BIS(ac-BENZOINOXIMO) DIOXOMOLYBDENUM(VI) AS A WEIGHING FORM FOR THE DETERMINATION OF MOLYBDENUM

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By

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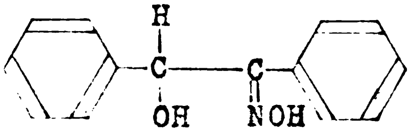
I. INTRODUCTION

A. Historical

1. Knowles' method and modifications

While working with α-benzoin oxime to determine the interferences in its use as a precipitant for copper, Knowles (10) discovered that in acid solution the reagent would quantitatively precipitate hexavalent molybdenum. From this he developed a gravimetric method for the determination of molybdenum.

The structure of the analytical reagent α-benzoin oxime is as follows:



Its molecular weight is 227.3 and it melts at 149-51°C. The oxime itself is insoluble in water, but soluble in alcohol, acetone and ether. The general reagent solution is composed of a one to two per cent solution in 95% ethanol. It selectively precipitates copper from an ammoniacal solution, and molybdate and tungstate from acid solution.

Knowles' method for molybdenum involves the precipitation of the complex from acid solution followed by ignition to molybdenum trioxide in a muffle furnace at 500-525°C. He states that the best acidity is approximately 5% sulfuric acid by volume, but up to

20% acid concentration is permissible. Hydrochloric or nitric acid may also be used when the use of sulfuric acid is inadvisable.

The method also calls for precipitation from a cold solution and addition of enough bromine to tinge the solution yellow. Both of these steps are to avoid reduction of hexavalent molybdenum by the reagent. Two to five times the theoretical amount of reagent is required for complete precipitation in this method. The theoretical amount according to Knowles is determined by the relationship of one molybdenum ion to three α-benzoin oxime molecules. However, no data or theoretical evidence is given to substantiate the postulation of this three to one complex.

Knowles also discovered that the precipitate can be filtered immediately or allowed to stand for ten minutes before filtration. If the precipitate is allowed to stand in contact with the solution for one-half hour or longer, low results are obtained. The most favorable wash solution is reported to be a 1% sulfuric acid solution containing a small amount of α-benzoin oxime.

Elements which cause difficulty in this precipitation from acid solution are columbium, silicon, palladium, tantalum and tungsten. Vanadium(V) and chromium(VI) also interfere if not reduced with

sulfurous acid before precipitation (9). Ferrous ammonium sulfate has also been suggested to reduce the vanadic and chromic acids (11).

Yagoda and Fales (17) applied the method to the determination of tungsten and molybdenum. Due to the difficulty of filtration of the complex formed, they unsuccessfully sought a substitute for α-benzoin oxime. They separated the molybdenum and tungsten by means of hydrogen sulfide. Since in the case of samples having a low molybdenum concentration the weight of the oxide was so small, they found a more suitable weighing form was thallous molybdate or thallous tungstate.

Taylor-Austin (16) used the method with a few modifications for the determination of molybdenum in cast iron. He states that three times the theoretical amount of reagent is used as determined by the relation that one molybdenum ion is equivalent to three α-benzoin oxime molecules, but also gives no basis for the formulation of such a complex. However this work shows that complex formation is incomplete in the presence of tartaric acid, and also that acetone may be successfully substituted as the reagent solvent.

S. W. Cravens et.al. (4) have developed the method to be used for the determination of molybdenum in steels in the presence of tungsten. After the precipitation of the molybdenum and tungsten with α-benzoin oxime the molybdenum is determined by the formation of the thiomolybdate in alkaline solution, followed by decomposition with dilute acid to the sulfide, and final ignition to the oxide.

Sterling and Spuhr (15) have also devised a method for molybdenum with certain modifications. The precipitated molybdenum- α-benzoin oxime complex is dissolved in ammonium hydroxide and hydrogen peroxide. The molybdenum is then reprecipitated from a lead acetate buffer mixture as lead molybdate. It has the advantage of providing a heavier weighing form than the oxide.

Arrington and Rice (1) ignite the complex to the oxide, dissolve the oxide in sulfuric acid, reduce the molybdenum in a Jones reductor, and titrate with standard oxidant.

A good review of most of these methods may be found in Flagg's, Organic Reagents, (6) and Blanco (3) has also published a review article on the determinations of molybdenum with α-benzoin oxime.

In all of these determinations an excess of two to five times the theoretical amount of α-benzoin oxime is added on the basis of a three to one complex. However, there has been no work done to establish that the complex is actually three to one, and no theoretical basis for the postulation of such a complex has been offered.

2. Molybdenum species present in acid solution.

It is also interesting to note that it has not been definitely established what molybdenum species is present in 5 to 20% acid solution. Both molybdenum and tungsten are reported to form isopoly acids of various complexities depending upon the pH of the solution (12). However molybdenyl sulfate, MoO_2SO_4, can be prepared by dissolving molybdenum trioxide in hot concentrated sulfuric acid and cooling the solution until the sulfate precipitates (8,14). The sulfate is very hygroscopic and is reduced by dust in the air to form a blue colored material, a molybdenum blue. Molybdenyl sulfate is reduced to a deep blue color when heated with pure metallic molybdenum. Nicholls, Saenger, and Wardlaw (13) have also shown the existence of molybdenyl sulfate in sulfuric acid solution.

The precipitate formed by molybdenum with 8-quinolinol in slightly acid solution has been definitely established and is employed as a suitable weighing form. The complex is bis(8-quinolinolo)-dioxomolybdenum(VI).(2).

This complex of molybdenum with 8-quinolinol is dried at 130°C. and weighed, while all the work done on the α-benzoin oxime complex indicates that it is incapable of being dried and weighed as such. In fact

Dupuis and Duval (5) ran thermal studies on the complex and found that it formed no stable material until the temperature reached about 550°C. where the complex was all converted to the oxide. This they determined to be stable to approximately 780° when sublimation began. They prepared the complex for these determinations exactly as outlined by Knowles.

B. Statement of Problem

1. Attempted volumetric method

The method of Knowles (10) for the determination of molybdenum with α-benzoin oxime is a gravimetric method involving ignition to the oxide which has an unfavorable gravimetric factor. The development of a volumetric method using the same reagent seemed quite desirable, and an attempt was made to develop an amperometric method using a small applied potential across a pair of platinum electrodes.

In acid media, from which molybdenum is quantitatively precipitated by α-benzoin oxime, the oxime was found to be quite active at a pair of platinum electrodes at a potential of 400 millivolts. This end point seemed to present a definite possibility for the development of a volumetric method using the "dead-stop" technique.

At this point, a review of the literature revealed that no actual determination of the composition of the complex had been carried out. Therefore Knowles original assumption of a three to one complex was followed, and solutions of molybdenum in 5% sulfuric acid, and α-benzoin oxime in 50% ethanol were made up accordingly. That is, a 0.0052 M molybdenum solution and a 0.0156 M α-benzoin oxime solution were made so that one ml. of each solution would be equivalent.

When twenty ml. of the molybdenum solution were diluted with 5% sulfuric acid and the α-benzoin oxime solution was added dropwise from a buret the results were very erratic. The first drop or two gave a large galvanometer deflection. The results after this were dependent upon the rate of addition of reagent. When the reagent was added rapidly the deflection increased, and with slow addition it decreased gradually.

An attempt to estimate the end-point by controlled rate of addition of the reagent to twenty ml. of the molybdenum solution was unsuccessful. The results of plotting ml. added against the galvanometer deflection (Figure 1) indicated a break at about fourteen ml. At the time, the results were inconclusive; however, they indicated the complex might be two to one instead of three to one as Knowles originally assumed.

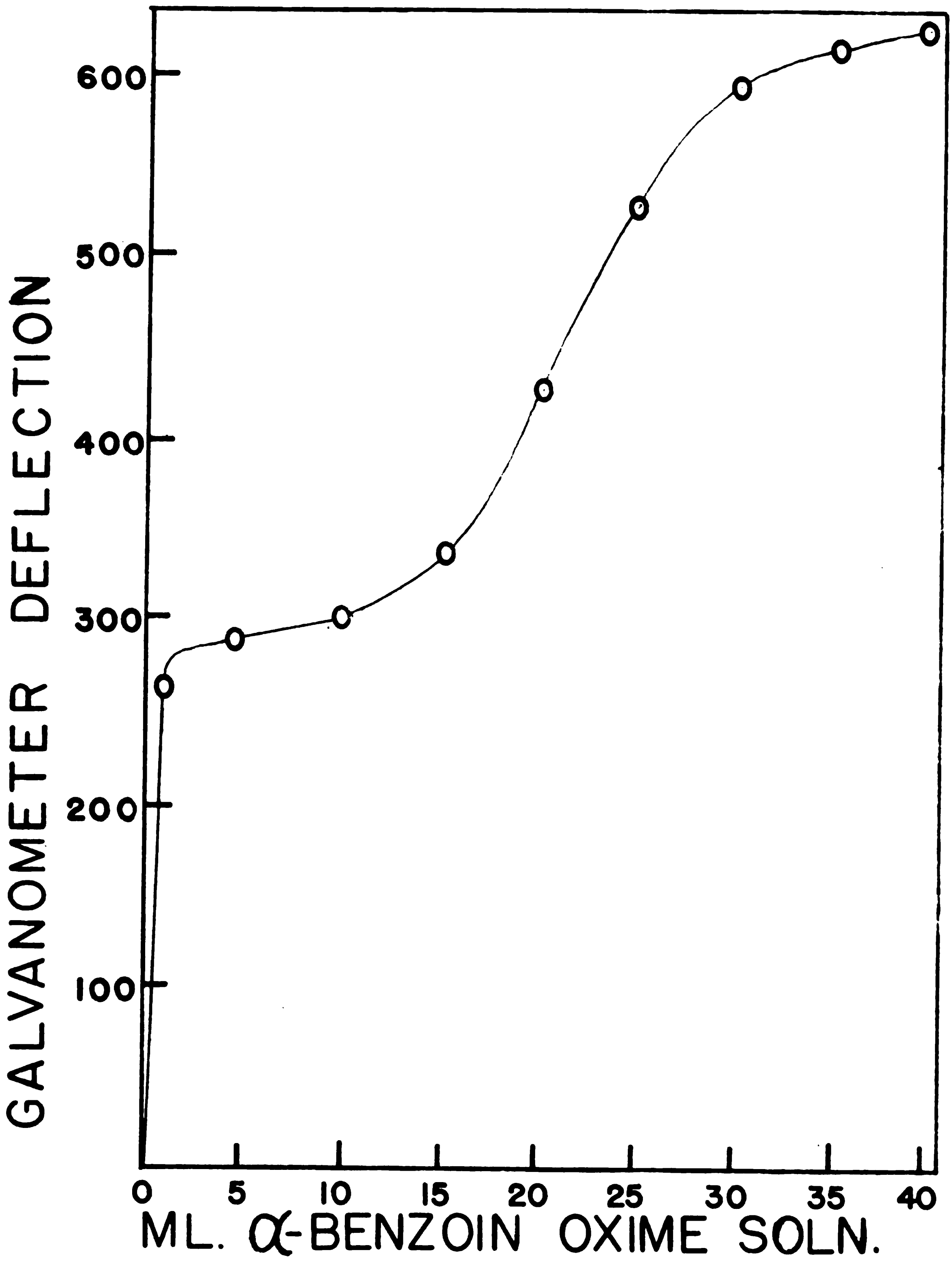

GALVANOMETER DEFLECTION
600
500
400
300
200
100
0
5
10
15
20
25
30
35
40
ML. α-BENZOIN OXIME SOLN.

FIGURE I.

2. Proposed modification of gravimetric method

At this point, the most logical approach appeared to be a study of the composition of the complex formed. As no basis could be found for the postulation of a three to one complex it was hoped that the determination of the actual composition would lead to a simplified gravimetric method. A method in which the complex could be dried and weighed as such would also have a much more favorable gravimetric factor than the oxide which is approximately two-thirds molybdenum.

A. Determination of Composition of Complex

1. Determination of % Mo

In order to revise the existing gravimetric method for the determination of molybdenum it was first necessary to establish the composition of the complex.

The method which was first attempted involved the precipitation of the complex according to Knowles method, drying and weighing the complex and then igniting the complex to molybdenum trioxide and reweighing. The first attempts at drying the complex in a 105°C. oven resulted in failure as the white precipitate turned to a black tarry mass. A melting point determination on some of the dried material yielded the following results. At 85°C. it turned yellow; at 95°, blue; at 100°, it melted to a pale yellow liquid; and at 104°C. it decomposed into a black tarry mass.

Since upon reduction Mo(VI) is reported (8) to form a material, molybdenum blue, of partially reduced molybdenum, it appeared that one of the steps in the melting process involved a reduction. As Knowles reported that the reagent will reduce some of the Mo(VI) at room temperature when no bromine is added, the preceding method was modified.

In order to avoid reduction by excess α-benzoin oxime, only one-half as much reagent was added as was theoretically necessary for complete precipitation. This could be done since the main purpose was recovery of pure complex and not quantitative precipitation. Also, the method of drying the complex had to be altered, so it was dried in a vacuum desiccator over concentrated sulfuric acid.

The following procedure was used. Forty ml. of 0.0052 M molybdenum solution in 5% sulfuric acid were cooled in beakers in an ice bath and then 20 ml. of 0.0156 M α-benzoin oxime solution were added dropwise to the beakers with constant stirring. The precipitates were allowed to stand for one hour in solution and then filtered through filter paper and washed with water. Some of the precipitate was then transferred to previously weighed silica crucibles. The precipitates were next dried to constant weight in a vacuum desiccator over concentrated sulfuric acid and finally ignited to the oxide and weighed. See Table I-A.

In all three cases the precipitates turned a spotty blue color during the drying process, and in sample 2 the blue coloration was quite intense.

Six more samples were precipitated exactly as before, the only difference being the fact that the precipitates were first allowed to dry overnight in the air before drying over concentrated sulfuric acid. Also, samples 4, 5 and 6 were treated with enough

TABLE I

ATTEMPTS TO ESTABLISH COMPOSITION OF COMPLEX

Sample	G. of Complex	G. of MoO_3	% MoO_3
A. Original attempts			
1	.0712	.0146	20.51
2	.0658	.0092	13.98
3	.0771	.0158	20.49
B. Effects of air drying and bromine addition			
1	.0602	.0135	22.43
2	.0631	.0145	22.98
3	.0751	.0172	22.90
4	.0560	.0125	22.32
5	.0792	.0180	22.73
6	.0516	.0112	21.71
C. Further tests on the effects of air drying			
1	.0587	.0126	21.39
2	.0662	.0154	23.35
3	.0550	.0130	23.64
4	.0480	.0109	22.71
5	.0662	.0158	24.17
6	.0766	.0185	25.56

bromine water to turn the solutions pale yellow. See Table I-B.

The precipitates after drying in air were still white, however after drying over the concentrated sulfuric acid they turned pale blue. This blue color faded during weighing.

In order to test the effect of air drying upon the results, six more samples were precipitated as before. Samples 1 and 2 were transferred immediately to the desiccator containing the concentrated sulfuric acid, samples 3 and 4 were first dried in the air for twelve hours, and samples 5 and 6 for seventeen hours before placing in the desiccator over sulfuric acid. They were all brought to constant weight and then ignited to the oxide. See Table I-C.

The results were so erratic on these determinations with each group yielding different results it began to appear that little could be done to obtain consistent results. The one remarkable feature being that in almost every case the precipitates acquired a blue coloration of varying intensity. This indicated the presence of excess reagent which was actively reducing the molybdenum.

In order to remove all of the oxime which might be present in the complex, the precipitation was carried out as before, the precipitates were allowed to stand for fifteen minutes, filtered and washed twice with five ml. portions of 95% ethanol. The precipitates were dried to constant weight in a 70°C. oven before ignition to the oxide. In this case there was no reduction of the molybdenum as no blue coloration appeared in the precipitate. See Table II-A.

A new melting point on some of this complex from which all excess reagent had been removed revealed that the complex itself was quite stable and melted sharply at 158-9°C.

Three more samples were run as above except that this time the complex was dried in a 105°C. oven to constant weight. See Table II-B.

TABLE II

DETERMINATION OF % Mo IN COMPLEX

	G. of Complex	G. of MoO_3	% Mo
A. Drying at 70°C.			
	.0783	.0193	16.65
	.0713	.0174	16.23
	.0739	.0182	16.42
B. Drying at 105°C.			
	.0764	.0188	16.40
	.0710	.0176	16.52
	.0799	.0195	16.45

2. Postulation of a structure for complex

Since the preceding results were reproducible and the complex formed appeared to be fairly pure, the original assumption of a three to one complex (10) appeared impossible. Therefore a new structure for the complex had to be postulated. There has been evidence given for the existence of an MoO_2^{++} ion in acid solution (3,13,14) which is especially supported by the precipitation of molybdenyl sulfate from cold concentrated acid solution.

The MoO_2^{++} ion has also been definitely established as the species which precipitates with 8-quinolinol from acid solution (2). This lead to the theory that the complex formed with α-benzoin oxime is actually bis(α-benzoinoximo)dioxomolybdenum(VI). See Figure 2.

The percentage of molybdenum in this complex is 16.51%. Therefore it seems quite probable that this is the actual structure of the precipitate.

The fact that Dupuis and Duval (5) stated that the complex was completely unstable until it had been completely ignited to the oxide is quite understandable. They prepared the complex according to the method postulated by Knowles which leaves a large amount of unreacted oxime in the precipitate. This excess reagent reduces the molybdenum in the complex and

BIS(α-BENZOINOXIMO)DIOXOMOLYBDENUM(VI)

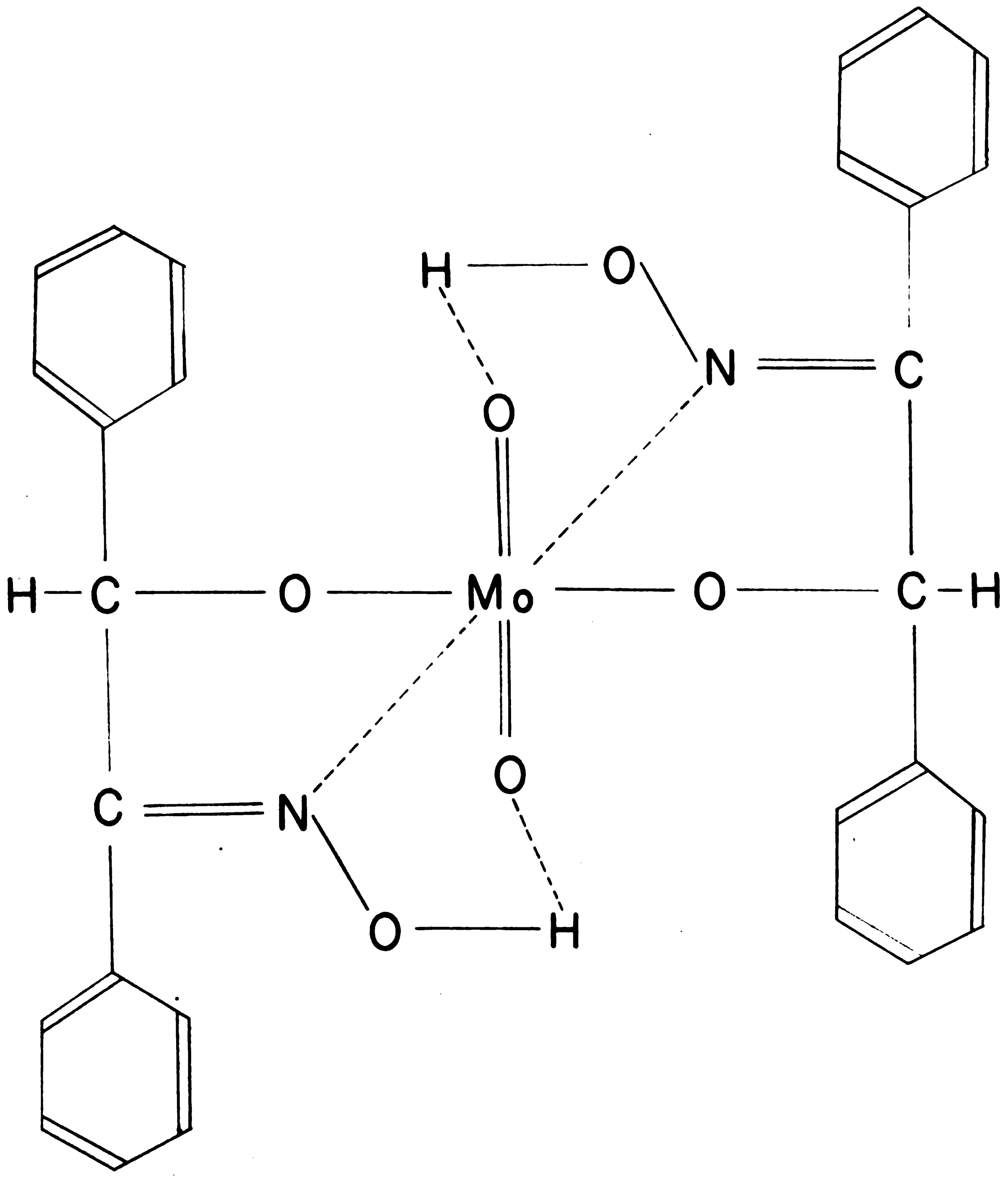


FIGURE 2.

renders it unstable to heat. Therefore in order to obtain a stable weighing form the excess reagent must be entirely removed.

B. Development of Gravimetric Method

1. Solubilities in acetone and ethanol

Up to this point ethanol had been used as the solvent for the oxime and also for washing the solution. Acetone has been recommended as a better solvent (16) and solubility tests, Table III, showed that it would be desirable to change to acetone as a solvent. These approximate figures showed that while there was no significant difference in oxime solubilities at 25% concentrations, the greater solubility of the oxime in 50% acetone would make this a more useful wash solution. The figures on the solubility of the complex in Table III may be slightly high, as the complex after evaporation of the solvent turned slightly blue indicating the possibility of a small amount of reagent in the complex. However the results indicated that acetone would be quite suitable for the reagent solvent and as a wash solution.

TABLE III

APPROXIMATE SOLUBILITIES OF REAGENT AND COMPLEX (GRAMS PER 100 ML. OF SOLUTION)

	% ethanol		
Substance	25	50	75
α-benzoin oxime	>0.2g.	0.3g.	1.25g.
	% acetone		
	25	50	100
α-benzoin oxime	0.2g.	1.9g.	13.5g.
molybdenum complex	.004g.	.006g.	.014g.

2. Precipitation with 10% excess reagent

The following solutions were then prepared to be used in the development of a gravimetric method using the complex as the weighing form. (1) A 3.7507g. sample of Merck Reagent Grade MoO_3, assay minimum 99.5% MoO_3, was dissolved in a small amount of dilute sodium hydroxide solution. It was then neutralized with sulfuric acid and diluted with water to one liter. The resulting solution was 0.0261 M, or contained 0.0500g. of molybdenum per 20 ml. of solution.

(2) Crude α-benzoin oxime from the Paragon Testing Laboratories was recrystallized twice from ethanol, and 5.9234g. of this purified, dried material were dissolved in one liter of 50% acetone. The resulting solution was 0.0261 M, or two ml. of α-benzoin oxime solution were equal to one ml. of molybdenum solution.

It was hoped that by adding only a 10% excess of reagent and washing with small portions of 50% acetone, complete precipitation could be effected and any excess oxime could be successfully removed. This would permit a simple weighing of the complex after drying in a 105°C. oven. The major advantages which would result from this method would be (1) a large decrease in the amount of reagent required, (2) elimination of the necessity of ignition to the oxide in a muffle furnace, and (3) a weighing form with a very favorable gravimetric factor, as molybdenum is only 16.51% of the total weight of the complex as compared to 66.65% when weighed as the oxide.

Two samples containing 20 ml. of the standard molybdenum solution (50 mg. of Mo) were pipetted into a beaker and one ml. of concentrated sulfuric acid was added to each. Forty-four ml. of the α-benzoin oxime in 50% acetone were added dropwise from a buret with constant stirring. This would be a 10% excess of oxime. The precipitates were filtered with suction on previously weighed sintered glass crucibles, being quantitatively transferred with water.

They were then washed twice with 5 ml. portions of 50% acetone and finally with a small amount of water. The precipitates were finally dried to constant weight in a 105°C. oven. The only difference in the two precipitations was that sample one was filtered immediately while sample two was allowed to stand overnight before filtration. See Table IV-A.

These results indicated the method might be quite successful as good results were obtained with the sample which was filtered immediately, and Knowles states that with his method low results are obtained if the precipitate is allowed to stand in contact with the solution for thirty minutes or more.

Six more samples containing 10 ml. of the molybdenum solution (25 mg. of Mo) and 10 ml. of water plus one ml. of concentrated sulfuric acid were precipitated by the addition of 22 ml. of the α-benzoin oxime solution dropwise from a buret. The precipitates were filtered immediately with suction on sintered glass crucibles and washed twice with five ml. portions of 50% acetone and then a small amount of water. The precipitates were again dried to constant weight in a 105°C. oven. See Table IV-B.

The above procedure was repeated using larger samples, i.e., 20 ml. of the molybdenum solution (50 mg. of Mo) were precipitated by the dropwise addition of 44 ml. of the α-benzoin oxime solution. Three smaller samples were also run using five ml. of the molybdenum solution (12.5 mg. of Mo) and 11 ml. of the oxime solution. In both cases the amount of reagent

TABLE IV

QUANTITATIVE PRECIPITATION OF MO WITH A 10% EXCESS OF REAGENT

	G. of Complex	G. of Mo Theor.	 Found	Error, g.
A. Original attempt				
	0.3032	0.0500	0.0501	+.0001
	0.2948	"	0.0487	-.0013
B. Further attempts on smaller samples				
	0.1513	0.0250	0.0250	.0000
	0.1513	"	0.0250	.0000
	0.1518	"	0.0251	+.0001
	0.1516	"	0.0250	.0000
	0.1514	"	0.0250	.0000
	0.1516	"	0.0250	.0000
C. Larger and smaller molybdenum samples				
	0.2991	0.0500	0.0494	-.0006
	0.3002	"	0.0496	-.0004
	0.2992	"	0.0494	-.0006
	0.0756	0.0125	0.0125	.0000
	0.0761	"	0.0126	+.0001
	0.0758	"	0.0125	.0000

added was an excess of 10% over the theoretical amount. See Table IV-C.

The results of these determinations indicated that it might not be sample size, but the concentration of acetone in the solution which caused low results with the larger samples.

3. Effects of varying acetone concentration

In order to determine the effect of varying the acetone concentration on the accuracy of the method, the following experiments were carried out. In all of the following determinations five ml. of the standard molybdenum solution were treated with 11 ml. of the α-benzoin oxime solution. The major difference being the amount of water added which altered the acetone concentration. The precipitations were all accomplished by the drop-wise addition of the reagent followed by immediate filtration. The precipitates were all carefully washed with two 5 ml. portions of 50% acetone and dried to constant weight in a 105°C. oven. See Table V.

These results indicate that the best results are obtained if the acetone concentration in the precipitating solution is limited to 15-20% acetone. Higher acetone concentrations tend to dissolve some of the complex and yield low results.

TABLE V

EFFECTS ON PRECIPITATION OF VARYING THE ACETONE CONCENTRATION

ml. H_2O added	ml. H_2SO_4 added	% Acetone in final solution	G. of Complex	G. of Mo Theor.	G. of Mo Found	Error, g.
0	0.5	33	.0740	.0125	.0122	-.0003
0	0.5	33	.0733	"	.0121	-.0004
5	0.5	25	.0742	"	.0123	-.0002
5	0.5	25	.0744	"	.0123	-.0002
10	1.0	20	.0751	"	.0124	-.0001
10	1.0	20	.0760	"	.0125	.0000
20	1.5	15	.0759	"	.0125	.0000
20	1.5	15	.0764	"	.0126	+.0001

4. Effects of varying reagent excess

Since it is almost impossible to decide when a slight excess of reagent has been added, the effect of the addition of a large excess of reagent had to be determined before this method could be applied to samples of unknown molybdenum content.

In the following determinations five ml. of the molybdenum solution (12.5 mg. of Mo) were used in each case. The oxime solution was added dropwise and the precipitate was filtered immediately. The precipitates were washed and dried as before. The only difference in each pair of samples was the amount of reagent that

was added. Since varying the amount of reagent added would also change the acetone concentration, the amount of water had to be altered to keep the acetone concentration of the resulting solution constant. The amount of sulfuric acid added was also varied to maintain a constant acid concentration. See Table VI.

TABLE VI

EFFECTS OF EXCESS REAGENT ON PRECIPITATION

ml. of oxime soln. added	% Excess of oxime	G. of Mo Theor.	G. of Mo Found	Error, g.
11	10	.0125	.0124	-.0001
11	10	"	.0123	-.0002
12.5	25	"	.0126	+.0001
12.5	25	"	.0125	.0000
15	50	"	.0124	-.0001
15	50	"	.0123	-.0002
20	100	"	.0124	-.0001
20	100	"	.0124	-.0001

Since these results indicated that a 100% excess of reagent could be tolerated without any appreciable effect on the results it seemed feasible to use a more concentrated oxime solution. This would allow a smaller volume of reagent to be used and aid in reducing the acetone concentration in the precipitating solution.

5. Effects of Fe(III), Cr(VI) and V(V)

After the allowable acetone concentration had been established and the fact that large excesses of reagent had no effect had been determined, the next step in devising a gravimetric procedure was to study the effects of the presence of other ions.

The materials which have been reported to cause difficulty in this determination of molybdenum (9) are columbium, silicon, palladium, tantalum, tungsten(VI), vanadium(V) and chromium(VI). The silicon may be filtered out before precipitation, but tungsten is quantitatively precipitated by the reagent. If tungsten is present, only the total molybdenum and tungsten content may be determined with α-benzoin oxime. Columbium, palladium, and tantalum are only occasionally found in significant quantities to cause difficulty. However, chromium and vanadium quite commonly occur in alloys with molybdenum. Both are reported to cause no difficulty if first reduced with freshly prepared sulfurous acid followed by boiling to eliminate the excess SO_2, (9) or if reduced with ferrous ammonium sulfate.

It was therefore desirable to determine the effects of iron(III) as well as chromium and vanadium in the precipitation of molybdenum followed by drying of the complex formed.

Before a study of the effects of other ions was started, a new α-benzoin oxime solution was prepared by dissolving 5.9234g. of the purified, dried reagent in 500 ml. of 50% acetone. The resulting solution was .0522 M, or one ml. of α-benzoin oxime solution was equivalent to one ml. of molybdenum solution. This new solution made it possible to minimize the acetone concentration during the precipitations.

Iron is reported to give no difficulty in the original method as outlined by Knowles and it was hoped that such would be the case here. To 10 ml. of the molybdenum solution (25 mg. of Mo) was added 25 ml. of water containing 2.5g. of analytical grade $Fe_2(SO_4)_3 \cdot xH_2O$ and 1.5 ml. of concentrated sulfuric acid. Twelve ml. of the new α-benzoin oxime solution were then added dropwise to precipitate the complex. The resulting precipitates were filtered as before through sintered glass crucibles employing suction. The resulting precipitates were then washed with two 5 ml. portions of 50% acetone containing five drops of concentrated sulfuric acid. The acid was used in the wash solution because the precipitates had a slight brown tinge indicating the presence of some ferric hydroxide after the quantitative transfer of the precipitate with water. The precipitates were finally dried to constant weight in a 105°C. oven.

The results obtained were very erratic and all quite high. However the high results were expected since all of the precipitates turned quite blue. This indicated reduction of molybdenum by the presence of some α-benzoin oxime which was not removed by the washing process. It was assumed at this point that the presence of the acid in the wash solution might cause incomplete removal of the excess reagent due to the reduced solubility of oxime in acid solution.

The washing procedure was then altered so the precipitates were first washed with a few ml. of 1% sulfuric acid, then a small amount of water, and finally two 5 ml. portions of 50% acetone. This method gave quite favorable results and indicated no interference by the iron. See Table VII.

To test the effects of chromium and vanadium, solutions of chromium trioxide and vanadium pentoxide were prepared by dissolving 0.2g. of chromium trioxide in 100 ml. of water and 0.8g. of V_2O_5 in 200 ml. of dilute sodium hydroxide followed by neutralization with sulfuric acid. Ten ml. of each of these solutions were added to ten ml. of the standard molybdenum solution followed by enough sulfuric acid to give the proper acid concentration. Sufficient freshly prepared sulfurous acid was then added to reduce the chromium or vanadium present. The solutions were heated to drive off the

TABLE VII

EFFECTS OF Fe, Cr, AND V ON PRECIPITATION

G. $FeSO_4 \cdot xH_2O$ added	G. CrO_3 added	G. V_2O_5 added	G. Mo		Error, g.
			Theor.	Found	
0.75			0.0250	.0250	.0000
"			"	.0259	+.0009
"			"	.0253	+.0003
"			"	.0249	-.0001
"			"	.0248	-.0002
"			"	.0249	-.0001
	.02		"	.0248	-.0002
	"		"	.0252	+.0002
	"		"	.0253	+.0003
	"		"	.0248	-.0002
		.04	"	.0256	+.0006
		"	"	.0251	+.0001
		"	"	.0251	+.0001
		"	"	.0253	+.0003
		"	"	.0252	+.0002
		"	"	.0254	+.0004
0.75	.02		"	.0248	-.0002
"	"		"	.0247	-.0003
"	"		"	.0248	-.0002
"	"	.008	"	.0254	+.0004
"	"	"	"	.0249	-.0001
"	"	"	"	.0250	.0000

excess sulfur dioxide, cooled to room temperature, and precipitated by dropwise addition of the α-benzoin oxime solution. The precipitates were filtered on sintered glass crucibles and washed with two 5 ml. portions of 50% acetone before drying in a 105°C. oven. The results indicated that chromium and vanadium should cause little difficulty if properly reduced. See Table VII.

Further tests were run in the same manner testing the effects of iron and chromium together, and the presence of all three. These results also indicated that little difficulty would be afforded by the presence of these three elements. See Table VII.

C. Application of Method to Steel Samples

1. General procedure

The results of all of these preceding experiments indicated that the development of a gravimetric method for the determination of molybdenum in non-tungsten steels would be quite feasible. Since tungsten is also quantitatively precipitated, the method was devised for the determination of molybdenum in the absence of tungsten.

The following method was employed in the analysis of molybdenum in several non-tungsten, National Bureau of Standards steel samples.

The reagent solution used for the precipitations in every case was prepared by dissolving 5.8g. of purified α-benzoin oxime in 500 ml. of 50% acetone, giving approximately a .05 M solution. One ml. of this solution was sufficient to precipitate approximately 2.5 mg. of molybdenum.

The weight of steel sample taken in each case was determined by the amount of molybdenum present. Each sample was selected to contain between 8 and 20 mg. of molybdenum. In every case, this gave a sample size between 2 and 5g.

The samples were dissolved in 100 ml. of hot 1:5 sulfuric acid and dilute nitric acid was carefully added dropwise to the hot solutions to oxidize the molybdenum and dissolve the carbon present. The solutions were then boiled to remove the oxides of nitrogen and filtered to remove any insoluble material. Two different methods were used with equal success to reduce any chromium or vanadium which had been oxidized. The first consisted of the addition of freshly prepared sulfurous acid followed by boiling to remove the excess sulfur dioxide. The second involved the addition of enough ferrous ammonium sulfate to reduce the chromium and vanadium present. While both methods proved equally satisfactory, the use of ferrous ammonium sulfate was probably the easier of the two.

After the solutions had completely cooled to room temperature the α-benzoin oxime solution was added dropwise with constant stirring. A 30 to 40% excess of reagent was added in each case. Although early experiments indicated that up to 100% excess of reagent could be tolerated, it was discovered that the larger volumes required in analysis of steels required longer for filtration and a large excess of reagent precipitated along with the complex. The difficulty of complete removal of all this oxime necessitated the use of smaller excesses of reagent.

The precipitates were then filtered on sintered glass crucibles. These filtrations and subsequent washings were found to require some practice in order to obtain successful results. It was necessary to keep as large a volume of solution in the crucibles as possible. This prevented the precipitate from settling to the bottom and forming a mat which would greatly reduce the rate of filtration. The quantitative transfer was accomplished with water, the amount of which had no apparent effect on the results.

Washing of the precipitates was accomplished with two 5 ml. portions of 50% acetone, which also required some practice. The wash solutions had to be carefully poured down the sides of the crucibles to completely wash away any reagent which was adhering to the sides.

The first portion also had to be added just before the final amount of water was filtered off. If this wasn't done the precipitated mat in the bottom of the crucible developed large cracks. The wash solution then filtered rapidly through these cracks affecting an incomplete removal of reagent and yielding high results. The samples which were incompletely washed were easily detected as they turned quite blue during the drying process.

The samples were dried to constant weight in a 105°C. oven. One-half hour was long enough to dry the smaller samples to constant weight, however slightly longer periods were required for the larger samples. The usual procedure followed was to dry the samples for one hour, weigh, and then continue drying for half hour periods until they reached constant weight. This procedure was followed as the complex exhibited a tendency to lose weight if allowed to dry for excessively long periods of time. The molybdenum was calculated as 16.51% of the complex.

2. Determinations on N.B.S. samples

The results of the determinations on the National Bureau of Standards samples are listed in Table VIII. It will be noted that in most cases there is quite good agreement with the accepted gravimetric determination for molybdenum.

TABLE VIII

DETERMINATION OF MOLYBDENUM IN N.B.S. STEELS

N.B.S. Sample			Sample,g.	Complex,g.	% Mo found
No.	% Mo.	Range			
106	0.164	0.159-0.174	5.0620	0.0497	0.162
			5.0063	0.0493	0.163
			4.9964	0.0492	0.163
			5.0576	0.0467	0.152
			5.0000	0.0490	0.162
					Ave. 0.160%
139	0.178	0.172-0.180	5.0135	0.0547	0.180
			5.0685	0.0565	0.182
			5.1995	0.0573	0.184
			5.1462	0.0542	0.172
			5.1698	0.0549	0.175
					Ave. 0.178
111A	0.222	0.216-0.229	1.0307	0.0143	0.218
			5.0256	0.0682	0.224
			5.0343	0.0683	0.224
			5.4211	0.0723	0.220
			5.0139	0.0640	0.212
					Ave. 0.220

TABLE VIII (CONT'D.)

N.B.S. No.	Sample % Mo.	Range	Sample,g.	Complex,g.	% Mo found
72b	0.222	0.216-0.228	5.1053	0.0648	0.209
			5.1551	0.0672	0.215
			5.0527	0.0633	0.207
			4.9976	0.0635	0.210
			5.0910	0.0719	0.233
					Ave. 0.215
159	0.414	0.405-0.420	3.9952	0.1007	0.416
			4.1585	0.1020	0.405
			3.9921	0.0996	0.412
			4.1141	0.1049	0.420
			4.0131	0.1024	0.421
					Ave. 0.415
135	0.575	0.560-0.582	2.9945	0.1024	0.565
			3.0437	0.1067	0.579
			3.0413	0.1055	0.573
			3.5101	0.1243	0.584
					Ave. 0.575
36	1.01	1.00-1.03	2.1052	0.1256	0.986
			2.1918	0.1335	1.014
			2.1219	0.1230	1.004
			1.9974	0.1217	1.006
			2.0570	0.1276	1.024
					Ave. 1.006

III. SUMMARY

Through the results of studies on the composition of the complex of molybdenum with α-benzoin oxime, the structure of the complex was established as bis(α-benzoin-oximo)dioxomolybdenum(VI).

Although this complex whose structure was heretofore unknown was reported to be 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. When the complex is weighed as such it contains 16.51% molybdenum as compared to 66.65% when weighed as molybdenum trioxide.

It was also shown that large excesses of reagent were not necessary, but that a 10% excess of the oxime was sufficient to quantitatively precipitate molybdenum for a 5 to 20% acid solution. This made possible the complete removal of excess reagent which was necessary to obtain the complex as 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. This method was applied with considerable success to seven non-tungsten steels from the National Bureau of Standards.

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