, and then with two ten ml. portions of chloroform. The extracts were combined in 50 ml. volumetric flasks containing three ml. of 0.1% quercetin in ethanol solution, and diluted to volume with ethanol. The absorbance of these solutions were then measured at 425 mμ with a spectrophotometer. The values ranged from 0.043 to 0.006 with some evidence of a break occurring. However, with such small absorbance values, very slight experimental errors give rise to large errors in the results. Therefore the results had very little value.

In order to obtain more intensely colored solutions, the above procedure was repeated with the exception that the combined extracts were collected in beakers and evaporated to dryness. The residues were then dissolved and transferred to ten ml. volumetric flasks with several small portions of ethanol. The quercetin solution was added, they were diluted to volume, and the absorbance measured at 425 mμ. The erratic results obtained were of no value.

The alternative extraction procedure seemed to be color development with toluene-3:4-dithiol as proposed by Jeffrey (14). However, before this was undertaken, it appeared desirable to determine, at least approximately, the maximum solubility of the tungsten complex in chloroform. For this purpose, a portion of chloroform was saturated with complex by shaking it overnight on an automatic shaker in the presence of excess tungsten complex. The solution was filtered, 150 ml. were pipeted into a previously weighed platinum dish, and evaporated to dryness on a steam bath. The residue was found to weigh 0.0180 gms, and thus the solubility of the tungsten-α-benzoin oxime complex to be 0.12 mg./ml. of chloroform.

On the basis of a proposed complex having the formula $WO_2(C_{14}H_{12}O_2N)_2$, which would be expected following the molybdenum work, this would make the concentration of a saturated chloroform solution 1.8×10^{-4} M. Under the conditions encountered in an extraction procedure, it would be impossible to saturate the chloroform layer, and thus the amount extracted would be less than 10^{-5} mole in 50 ml. In order to successfully apply the proposed extraction procedure for determining the tungsten:α-benzoin oxime ratio the oxime concentration would necessarily be below 1×10^{-4} M. The possibility of successfully extracting the tungsten with an oxime solution of such low concentration seemed improbable. Some other common solvents, such as benzene, carbon tetrachloride, ethyl ether, and ethyl acetate, showed even less promise. Therefore, a gravimetric procedure was devised for establishing the α-benzoin oxime:tungsten ratio.

C. Precipitation Experiments

1. Establishing tungsten:α-benzoin oxime ratio of complex. The gravimetric procedure developed was very similar to the attempted extraction procedure. It involved the precipitation of a constant amount of tungsten with varying amounts of α-benzoin oxime. It was postulated that the weight of the complex formed would increase with increasing oxime addition. This should occur until sufficient oxime is added for precipitation of the amount of tungsten chosen. Further addition of reagent beyond this point should result in no further increase in the weight of precipitate. Therefore, a plot of weight of precipitate versus mole ratio of tungsten to reagent will yield a break when equivalent amounts are present.

For this purpose a solution of 1×10^{-2} M. sodium tungstate which was also 1×10^{-2} M. in phosphate and 4% in sulfuric acid was made up. This provided just a slight excess of phosphate to prevent precipitation of tungstic acid. Ten ml. portions of this solution were precipitated with varying, measured portions of α-benzoin oxime. The precipitation procedure followed was the same as described in the section on procedures. The flocculent white precipitate, which filters more easily than the molybdenum complex, was filtered onto 30 ml., medium porosity, sintered glass crucibles. The results obtained are recorded in the first half of Table II. They show that either precipitation of tungsten with α-benzoin oxime is far from complete, or the presence of phosphate interferes in the complex formation.

TABLE II

PRECIPITATION OF TUNGSTEN WITH VARYING AMOUNTS OF α-BENZOIN OXIME

$WO_4^{=}$, mmole	α-Benzoin Oxime, mmole	Complex, Gm. Formed	Complex, Gm. Theoretical for $WO_2(C_{14}H_{12}O_2N)_2$
Precipitation from 1 x 10^{-3} M. PO_4 solution			
0.100	0.040	0.0014	0.0267
0.100	0.100	0.0042	0.0401
0.100	0.160	0.0026	0.0535
0.100	0.220	0.0029	0.1337
0.100	0.280	0.0040	0.1337
0.100	0.340	0.0047	0.1337
0.100	0.400	0.0038	0.1337
Precipitation from 0.1 M. F^{-} solution			
0.100	0.040	0.0168	0.0267
0.100	0.060	0.0351	0.0401
0.100	0.080	0.0499	0.0535
0.100	0.100	0.0618	0.0699
0.100	0.120	0.0736	0.0802
0.100	0.140	0.0861	0.0934
0.100	0.160	0.1005	0.1070
0.100	0.180	0.1091	0.1303
0.100	0.260	0.1300	0.1337
0.100	0.300	0.1322	0.1337
0.100	0.340	0.1324	0.1337

To check on the interference by phosphate, the exact procedure was repeated with the exception that the phosphate was eliminated, but the solution was made 0.1 M. in potassium fluoride. This last was necessary to avoid precipitation of tungstic acid. The results of this set of experiments are recorded in the last half of Table II, and the results are plotted in Figure 3.

The sharp break in the plot illustrates that the tungsten complex contains two α-benzoin oxime molecules per tungsten atom, just as in the case of the molybdenum. From the results in the last half of Table II it may also be seen that in the absence of excess reagent the precipitation is not complete just as for molybdenum. However, even with the addition of excess reagent, the results remain slightly low. Such is not the case with molybdenum. It is also obvious from a comparison of the first and last half of Table II that phosphate must be absent for the precipitation of tungsten.

The above results were not enough to establish the formula of the complex as $WO_2(C_{14}H_{12}O_2N)_2$ without knowing the per cent tungsten in the compound. This was accomplished using the method described in the section on procedures. The results are listed in Table III.

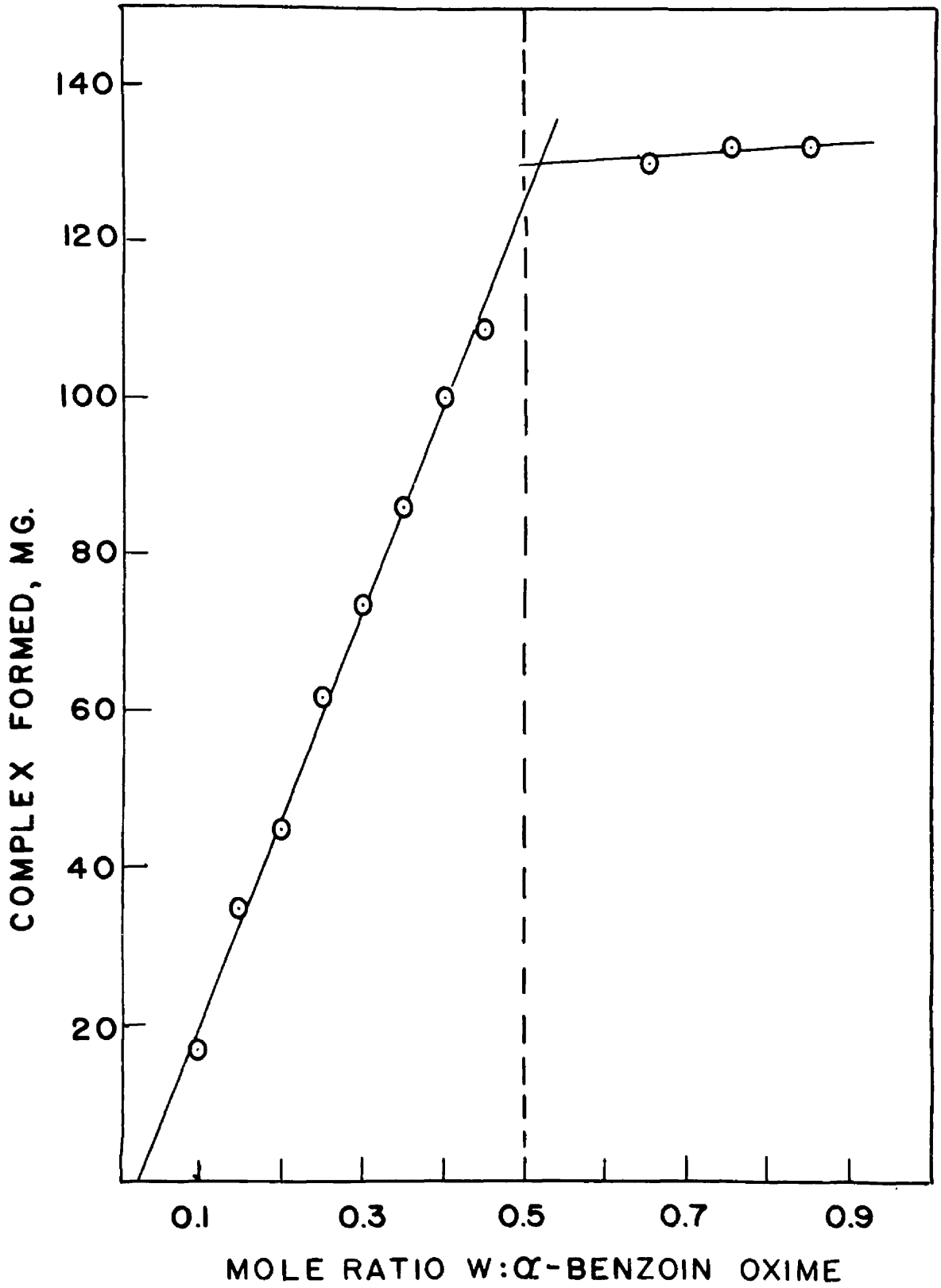


Figure 3. Precipitation of Tungsten Complex with Varying Amounts of α-Benzoin Oxime.

TABLE III

DETERMINATION OF PER CENT TUNGSTEN IN α-BENZOIN OXIME COMPLEX

Complex, Gm.	0.1848	0.1949	0.2073	0.1987	0.1720
WO_3, Gm.	0.0645	0.0681	0.0715	0.0689	0.0691
Per Cent W in Complex	27.68	27.70	27.42	27.50	27.59
Average			27.58		

The per cent tungsten calculated for the postulated $WO_3(C_{14}H_{12}O_2N)_2$ is 27.51%. The average of the experimental results is within two parts per thousand of the theoretical, and therefore within experimental error. The combined results of these experiments is enough to establish the formula of the complex as $WO_3(C_{14}H_{12}O_2N)_2$.

2. Attempted gravimetric procedure. In order to assist in establishing a gravimetric procedure for tungsten, the solubility of the complex in varying acetone concentrations was determined. This was accomplished by evaporating 150 ml. of a saturated solution in a platinum dish and weighing the residue. These solubility measurements were not carried out with great precision since relative and not absolute values were all that were required. A 50% acetone solution saturated with tungsten complex was found to contain 0.30 mg./ml. of the complex. For a 25% solution, the value dropped to 0.19 mg./ml. and for 15% acetone it was found to be only 0.02 mg./ml. This solubility in 15% acetone is even

slightly less than that exhibited by the molybdenum complex, and should thus cause no difficulty in a gravimetric procedure.

In the first attempt at a gravimetric precipitation, a slight excess of fluoride was added and the solutions were acidified with hydrochloric acid. Due to formation of tungstic acid, solid potassium fluoride was added until the precipitate dissolved before addition of the α-benzoin oxime solution. The results obtained showed that less than half of the tungsten was recovered. Therefore, in succeeding experiments, sulfuric acid was used so that the amount of fluoride could be held down.

For this study, a 0.0272 M. tungstate solution was prepared so that one ml. would contain 5.00 mg. of tungsten. The reagent solution was made up 0.0272 M. in α-benzoin oxime and 50% acetone. One ml. of this solution was thus required for the precipitation of 2.50 mg. of tungsten. Before acidification of aliquots of the above tungstate solutions equal volumes of 0.136 M. potassium fluoride were added. This provided a 20% excess of fluoride ion for $WO_2F_4^{=}$ formation.

Using these solutions and the precipitation procedure previously described, the precipitation of tungsten was fairly successful with the results in all cases being a few milligrams low. However, when the effect of the fluoride was checked by omitting fluoride and carrying out the precipitation immediately upon acidification, the recovery of tungsten was less than half. The results were found to be low also when a deficiency of fluoride was added. The same was found to be true

when ferric ion was added to a solution containing the slight excess of fluoride. In every case of low results, complex was observed to form in the filtrate after filtration, the flocculent white precipitate being easily distinguished from the needle-shaped crystals of excess reagent. This was observed even when the precipitates were allowed to stand for a half hour before filtration. Longer standing time could not be tolerated because beyond this the excess reagent crystallized out and can not be removed with washing.

The apparent effect of fluoride ion upon the precipitation made it advisable to check the precipitation in solutions of varying fluoride ion concentration.

Two sets of samples were run, with 5 ml. of tungstate solution, or 25.0 mg. of tungsten, and 10 ml. of tungstate solution, or 50.0 mg. of tungsten. To each of these solutions were added varying amounts of fluoride ion before precipitation. The precipitation procedure was carried out in the usual manner, and the weight of tungsten calculated from the weight of the complex obtained. Since the results of these experiments are more significant graphically they have been plotted in Figure 4, and the data recorded in the Appendix. To make the plot more meaningful, the weight of tungsten recovered has been plotted as a function of the mole ratio of fluoride to tungstate.

The results of these experiments are quite significant. They show that where there is a deficiency of fluoride ion for conversion to $WO_2F_4^=$ the precipitation of the tungsten is far from complete.

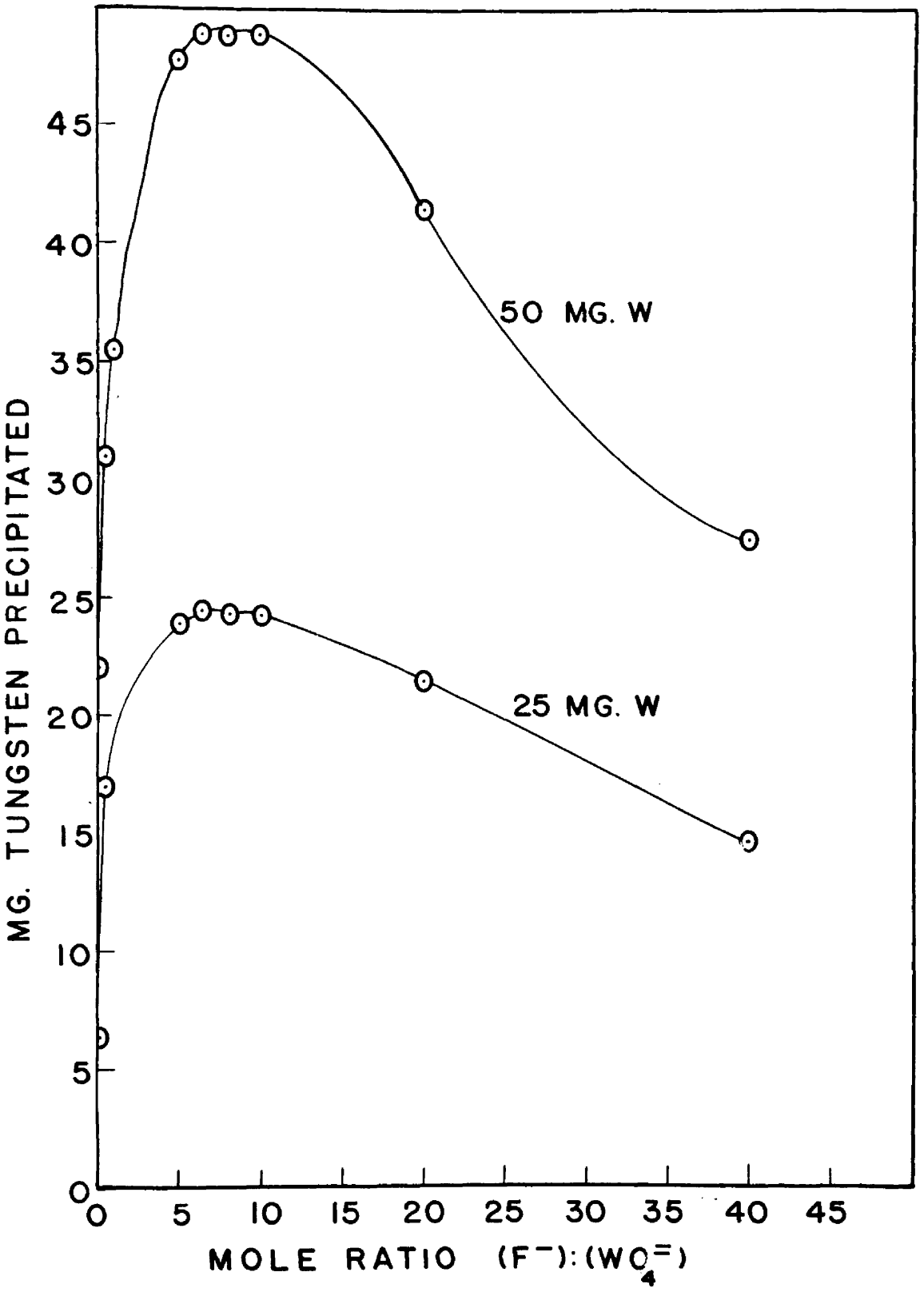


Figure 4. Effect of Fluoride Ion Concentration on Tungsten Precipitation.

Also as the fluoride ion concentration is greatly increased, the fluoride complex is stabilized again yielding far from complete precipitation.

These factors make the quantitative precipitation of tungsten with a small excess of α-benzoin oxime impossible. In order to have the mole ratio of fluoride to tungsten correct for the region where the precipitation is almost quantitative it would be necessary to know quite closely the tungsten content of the sample before precipitation. Even for cases where this were true, control of the fluoride ion would be almost impossible due to the presence of the large number of other elements, such as iron, which also form fluoride complexes.

On the basis of these results it is difficult to understand how the combined precipitation first proposed by Ingods and Wales (30) has been successful. However, if the precipitation conditions are considered this too becomes understandable. The combined precipitation is carried out from an acid solution to which no complexing agents have been added. This is the situation in which insoluble hydrated tungstic acid is readily formed. In addition to this, the extremely large excess of reagent added results not only in the complete precipitation of the molybdenum complex, but also in partial precipitation of the tungsten complex, and excess reagent. Due to the flocculent nature of these complexes, the formation of all this precipitate could quite easily carry down the hydrated tungstic acid, which is quite often colloidal. Since the precipitate in this method is not weighed, the nature of the

precipitate is not important. This could quite easily explain why these authors reported a negative error on all determinations run on pure sodium tungstate solutions and not on steel samples. In the absence of the large amount of molybdenum complex, it would be quite logical for a portion of tungsten to remain unprecipitated.

Although no new methods of determination for tungsten resulted from this study it can be readily explained why the existing methods are successful. The gravimetric method has just been discussed. The colorimetric method works because toluene-3:4-dithiol is such a sensitive indicator that only microgram quantities of tungsten are required. Thus with these extremely small quantities no solubility problem of the complex in chloroform is encountered. In addition to this, the formula for the tungsten-α-benzoin oxime complex has been established, and some interesting data on the tungsten species in acid solution containing fluoride has been recorded.

Finally on the basis of the insolubility of the tungsten complex, and the great decrease of complex formation in the presence of phosphate, the newer extraction method has been revised to be specific for molybdenum. This was described in the molybdenum section.

V. CHROMIUM

A discussion of the results of the chromium experiments can be done very briefly, as the work was entirely unsuccessful.

A. Extraction Attempts

Although no reported interference by chromium has been reported for extraction procedures employing α-benzoin oxime, it was necessary to check the extraction over a range of acidity values. For this purpose, use was made of the colorimetric method for chromium using the deep red color developed by diphenylcarbazide. This method is described in Analytical Chemistry of the Manhattan Project (15). A series of solutions of varying acidity were prepared containing 0.05 mg. of chromium per ml. Ten ml. portions of these solutions were extracted with ten ml. of 0.1% α-benzoin oxime in chloroform. The extracts were drawn off into 100 ml. volumetric flasks containing ten ml. of 0.1% diphenylcarbazide in ethanol and ten ml. of water. One drop of 6N. HCl was added to each, and they were diluted to volume with ethanol. For an estimate of the amount of chromium extracted, the following standard was prepared. Ten ml. of the chromium solution, 0.05 mg./ml., was pipeted into a 100 ml. volumetric flask. To this were added 10 ml. of the 0.1% α-benzoin oxime in chloroform solution, ten ml. of the diphenylcarbazide solution, and one drop of 6 N. HCl, and it was diluted to volume with ethanol. This gave exactly the same composition of solution as for the samples, and would correspond to 100% extraction of the chromium. The absorbance was then measured at 540

mμ, the peak absorbance for the red-colored complex formed. The results are recorded in Table IV.

TABLE IV

ABSORBANCE OF DIPHENYLCARBAZIDE COMPLEX OF CHROMIUM EXTRACTED WITH α-BENZOIN OXIME AT VARYING ACIDITIES

	Acidity						
	pH				Per Cent HCl		
pH, or acidity	5.8	3.4	2.1	0.7	1.0	2.5	5.0
Absorbance	0.008	0.007	0.009	0.019	0.022	0.021	0.024

Absorbance of standard corresponding to 100% extraction = 1.80

From these results it may be seen that even in higher acid concentration the amount of chromium extracted is only approximately 1% of that present. Whether this lack of extraction is due to non-formation of complex, insolubility of the complex formed, or reduction of chromium by reagent could not be determined since it was impossible to obtain any pure complex for solubility measurements. This will be shown in the next section.

B. Precipitation Attempts

To check on the complex formed by precipitation of chromium (VI) with α-benzoin oxime, a solution of potassium chromate in 5% hydrochloric acid was prepared. The chromium in a sample of this solution

was precipitated by the drop-wise addition of a solution of α-benzoin oxime in 50% acetone. At first, an orange precipitate started to form, but as further reagent was added, it turned to a greenish-brown gummy residue which could not be filtered, as it was absorbed into the filter paper. It was also found that when the addition of reagent was halted with the first appearance of orange precipitate, the same phenomena was observed. The reason for these results is because of the stronger oxidising power of chromium (VI) in acid solution. This results in reduction of the chromium by the α-benzoin oxime. Therefore, α-benzoin oxime is of no use and gives no clean-cut reactions to yield a stable complex with chromium. It is therefore fortunate that the interference of chromium in other reactions can be eliminated by the previous reduction of the chromium (VI) to a lower valence state.

VI. VANADIUM

The study of the reactions of vanadium with α-benzoin oxime proved to be much more difficult than for molybdenum and tungsten. The greater complexity exhibited by acid solutions of vanadium (V) accounts for the increased difficulty in obtaining results which could be correlated with literature data.

A. Precipitation Attempts

1. pH effects in precipitation. The literature data have quite definitely established the fact that in fairly strong acid solutions, that is, beyond the isoelectric point at pH 2.2, the major species in solution is the VO_2^+ cation. This offered the possibility of formation of $VO_2(C_{14}H_{12}O_2N)$ as the complex. At least this would be expected on the basis of the established formulas for molybdenum and tungsten complexes.

To check this a portion of α-benzoin oxime was added to a series of vanadium solutions at varying pH values. The results were checked by observing the solutions. At pH values from 9 to 6, no precipitate formed. At pH 4.0 the formation of a slight amount of precipitate made the solution cloudy. At pH 2.8 a quantity of dark yellow precipitate formed. A much larger mass of this flocculent yellow precipitate formed at pH 2.0. When the acidity was increased so the value of the pH fell below 1.5, no complex was observed to form with the addition of α-benzoin oxime. This showed that precipitation occurs in the region of the isoelectric point. It also indicated that beyond the isoelectric point where the major species is VO_2^+, no precipitation occurred.

2. Attempt to characterize precipitate. On the basis of these results, an attempt to establish the per cent vanadium in the yellow precipitate was undertaken. A solution of sodium vanadate was adjusted to pH 2, and less than the theoretical amount of α-benzoin oxime was added. The dark yellow precipitate was filtered and washed with 50% acetone. The per cent vanadium was determined according to the previously discussed procedure. The only variable in the original procedure was the method of drying the complex, a number of which were used. It was dried in an oven at temperatures of 130°, 105°, and 75° C., as well as at room temperature in a vacuum desiccator for various samples. The precipitates which were oven dried attained constant weight only after numerous periods of drying, and in most cases showed evidence of decomposition by turning gray in color. The results obtained were erratic, and could not be reproduced. The values for per cent vanadium varied from 22.2 to 14.1. The lower values were obtained for drying in a vacuum desiccator and drying at 75°C. This could indicate water being driven off at the higher temperatures. In addition to this when the melting point of the compound was determined, the complex turned from yellow to gray between 115° and 130° C. This could also indicate the loss of water from the structure of the complex.

Since it was also possible that the presence of excess reagent could cause this color change by reduction of the vanadium, the following experiment was carried out. The yellow complex precipitated as before was thoroughly washed with several portions of acetone, then

with water, and finally with more acetone. The complex was then dried to constant weight in a vacuum desiccator for determination of the per cent vanadium. Results determined in this manner gave vanadium percentages between 14 and 15%. Heating these samples above 100°C. also resulted in the color change, thus indicating loss of water.

Although the preceding experiment did not succeed in accurately establishing the amount of vanadium in the yellow complex it lead to another discovery. Washing with pure acetone of course resulted in dissolving a large portion of complex. When these filtrates were allowed to stand for several hours there appeared a large amount of flocculent white precipitate. This could easily be differentiated from the needle-shaped crystals of α-benzoin oxime. It therefore became evident that vanadium forms two distinct complexes with α-benzoin oxime, a white form and a yellow form.

Since little success was encountered in determining the exact vanadium content of the yellow form, attention was focused on the white precipitate. It was found that this could be quite easily prepared by precipitating the yellow complex and allowing the precipitate to stand overnight. This resulted in a conversion to the white precipitate. This could be explained when it was found the solubility of the yellow material in acetone solutions was much greater than the white. It therefore appears that the yellow precipitate is formed much more rapidly but due to its greater solubility is converted to the white species which forms more slowly, but has a lower solubility.

When these precipitates which formed on overnight standing were filtered, dried, weighed, and ignited to the oxide, the vanadium content was found to vary from 14.95% to 15.57%. However, it soon became apparent that the erratic results were due to the presence of excess reagent which precipitated during the period of overnight standing. Therefore complex prepared in this fashion was precipitated and thoroughly washed with pure acetone. When this was done successive experiments gave values of vanadium of 16.43, 16.53, 16.40 and 16.56%. The average of 16.48% clearly indicates that this white material is the originally postulated $VO_2(C_{14}H_{12}O_2N)$ which would contain 16.47% vanadium. The yellow precipitate must then be a precipitate of some polymerized vanadium form which is in equilibrium with VO_2^+ at the isoelectric point.

If the above were actually the case, the white species would be expected to form directly at lower pH values, and at higher pH values there should be no conversion of the yellow to white precipitate. It was found that when precipitation was carried out at values below pH 1.5 no yellow precipitate was formed. However, after standing for several hours precipitation of the white species took place. When the precipitation was carried out at pH 3, the yellow precipitate formed immediately. Allowing the solution to stand for several days resulted in no conversion to the white species. This further verifies the suggested explanation for the phenomena observed.

3. Correlation of results with literature data. Formation of the white precipitate having a vanadium content corresponding to

$VO_2(C_{24}H_{22}O_2N)$ was expected on the basis of species studies in acid and the results of molybdenum and tungsten experiments. However, it was hoped that a quantitative procedure could be worked out from this in which the precipitate is dried and weighed. This is impossible, because due to the long period of standing required, excess oxine also precipitates from solution. The amount of acetone required to remove the excess reagent will also dissolve a quantity of the precipitate. The only possibility would be the long involved procedure first worked out for molybdenum. That is, using final ignition of the precipitate to V_2O_5 in a muffle furnace.

The erratic results obtained in attempts to determine the vanadium content of the yellow species are now easily explained. The precipitate appears to contain structural water which is driven off at normal drying temperatures. In addition to this, the length of time before filtration would have an appreciable affect upon the amount converted to white $VO_2(C_{24}H_{22}O_2N)$. The greater solubility of the yellow complex, in addition to these other factors also made it impossible to develop a gravimetric procedure based on precipitation of the yellow form.

The most important contribution of this portion of the study is the correlation it provides concerning the species studies at the isoelectric point of pH 2.2. Rossotti and Rossotti (26) have correlated their experimental results with earlier work done to show that at the isoelectric point, the equilibrium is

$$10\ VO_2^+,\ aq. + 8\ H_2O \rightleftharpoons H_3V_{10}O_{28}^{-4},\ aq. + 14\ H^+.$$

They reported their data corresponded to the equilibrium proposed by Hazel, McMabb, and Santini (11),

$$VO_2^+ \rightleftharpoons (VO_2^+)_q(OH^-)_p \rightleftharpoons V_{10}O_{27}^{-4}$$

(where $q > 10$ and $p < q$).

However, they reported no evidence for the highly polymerized cationic species proposed in this equilibrium.

This present work very strongly indicates that such a cationic species must be involved in the equilibrium. Since α-benzoin oxime forms complexes with cations only, MoO_2^{++}, WO_2^{++}, Cu^{++}, Pd^{++}, there must be two cationic species involved in the equilibrium. The highly polymerized species postulated by Hazel, McMabb and Santini would be capable of forming a highly polymerized α-benzoin oxime complex, containing structural water. Heating this complex could result in splitting out of water. This in turn could result in degradation of the polymer causing the color change observed in heating.

At any rate, the results show that the simple VO_2^+ ion is indeed involved in the equilibrium at the isoelectric point, and exists at greater acidity values. They also give good evidence of the presence of another cationic species existing in this acidity region. Thus strengthening the results published by Hazel, McMabb and Santini, the only ones to have postulated such a cationic species.

B. Extractions

1. Original attempts. A great deal of difficulty was encountered in the development of an extraction procedure for vanadium since much of the work was done before and simultaneously with the gravimetric experiments. Once the presence of two distinct species became evident, the work was greatly simplified.

With vanadium as well as tungsten and molybdenum, a determination of the oxine to metal ratio by the method of continuous variations was found to be impossible. With molybdenum and tungsten absorption of the complex in the ultra-violet occurred at the same wave-lengths as that of the oxine. With the vanadium complex, absorption occurs in the visible in the same wave-length region as that for vanadate ion in acid solution.

However, the possibility of developing an extraction procedure with spectrophotometric measurement based on the yellow colored complex formation seemed quite plausible. The yellow colored complex exhibited an absorption in the visible below 500 mμ. The absorbance at 450 mμ was quite satisfactory for measurement. However, a great number of extraction procedures gave very little success. The reasons for this became obvious as the work progressed.

The reasons for the failure of this work are as follows. (1) The extraction of the vanadium is dependent upon the pH, with the maximum extraction occurring at the isoelectric point, pH 2.2. (2) Extraction is time dependent, with the maximum occurring with ten minute shaking

on the automatic shaker. (3) The yellow colored complex is not stable but fades progressively over relatively short periods of time. Both of these latter difficulties may be attributed to conversion of the yellow complex to the unpolymerized white species. The white species exhibiting no visible absorption and also decreased solubility in chloroform. (4) Larger amounts of vanadium in the presence of excess α-benzoin oxime in the chloroform medium undergo reduction as evidenced by a color change from yellow to green. This occurs if the solutions are allowed to sit for any length of time, but does not occur rapidly.

On the basis of these difficulties and with the knowledge of the instability of the yellow species determined gravimetrically, a new procedure was developed.

Since it appeared that vanadium could be successfully extracted by α-benzoin oxime into chloroform, the major difficulty appeared to be the development of a stable color. A colorimetric method (28) involving the red color of the vanadium 8-quinolinolate complex in the presence of ethanol has been quite successful. According to this method the absorption is measured at 550 mμ where the molybdenum complex does not absorb. This resulted in the only interference being ferric ion. Taking advantage of this colored complex formation, which was also observed to occur in the vanadium-α-benzoin oxime-chloroform extracts upon addition of 8-quinolinol and ethanol, the following procedure was developed.

2. Development of colorimetric method. A ten ml. portion of vanadium containing solution, adjusted to pH 2.2 with hydrochloric or sulfuric acid, is pipeted into a 60 ml. separatory funnel. Ten ml. of a 0.1% α-benzoin oxime in chloroform solution is added, and the mixture is shaken for one minute. The chloroform layer is immediately drawn off into a 100 ml. volumetric flask containing 10 ml. of a 0.1% solution of 8-quinolinol in ethanol. The vanadium solution is then extracted with two successive ten ml. portions of 0.1% α-benzoin oxime solution in chloroform. Each of these solutions are shaken for several minutes before the organic layer is combined with the contents of the volumetric flask. The final extraction is carried out with a ten ml. portion of chloroform. Twenty ml. of ethanol are added to the combined extracts, and the solution is diluted to 100 ml. with chloroform. The absorbance of the solution is measured at 550 mμ against a blank containing everything but the vanadium.

Extractions carried out in this manner were found to obey a Beer's Law plot for solutions containing from 5 to 80 micrograms of vanadium per ml. of solution. The 8-quinolinol test for vanadium, as outlined by Feigl (7), gave negative results. Since the concentration limit for the method is 1:500,000, the evidence for quantitative extraction is quite good.

This procedure was used to establish the α-benzoin oxime:vanadium ratio according to the extraction method previously described for molybdenum. The vanadium extracted was determined colorimetrically using the 8-quinolinol method just described.

For this purpose a series of vanadium solutions at pH 2.2 and of concentrations from 1.0×10^{-3} to 2.75×10^{-3} M. were prepared. Ten ml. portions of these solutions were extracted with two 10 ml. portions of 1.0×10^{-3} M. α-benzoin oxime in chloroform and one 10 ml. portion of chloroform. The color was developed on the combined extracts by the method just described.

A plot of the absorbance versus the mole ratio of vanadium to α-benzoin oxime is shown in Figure 5, the data for which are given in the Appendix. The absorbance values show less than complete extraction due to extraction with more dilute α-benzoin oxime solution. However, the definite break occurring at 2×10^{-2} millimole of vanadium by extraction with 2×10^{-2} millimole of α-benzoin oxime definitely establishes the α-benzoin oxime:vanadium ratio as 1:1. This corresponds to the results anticipated.

The colorimetric method for vanadium had been proposed originally as an attempt to determine the vanadium:α-benzoin oxime ratio. However, due to the adherence to Beer's Law plot in the concentration range stated, it was deemed possible that it could be used for a quantitative method. The major advantage of this method over the direct extraction of the 8-quinolinol complex as proposed by Talvitii (28) would be that no extraction of iron would occur. This would eliminate the necessity of removing iron before the extraction of vanadium.

For this purpose, a vanadium solution was made up at pH 2.2 which, as the result of several determinations by this method, on the pure

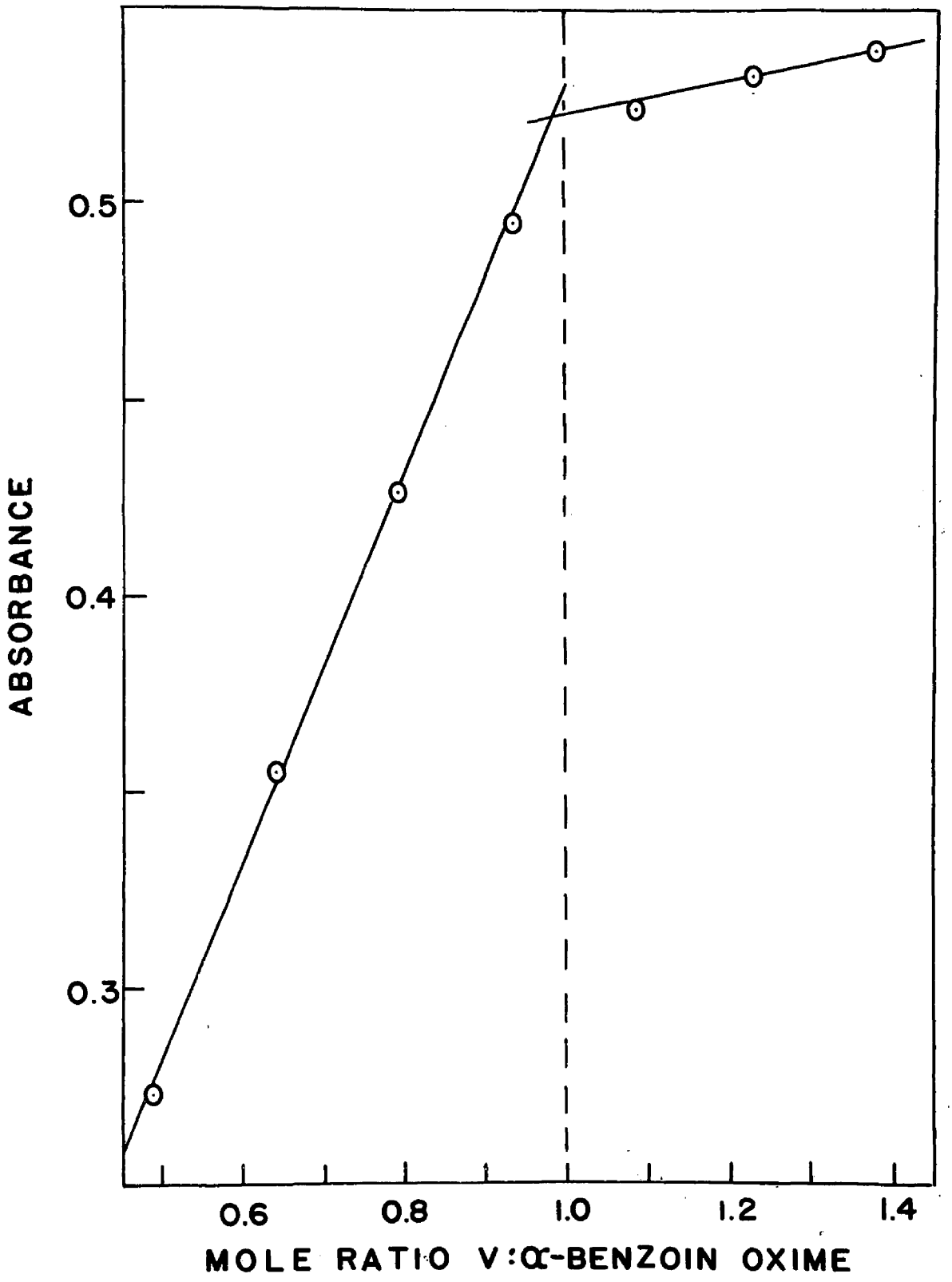


Figure 5. Determination of Vanadium:α-Benzoin Oxime Ratio by Extraction.

solution, was found to contain 0.0b9 mg./ml. of vanadium. To ten ml. portions of this solution were added a wide variety of elements commonly occurring with vanadium, and the vanadium was determined according to the procedure outlined. The effects of these various ions are shown in Table V.

The results show that the only serious interference occurred in the case of antimony. The major difficulty in this case was the precipitation of hydrated antimony oxide from acid media. This precipitate which was at first white soon appeared to have a yellow color. This yellow color became more intense as the solution aged. This indicated that the antimony was removing the vanadium from solution in some manner. This also explains why the negative error in the second experiment in the presence of antimony is almost twice as great. The same solution was used in both cases, but the second sample was run after the solution was allowed to stand for twenty-four hours. Bismuth and uranyl ion also show a certain amount of interference.

It is also interesting to note that only negative errors were encountered when interferences were present, and this only when ions capable of heteropoly acid formation with vanadium were present. This indicates that heteropoly acid formation makes extraction slightly more difficult.

The main advantage of this method is shown by the results obtained in the presence of ferric ion. By this method a simple extraction procedure is all that is required with no previous removal of iron.

TABLE V

EFFECT OF VARIOUS IONS ON THE DETERMINATION OF VANADIUM

Quantity, Mg.	Ion	Vanadium, Mg. Present	Found	Difference
2.50	Mo (VI)	0.49	0.48	-0.01
			0.47	-0.02
	W (VI)		0.47	-0.02
			0.46	-0.03
	Cr (VI)		0.49	-0.00
	Mn (VI)		0.49	0.00
	Cu (II)		0.49	0.00
	Si (IV)		0.47	-0.02
			0.47	-0.02
	Bi (III)		0.46	-0.03
			0.45	-0.04
	UO_2^{++}		0.46	-0.03
			0.46	-0.03
	Sb (III)		0.43	-0.06
			0.35	-0.14
1.25	$PO_4^{\equiv}$		0.49	0.00
			0.49	0.00
	Fe (III)		0.49	0.00
	Al (III)		0.49	0.00

It is therefore a simple, rapid method for small amounts of vanadium which can be carried out in the presence of most common elements.

VII. SUMMARY

The α-benzoin oxime complexes of vanadium, molybdenum, and tungsten have been thoroughly studied. An attempt to do the same with chromium was found to be impossible due to the preferential reduction of chromium by the reagent. The methods employed for these studies involved both precipitation and extraction techniques.

The molybdenum complex has been determined to be bis(α-benzoinoximato)-dioxomolybdenum (VI), $MoO_2(C_{14}H_{12}O_2N)_2$, and for tungsten, bis(α-benzoin-oximato)dioxotungsten (VI), $WO_2(C_{14}H_{12}O_2N)_2$. Vanadium has been found to form two different complexes, a white precipitate and a dark yellow precipitate. The white form has been established as α-benzoinoximato-dioxovanadium (V), $VO_2(C_{14}H_{12}O_2N)$. The yellow form, also containing one α-benzoin oxime molecule per vanadium, is the result of complex formation between α-benzoin oxime and some highly polymerized vanadium species. The formation of all these complexes has been correlated with literature data concerning the species of these metals in acid solutions.

For molybdenum, the most complete complex formation occurs in solutions containing from 5 to 20% mineral acid. For tungsten the most complete formation has been found not only to require an acid solution, but also a mole ratio of fluoride to tungsten ion between 7:1 and 10:1. This has been explained on the basis of the availability of WO_2^{++} from the fluoride complex.

For vanadium, the yellow, or polymerized form, has been found to form more readily and completely at the isoelectric point of pH 2.2. Although the white form also precipitates in this region, it was impossible to determine the best acidity for its formation. This was

due to the fact that the rate of formation of $VO_2(C_{14}H_{12}O_2N)$ is so slow that its precipitation also results in the precipitation of some reagent from solution. Therefore, it was impossible to check for completeness of precipitation of the white precipitate by gravimetric methods.

As a result of the study, a number of factors concerning the use of α-benzoin oxime as an analytical reagent for these elements have been determined.

Molybdenum may, as determined earlier, be quantitatively precipitated by α-benzoin oxime from acid solution. When the precipitation is done properly, the complex may be dried and weighed and the molybdenum determined as 16.51% of the complex.

Tungsten can not be determined in this same manner since the precipitation is not quite complete even when the fluoride ion concentration has been accurately adjusted to give optimum precipitation conditions. The success of the earlier method for the combined precipitation of molybdenum and tungsten probably results from carrying down of hydrated tungstic acid by the combined complexes and the excess reagent.

It has also been found impossible to determine vanadium by the same type of gravimetric procedure employed for molybdenum. The reason for this being the fact that the yellow precipitate is not a stable form, and the length of time required for complete precipitation of the white form results in precipitation of excess reagent. This excess reagent can not be removed by washing without the loss of complex.

On the basis of the studies completed, the newly proposed extraction procedure for molybdenum (10) involving final color development with quercetin has been revised. This revision has resulted in making the method specific for molybdenum. It may now be employed even in the presence of moderate amounts of tungsten.

No new extraction procedures for the determination of tungsten have been possible on the basis of the work completed. The major difficulty is the extreme insolubility of the tungsten complex, and the fact that it does not extract as a colloidal precipitate into chloroform as the molybdenum complex does.

As a final result of the study completed, an extraction procedure for the determination of vanadium has been developed. This method involves extraction of the vanadium complex into chloroform from a solution at pH 2.2. The vanadium complex of 8-quinolinol is developed directly in the presence of the α-benzoin oxime and the absorbance measured. The concentration range for successful extraction is from 5 to 80 micrograms per ml. The only serious interference is caused by antimony where the formation of a precipitate of hydrated antimony oxide is found to carry down vanadium. Bismuth and uranyl ion also cause a slight negative error.

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APPENDIX

DATA FOR FIGURE 1

Extraction of Molybdenum with 2×10^{-2} Millimole of α-Benzoin Oxime in Chloroform

$MoO_4^{=}$, mmole.	Absorbance of Quercetin Complex	
	From 5% HCl	From pH 2.2
1.8×10^{-2}	0.670	0.530
1.5×10^{-2}	0.668	0.516
1.2×10^{-2}	0.662	0.502
1.0×10^{-2}	0.639	0.484
0.8×10^{-2}	0.581	0.417
0.5×10^{-2}	0.380	0.260
0.2×10^{-2}	0.195	0.133

DATA FOR FIGURE 4

Effect of Fluoride Ion on Tungsten Precipitation

W taken, G.	$[F^-]/[NO_4^{--}]$	W Ppted., G.
.0250	0	.0063
	0.5	.0170
	5	.0239
	6.6	.0245
	8	.0243
	10	.0243
	20	.0215
	40	.0146
.0500	0	.0221
	0.5	.0310
	1	.0355
	5	.0478
	6.6	.0490
	8	.0488
	10	.0489
	20	.0415
	40	.0275

DATA FOR FIGURE 5

Extraction of Vanadium with 2 x 10^{-2} Millimole of α-Benzoin Oxime in Chloroform

V, mmole.	Absorbance of 8-Quinolinol Complex
2.75 x 10^{-2}	0.540
2.45 x 10^{-2}	0.534
2.16 x 10^{-2}	0.525
1.86 x 10^{-2}	0.496
1.57 x 10^{-2}	0.427
1.28 x 10^{-2}	0.356
0.98 x 10^{-2}	0.273