

A Study of Some Methods of Separation And Determination of Molybdenum.

by

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Chapter I

INTRODUCTION

In the past fifty years or so, molybåenum has come into considerable prominence. Up to the beginning of the last World War, its main uses were in connection with the manufacture of magnet steels and of chemical salts such as ammonium molybdate and molybåic acid. However with the World War molybdenum became important owing to its use in a number of special steels. During this period a vast amount of experimental work was undertaken and a more extensive search was made for molybåenum deposits. While the industrial application of molybåenum has been extensive in the last decade or so, the demand for it will doubtless be further increased by the present war. With this thought in mind a study of the available methods of analyses for molybåenum was undertaken.

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Chapter II

Review of Methods of Analyses for Molybdenum

1. Materials Containing Molybdenum.

There are a number of ores (1) containing molybdenum and of these molybdenite (MoS_2) and wulfenite ($PbMoO_4$) are the two principal ones. Frequently associated with the molybdenite is the mineral molybdite, or molybdic other ($Fe_2O_3.3Mo$ $O_3.7\frac{1}{2}H_2o$). This is an oxidation product of the sulphide. Molybdenite is usually found in flakes somewhat similar to graphite, while wulfenite crystallizes in tables which are usually yellow or orange, although they may have a reddish tinge. Molybdite is a canary yellow mineral and powellite ($CaMoO_4$), which is not a commercial mineral, is frequently associated with tungsten.

In analyses we are also concerned with molybdenum in alloy steels, ferro compounds and chemical reagents such as ammonium molybdate, molybdic oxide and many others.

2. Preparation of Sample for Analysis

The decomposition of ores, alloy steels or the commercial products of molybdenum commonly encountered, usually offers very little difficulty. If the ores or chemical products are ground to minus 100 mesh fineness, this will usually be sufficient. However oxide ores and ferro-alloys generally require much finer grinding than sulfide ores(2). For sampling ores the general process of "coning and quartering" is usually suitable.(3) However in the case of molybdenite ore uneven distribution of the element molybdenum may be caused by the flaky structure of the mineral.

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There are two general methods of attacking an ore for analysis, by acid and by fusion. In decomposition by acid, the choice of the acids selected for decomposition depends upon the nature of the ore and the subsequent determination to be made.

In treating wulfenite, the $PbMoO_4$ mineral is best effected by a mixed acid treatment, since HNO_3 or HCl alone will not dissolve wulfenite to any appreciable extent. The acid mixtures recommended for ores containing this mineral are a combination of HNO_3 , HCl and H_2SO_4 , or a combination of HNO_3 and H_2SO_4 . (2)

If the mineral is powellite $(CaMoO_4)$ the use of acid is inadmissable and in this case, fusion methods are generally used. (4)

Molybdenite yields readily to the action of strong nitric acid and aqua regia which oxidizes the molybdenum and sulfur to molybdic and sulfuric acids. (4) The most effective decomposition of the ore was obtained in this case by using the acid combination H_2SO_4 and HNO_3 .

In treating the ores by fusion methods a complete decomposition can be obtained. This process is somewhat more cumbersome than the acid treatment and in some cases if care is not taken in the fusion mixture, considerable time is involved in separating the fusion mixture from the crucible. Nevertheless it has an advantage (2) and parts of other interfering elements are precipitated out of solution. For the decomposition of a molybdenite ore, a mixture of Na₂CO₃ and NaNO₃ is very effective and provides an effective decomposition of the ore.

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A combination treatment, using an acid digestion, followed by a fusion of the residue is very often necessary as a small percentage of the molybdenite may be held in the silicious residue. However, this may in most cases be omitted if special care is used in the acid treatment so that all the molybdenite is oxidized.

3. Methods of Separation.

The analysis of molybdenum products is frequently difficult owing to the munber of other elements that may be associated with this metal. Some of the ores and steels are complicated. Elements that may be encountered in the determination of molybdenum are as follows: cobalt, chromium, nickel, iron, manganese, tungsten, vanadium, titanium, zirconium, copper, zinc, carbon, silicon, phosphorous, arsenic, antimony, and bismuth.

In the volumetric procedures the elements that offer the greatest interference are iron, chromium, tungsten, vanadium, titanium, zirconium, copper, arsenic and antimony. The remaining elements are either not reduced or are eliminated in the acid decomposition forming insoluble salt (PbSO₄, etc.) which can be filtered off.

If the molybdenum is to be determined gravimetrically, all of these elements have to be first removed as they will appear in the ignited precipitate.

(a) Removal of Iron.

If iron is present to any appreciable amount, the precipitation of the ferric hydroxide and the filtration of the precipitate becomes somewhat tedious.

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The precipitation of the iron as well as the aluminum by an excess of concentrated ammonium hydroxide has been found satisfactory if at least two precipitations are made. The excess ammonia is removed by boiling and the resulting ferric hydroxide is filtered off. However boiling off the excess of ammonia should be avoided if possible as an insoluble basic ferric molybdate of an uncertain composition is liable to form.

 $3(NH_4)_2MoO_4$ Fe₂(SO₄)₃ (NH₄)₂SO₄ Fe₂(MoOH)₃ (2) However this ferric molybdate can be dissolved by an excess of ammonia or caustic.

(b) Removal of P, As and Sb.

In an ordinary analysis for molybdenum enough ferric salt is usually present to prevent interference from phosphorous, arsenic or antimony, since the addition of the ammonia precipitates them with the iron group. (5) If much of these elements are present, they can be effectively removed with the iron and aluminum precipitate by the addition of a measured excess of ferric chloride. (2)

If the phosphates of Group III and fixed alkalies are present, they are precipitated with Group III metals by ammonium hydroxide in the usual course of analysis. Of the phosphates of the metals of Group III, IV, and V, those of aluminum and iron are insoluble in acetic acid while chromium phosphate is only dissolved with difficulty. The phosphates of the remaining metals of these groups are readily soluble in acetic acid. Ferric phosphate is somewhat soluble in a solution of ferric acetate, so that the

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separation of phosphorous is better performed in an ammoniacal solution than in an acetate solution, if calcium, magnesium, or barium is not quantitatively desired in the filtrate. (2)

(c) Removal of Barium, Strontium, and Calcium.

Barium, strontium, and calcium form molybdates in neutral solutions and thus have to be eliminated in a gravimetric procedure. Barium readily forms a molybdate, even in a slightly acidified (acetic) solution without much boiling. Barium, however can be completely removed with sulfuric acid in the same manner as the lead is removed. The amounts of strontium encountered in any material associated with molybdenum need not be considered. Calcium may occur as calcite in some molybdenum samples, but under the conditions of precipitating molybdenum, the presence of 20cc. of acetic acid will keep this in solution. (2) If the material, however, should contain much lime, it is best to remove it from the solution by sodium carbonate.

(d) Removal of Copper.

This separation from molybdenum in solution is made by potassium or sodium sulpho-cyanate after first being reduced with sulfur dioxide in a weak sulfuric acid solution. (6) Another procedure recommended for the removal of copper is by adding pure shot zinc to the solution, thus reducing the molybdenum in solution and precipitating the copper. (2)

(e) Removal of Chromium.

Chromium (2) can be separated from molybdenum by acidifying the solution with hydrochloric acid and reducing

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the chromate with SO_2 . The molybdenum remains unreduced if acid concentration is about ten per cent by volume. Ammonium or sodium hydroxide will then precipitate out the chromium if boiled for at least twenty minutes (NH₄Cl aids the precipitation and decreases the solubility of the precipitate similar to Al(OH)₃ precipitate.). Chromium when in a reduced condition forms no precipitate in the acetic acid solution by $Pb(C_2H_3O_2)_2$ under suitable conditions.

(f) Sulphide Precipitation.

In some cases where the individual separations do not suffice for complete separation, precipitation of molybdenum itself by hydrogen sulphide becomes necessary. In this case of the solution is made alkaline and then hydrogen sulphide gas bubbled into the solution under pressure, a quantitative separation can be obtained from aluminum, chromium, iron, zirconium, zinc, nickel, cobalt, manganese, titanium, lead, bismuth, copper, cadmium, and the rare earths, since these form insoluble sulphides and hydroxides and thus can be filt-The molybdenum and tungsten as well as traces of ered off. arsenic, antimony, and tin are not precipitated by hydrogen sulphide in an alkaline solution. By adding a small amount of tartaric acid and acidifying with sulfuric acid, the sulphides of molybdenum along with the metals of the arsenic group precipitate out on the addition of hydrogen sulphide under pressure, thus separating molybdenum from tungsten, tin, the alkaline earths, and alkali metals.

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Molybdenum along with arsenic and antimony can now be separated from the insoluble sulphides of Group II by ammonium sulphide. The arsenic can then be separated by volatifization (7) and the antimony by granulated lead. (7)

This separation, however, is very often inaccurate due to the reduction of the molybdenum by the hydrogen sulphide in acid medium, thus preventing the molybdenum from precipitating. Also as one can see, it is a time consuming operation and required considerable technique. (8)

Yagoda and Fales, in order to circumvent the described difficulties in the quantitative precipitation of pure molybdenum sulphide, conducted investigations on the means of increasing the concentration of the hydrogen sulphide in the system. They found that the solubility of hydrogen sulphide gas in water at 0°C is more than twice that at 25°C and that molybdenum sulphide can be quantitatively precipitated in a formic acid medium by initiating the reaction at a low temperature and maintaining a high concentration of hydrogen sulphide in the solution. It was noted here that a quantitative separation of the sulphide in the presence of tungsten can be effected in a solution whose pH is adjusted to 2.9 by a buffer mixture consisting of ammonium formate, tartrate and formic acids.

(g) Precipitation with Alpha Benzoin Oxime.

F. Feigl, (9) in the course of investigating certain organic reagents, discovered that the compound alpha benzoin oxime, $C_{6}H_{5}$ -CH-C-C₆H₅ could be used for the de-*I H* OH NOH

termination of copper.

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He succeeded in obtaining a quantitative determination of copper in the presence of nickel and the ammonia precipitable metals (Fe, Al, etc.) using this reagent.

About ten years later H. B. Knowles, (10) in a search for a rapid method for the determination of molybdenum, discovered that it could be quantitatively precipitated in acid solution by the addition of alpha benzoin oxime and the precipitate ignited to MoO₃.

This proved to be a very satisfactory method as the only other elements that were precipitated in mineral acid solution with alpha benzoin oxime were tungsten, palladium, sexivalent chromium, quinquivalent vanadium, and tantalum. Since sexivalent chromium and pentavalent vanadium can easily be reduced by sulfurous acid before the precipitation of the molybdenum, and palladium and tantalum only rarely occur, they can generally be disregarded as interfering. It was also found that columbium and silica, in addition to the already mentioned elements, contaminated the precipitate and must be removed before the precipitate of molybdenum could be determined by weighing, or else deducted.

Conditions Under Which Good Results Were Obtained by H. B. Knowles:

<u>Permissible Acidity</u>: The solution must be distinctly acid with either HCl, HNO_3, H_3PO_4 , or H_2SO_4 (preferable except when used in the presence of lead or tin). Five per cent by volume was found to be preferable, although good results were obtained in solutions containing as much as twenty per cent by volume.

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(b) <u>Temperature of the Solution</u>: Best precipitations were obtained at temperatures below 10[°]C and adding sufficient bromine water to faintly tinge the solution after addition of the reagent. These conditions are necessary as it was noted that at higher temperatures, the sexivalent molybdenum is liable to be reduced before it is precipitated.

(c) <u>Amount of Reagent Required</u>: Two to five times the theoretical amount of reagent provided an adequate excess.

(d) Time Necessary for Complete Precipitation:

Filtrations were best performed at the end of ten minutes during which time the solution was frequently stirred. Low results were obtained if left for thirty minutes.

(e) <u>Washing the Precipitate</u>: Cold dilute sulfuric acid (1/1 by volume) containing a small amount of alpha benzoin oxime was found to be the best wash solution.

Procedure Recommended by Knowles for General Use:

Prepare a solution containing 10 ml. of H_2SO_4 (sp. gr. 1.84) in a volume of 200 ml. and not more than 0.15 gr. of sexivalent molybdenum. If vanadates or chromates are present, add sufficient prepared H_2SO_3 to reduce them and heat to boiling until the odor of SO_2 can no longer be detected. Chill the solution to about 5°-10°C. Stir and add slowly 10 ml. of a solution of 2 gr. of alpha benzoin oxime in 100 ml. of alcohol and 5 ml. extra for each 0.01 gr. of molybdenum present. Continue to stir the solution, add just sufficient bromine water to tint the solution a pale yellow and then add a few milliliters of the reagent. Allow the beaker and contents to remain in a cooling mixture 10-15 minutes with occasional stirring. Stir in a little macerated pulp and filter through a paper of close texture, such as S&S. No-589 Blue Band. Wash the precipitate with 200 ml. of a cold, freshly prepared solution containing 25-50 ml. of the prepared reagent and 10 ml. of H₂SO₄ in 1,000 ml. On standing, the filtrate will deposit needlelike crystals if sufficient reagent has been employed.

Transfer the washed precipitate to a weighed platinum crucible, cautiously dry and char without flaming over a very low gas flame and then ignite to a constant weight in an electric muffle at 500°-525°C.

Knowles found that it is best to remove the silica in umpire analysis before proceeding with the precipitation of molybdenum rather than to treat the final precipitate with sulfuric and hydrofluoric acids, because of the uncertainty of completely decomposing molybdenum sulfate at the temperature of ignition. The ignited oxide of molybdenum is dissolved in warm dilute ammonium hydroxide. If an insoluble residue remains, it must be filtered off, ignited and weighed and the weight subtracted.

The above procedure offered an accurate and convenient method for the separation and determination of molybdenum in the presence of all interfering elements with the exception of tungsten.

(h) Separation from Tungsten.

The precise analysis of materials containing tungsten and molybdenum is complicated by the fact that in

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separating tungstic acid, the precipitate is always contaminated by appreciable quantities of molybdenum.

The usual method for the quantitative precipitation of tungsten (4) is by the addition of a solution of cinchonine in hydrochloric acid. The precipitate is ignited and weighed as tungstic oxide. The determination of molybdenum in the filtrate, however, gives low results unless a correction is applied for the molybdenum carried down with the tungsten. This may be done by bringing the tungstic oxide again into solution and estimating the molybdenum colorimetrically.

A number of other methods have been proposed for the separation of tungsten and molybdenum. Pechard heated the mixture of tungstate and molybdate (11) in a combustion furnace at a temperature between $250^{\circ}-270^{\circ}$ C. while passing a current of dry hydrochloric acid gas over them. The molybdenum is volatilized as MoO_3 .2HCl and collected in a cool part of the apparatus, while the tungsten oxide remained. This method is obviously unsuitable for routine analysis.

Rueginberg and Smith (12) employed concentrated sulfuric acid to separate the molybdenum from a mixture of the hydrated tungstic and molybdic acids. This was known as the Hommel (13) process and it consisted of heating the freshly precipitated oxides MoO_3 and WO_3 with sulfuric acids. The former passes into solution while the latter remains insoluble. They obtained the most satisfactory results by first digesting the oxides in a porcelain dish over a naked flame for about half an hour, then cooling the solution

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down and diluting up with water. The tungstic acid precipitate is filtered off. The separation by this method is not very satisfactory.

Merrill (14) used a similar procedure, employing selenium oxychloride as the solvent. He found that a mixture of 5cc. of conc. sulfuric acid and 25cc. of selenium oxychloride (SeOCl₂) will dissolve 1 gr. of MoO_3 in fortyfive minutes at the boiling point. However, the per cent of tungsten should not exceed ten per cent.

Marbaker (15) provided a means of separation by using Mdivanis reagent $(50g.SnCl_2.2H_20$ in 200cc. conc. HCl) to precipitate the tungsten out of solution. His procedure consisted of boiling the tungstates and molybdates of sodium and adding Mdivanis reagent in proportion of 20cc. for each 0.15 gr. of WO₃ present. The solution mixture is boiled for 3 minutes, filtered and the blue precipitate (V_2O_5) washed with hot five per cent hydrochloric acid.

Since the time of Heinrich Rose, (16) who discovered that molybdenum can be precipitated free from tungsten in solutions containing tartaric acid, considerable amount of work has been done on this method. However, the disadvantage of the separation by means of hydrogen sulfide is that the precipitation is usually incomplete owing to the reduction of part of the molybdenum by the reagent to a lower valency state in which the ions can no longer form insoluble sulfides. (4) The tartaric acid is required to keep the tungsten in solution by the formation of a soluble complex with the tungstic acid, and its subsequent removal, which becomes necessary if the filtrate is to be analyzed further, is a difficult and time

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consuming operation.

Arrington and Rice (17) made a rather complete survey of the methods available for the separation of tungsten from molybdenum and they concluded that the precipitation of molybdenum as the tri-sulphide by the method of Yagoda and Fales, which has already been mentioned, effects a better separation of molybdenum from tungsten than does the precipitation of the latter element as tungstic acid or cinchonine tungstate. However, they noted that the relative amounts of tungsten and molybdenum may reach a point where the molybdenum tri-sulphide carries down a little tungsten.

Gottlieb and Lang (18) avoided the difficulty of separating molybdenum and tungsten by developing a selective oxidation method by which the molybdenum is determined volumetrically in the presence of tungsten. The molybdenum in HCl solution is reduced to the pentavalent state with stannous chloride. Tungstic acid is prevented from precipitating in the acid solution by adding sodium fluoride to form a soluble complex. Any tungsten that is reduced by the stannous chloride is re-oxidized with bromine, which does not oxidize the molybdenum, and the excess bromine is removed by adding sodium arsenite. The molybdenum is then titrated with standard vanadate solution which does not oxidize either bromide or arsenite.

4. Methods of Determination of Molybdenum.

Until the discovery of the use of alpha benzoin oxime as a precipitant for molybdenum, there was little to choose from for the accurate determination of molybdenum between the volumetric method in which molybdenum is reduced

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by zinc in the Jones reductor, caught under a solution of ferric sulphate and titrated with a standard solution of potassium permanganate and the gravimetric method in which it is weighed as lead molybdate. As both of these methods are affected by practically the same interfering elements, the choice between them is a matter of convenience.

(a) Gravimetric Methods.

(1) The estimation of molybdenum as PbMoO₄ has been found to be undeniably one of the best methods for the gravimetric determination of molybdenum. This procedure was first suggested by Chatard (19) and studied by many others, notably by Brearley, (20) Weiser, (21) Bonardi, (2) and by Arrington and Rice. (22)

The precipitation is usually made by the slow addition of a lead acetate to a hot dilute acetic acidammonium acetate solution containing the molybdenum. The lead molybdate formed is stable at high temperatures and no special precaution is necessary on igniting. Due to the stability of the PbMoO₄ and the formation of a compound having a high molecular weight, this method became the standard procedure of gravimetric analysis in the majority of chemical laboratories.

(2) The precipitation of molybdenum (22a) in acid solution as the sulphide followed by ignition to the oxide, MoO₃ is not quite as satisfactory a method as that of PbMoO₄.
(22b) The precipitation of molybdenum without pressure is incomplete unless repeated several times. (23) Also this method is not reliable for low-grade materials, assaying around 0.10 per cent molybdenum. (2)

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Too many factors, unless accurately observed, will give erroneous results, especially in igniting and weighing as the di-sulphide or tri-oxide. The sulphide method is applicable, however, to certain classes of materials that require several determinations to be made on one weighing and may also be used when the sulphide contains no other interfering sulphides or impurities.

(3) There are a number of other gravimetric procedures for the determination of molybdenum, but these are of little value. However, the precipitation by mercurous nitrate in a nearly neutral solution of sodium carbonate is capable of giving good results in pure solutions of molybdenum. (24) (25) This method requires the same care in igniting the mercurous molybdate to 100_3 , in which form it is weighed, as in the sulphide method. In addition chromium, vanadium, tungsten, phosphorous, and arsenic are also precipitated by this reagent and interfere. The precipitation as AgMoO4 in the presence of silver nitrate was also found to be accurate for the determination of molybdenum in pure alkali molybdates.⁽²⁶⁾

Perkins descibed a gravimetric procedure involving the following reaction: (27)

2 MoO₃+ 4KI+ 4HCL \rightarrow 2MoO₂I+ HKCL+ H₂O+ I₂ The liberated iodine is combined with electrolytic silver, forming silver iodide which is weighed.

H. B. Knowles' method (10) employing alpha benzoin oxime as the precipitant has already been described. It serves to separate molybdenum from most other elements except tungsten and the precipitate may be ignited at 500° - 525° C. to MoO₃ and weighed.

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For accurate results, the temperature during the ignition must be closely controlled and a correction must be made by dissolving the MoO₃ in ammonia and filtering off, igniting and weighing any insoluble residue. To avoid these complications Sterling and Spuhr (28) combined the alpha benzoin oxime separation with the lead molybdate precipitation. They dissolved the alpha benzoin oxime precipitate, without ignition, in ammonia, filtered off the insoluble residue and then precipitated the molybdenum as lead molybdate.

(b) Volumetric Methods.

The precipitation of molybdenum as lead molybdate may be carried out volumetrically as well as gravimetrically. This is, however, less reliable than the procedures which depend on the preliminary reduction of the molybdate, followed by titration with a standard oxidizing agent. The standard solution used may be potassium permanganate, potassium dichromate, ceric sulfate, potassium iodate, or ammonium vanadate. The preliminary reduction of the molybdenum may be either to the trivalent or the quinquevalent state. Reduction to the trivalent state is most readily effected with zinc in the Jones reductor. Reduction to the pentavalent state may be brought about by mercury, silver, or stannous chloride.

(1) Volumetric Precipitation of Lead Molybdate.

The titration with lead acetate is the reverse of Alexanders ammonium molybdate method for the determination of lead and has the same limitations. The molybdate solution after being acidified with acetic acid - the mineral acid

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having been previously suppressed by ammonium or sodium acetate - is heated to boiling and titrated with lead acetate solution (20 grams per liter) until a drop of the solution fails to give a yellow tint with dilute tannic solution on a spot plate. (29) (30) (31) This process was found to be shorter than the gravimetric one, and on pure solutions is equally accurate. It is, however, unreliable when working with low grade ores, owing to a large amount of dissolved salts. (2)

(2) Reduction in Jones Reductor.

The reduction of molybdenum with zinc (32) in the Jones reductor provided with a solution of ferric sulfate in the receiver, followed by a titration with a standard solution of permanganate, leaves nothing to be desired as regards accuracy and convenience according to Hillebrand and Lundell. (4) It was formerly believed that reduction with zinc gave low results because of incomplete reduction of the molybdenum to the trivalent stage. However, Randall (33) in 1907 showed that the low results were due to partial reoxidation by air and that this can be overcome by collecting the solution as it leaves the reductor in one of ferric sulfate. Further evidence was given by Carriere and Lautie (34) and Th. Doring (35) to prove that the reduction of molybdic acid by zinc and sulfuric acid leads to the trivalent molybaenum and nothing else when air is excluded. The reduced molybdenum is oxidized by the ferric sulfate to a more stable intermediary compound with the formation of a reducing equivalent of ferrous sulphate.

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Phosphoric acid is used during the titration to bleach the color of the ferric sulphate. It was formerly the practice to add a few grams of granulated zinc to the molybdenum solution contained in a flask so arranged to allow for the replacement of its atmosphere of air by an atmosphere of carbon dioxide during the reduction of the molybdenum. However, the foregoing technique is seldom used to-day as the result of the development of the Jones reductor. (36) This (37), (36), (2), (38) consists of a cylindrical glass tube having a length about 22 cm. and an internal diameter of about 1.8 cm. At its top end, it is enlarged so as to form a reservoir of about 100 cc. capacity at its lower end, it is constricted and drawn out into a smaller tube about 15 cm. long and 0.6 cm. internal diameter. This small tube is provided with a stopcock and is connected to a suction flask. J. Bonardi (2) states that the internal bore should not be greater than five eights of an inch and should be about twenty to thirty inches long. Shorter reductors and larger bores give unsatisfactory results as the molybdenum solution was not completely reduced by passing the solution through a second time and requires a larger blank correction.

The titration of the reduced solution is made in the usual way with potassium permanganate which serves as its own indicator. Ceric sulfate solution may be used with ortho phenanthroline-ferrous complex as indicator, or potassium dichromate or ammonium vanadate may be used with diphenylamine or barium diphenylamine sulfonate as indicator.

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(3) Reduction with Mercury or Silver.

Chilesotti (39) in 1906 first observed that mercury would reduce a molybdic acid solution to the trivalent state, if the hydrochloric acid concentration was about 9N. This fact was carried no further than the preliminary observations until 1921, when McCay and Anderson (40) observed qualitatively that molybdenum solutions were reduced by mercury. Fourster and Fricke (41) prepared pentavalent molybdenum by electrolytic reduction and Stehlik (42) studied the volumetric estimation of molybdenum by potentiometric oxidation of the guingue- to the sexivalent state with ceric sulfate or potassium permanganate using stannous chloride as a reducing agent. But it was not until 1936 when an accurate procedure was devised for the quantitative reduction of the molybdenum to the quinquivalent state. This procedure was developed by Furman and Murray (43) (43a) and they showed that the relative instability of the quinquivalent molybdenum is evident from the following data:

Quinquivalent Molybdenum in 2N.HCL

 Days
 0
 2
 8
 14
 44
 202

 Normality
 0.08092
 0.07978
 0.0785
 0.07565
 0.06981
 0.00505

 Guinquivalent Molybdenum in 4N.HCL

Days 0 1 3 4 5 6 Normality 0.1356 0.1353 0.1344 0.1325 0.1315 0.1298 From the foregoing data they were able to show that quinquivalent molybdenum solutions are relatively unstable over extended periods of time, but the solutions are not appreciably oxidized in six or eight hours. From these data they also showed that it was possible to work with pentavalent molybdenum

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solutions without precaution to exclude air, if the solutions are to be oxidized within a short time. However, they concluded that the solution must be above 1 N. HCl, for the quinquivalent molybdenum was very unstable in neutral solutions and tends to deposit molybdenum blue. For the best results they found that the acid concentration must be between 1.5 N. and 3.5 N. HCl for if the concentration is below 1.5 N. molybdenum blue deposits out and if above 3.5 N. reduction to the trivalent state is apparent.

The Procedure Recommended by Furman and Murray.

The molybdate solution is transferred to a flask and made exactly 3 N. with conc. hydrochloric acid and then 25 cc. of metallic mercury is added. The solution mixture is then shaken vigorously for five minutes to obtain complete reduction of the molybdenum to the quinquivalent state. The solution is then decanted off through a filter paper and the mercury washed five times with 20 cc. portions of (1/5) hydrochloric acid and the filtrate titrated colorimetrically with ceric sulfate, using ortho phenanthroline as an indicator.

They found in their analyses that ammonia and phosphate salts had no effect on the results while arsenates had no effect up to 0.25 gr. quantity. However, other reducible elements had to be first separated as they were partially reduced by the mercury. Copper ions also had to be entirely removed as they catalyzed auto-oxidation of the quinquivalent molybdenum. (44)

The use of metallic silver as a reducing agent for obtaining pentavalent molybdenum was first suggested by Hoenig (45) in 1915 and by Edgar and Kemp (46) in 1918.

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However, this was not efficiently developed until 1934 when Walden, Hammett and Edmonds (47) devised a silver reductor and a new quantitative procedure for the determination of iron. Later on with the investigation of the reduction of molybdate in acid solution by Foerster, Fricke and Hausswald, (48) who represented the reaction by the following equation:

 $Mo0_2^{++} + 2H + C \rightleftharpoons Mo0^{+++} + H_2^{0}$

and measured the molal oxidation potential in 2,4 and 8 M. HCl Birnbaum and Walden (49) succeeded in devising a quantitative procedure for the determination of molybdenum by reducing with the silver reductor to the quinquivalent state and titrating with ceric sulfate.

(4) Other Volumetric Procedures.

Knecht and Atack (50) proscribed a reduction method which depends upon the reduction of molybdenum to MoCl₃ by zinc and hydrochloric acid in an atmosphere of carbon dioxide, the reduced solution being titrated with methylene blue. They claimed the reaction occured in two distinct stages, represented by the equations:

 $2\text{MoCl}_{3} + 2\text{HCl} + 0 \longrightarrow 2\text{MoCl}_{4} + \text{H}_{2}0 \quad (\text{and})$ $2\text{MoCl}_{4} + 2\text{HCl} + 0 \longrightarrow 2\text{MoCl}_{5} + \text{H}_{2}0$

This method never obtained any industrial importance as it required too much attention and did not seem to offer rapid solution. Another of the volumetric procedures recommended was the titration with ferric chloride after reduction with titanium chloride. (51) This method like the titration with methylene blue is too delicate an operation and unless kept within restricted limits is unreliable.

In the iodometric method the solution containing molybdenum trioxide is boiled in the presence of potassium iodide and hydrochloric acid, the volume having defined limits. Free iodine is liberated and can be expelled while the molybdenum is reduced to a lower oxide. The reaction is as follows:

 $2MoO_3 + 4KI + 4HC1 \longrightarrow 2MoO_2I + I_2 + 4KC1 + 2H_2O$

 $2MoO_3 + 2HI \longrightarrow MO_2O_5 + I_2 + H_2O_5$

The reoxidation of the molybdenum can be affected by a standard iodine solution, performed in a solution previously neutralized by sodium bicarbonate, and in the presence of tartaric acid to prevent precipitation during the neutraliz-The excess of iodine which has been added is then ation. titrated back with a standard sodium arsenite solution. The reoxidation is then done by standard permanganate whose excess is titrated with standard arsenite, and then reoxidized again with a standard iddine solution, using starch as an indicator. For detailed explanation of this procedure, the reader is referred to the following authors in whose work will be found all the information bearing upon the sub-Scott, (38) Gooch and Fairbanks, (52) Gooch and Pulman. (53) ject. Treadwell and Hall (54) state that the method finds no practical application, since it is difficult to obtain a quantitative reduction in accordance with the above equation. This procedure offered very little encouragement in view of

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the delicate reactions and manipulations involved and hence it obtained little commercial value.

The method of titration with potassium iodate was described by Andrews (55) and perfected by Jamieson (56) for determining molybdenum. The reactions may be represented as follows:

 $KIO_3 + MO_2O_3 + 2HC1 \longrightarrow MO_2O_5 + IC1 + KC1 + H_2O$

 $3KIO_3 + 2Mo_2O_3 + 6HCl \longrightarrow 4MoO_3 + 3ICl + 3KCl + 3H_2O$ This method also offered very little practical application as it required much painstaking experimentation to standardize accurately the many factors involved, besides taking care of the interfering elements that are found to be present in the routine analysis of an ore.

(c) Colorimetric Methods.

There have been several colorimetric methods proposed which have a fair degree of accuracy, but are only applicable in estimations. Among the most noted of these methods are the potassium xanthate procedure (57) (59) and the cyanate (58) (59) procedure. As these are only good for an estimation of small amounts of molybdenum, they have become of little value in the analytical laboratory except in estimations.

-25-Chapter III Experimental

1. Analysis of Molybdenite Ore.

By way of preliminary to the study of methods of analysis for molybdenum, a sample of a molybdenite ore was obtained and analyzed by the standard volumetric method recommended by the U. S. Bureau of Mines. The results obtained were high and variable, and considerable time was spent in locating the source of the discrepancies. They were at last traced to incomplete elimination of nitric acid from the solution before reduction and titration of the molybdenum. Following this, a comparison was made with a shortened procedure in which the molybdenum was determined directly in the filtrate from a hydroxide precipitation of the iron. Some experiments were also made on the effect of the size of sample taken for analysis.

The ore that was used was supplied through the kindness of Dr. F. F. Osborne of the Department of Geology. It contained pyrite, biotite, quartz, feldspar, and from 2 to 4% molybdenite. It was first ground to minus 100 mesh fineness and analyzed by the U. S. Bureau of Mines procedure which is as follows:

Method of Solution of Molybdenite.

From 0.5 to 5 grams of the finely pulverized sample, the weight used varying with the grade of the ore or concentrate, are treated with from 10 to 35 cc. of nitric acid (sp. gr. 1.42) and 7 to 10 cc. of sulfuric acid (sp. gr. 1.84) in a 250 cc. beaker provided with a watch-glass cover. It is then digested at a temperature somewhat below boiling until most of the MoS_3 appears to have been decomposed and then evaporated to white fumes. The solution is cooled and 50 cc. of water added to it and then it is boiled briskly for a few minutes until all of the salts have dissolved. The residue is then filtered and washed with hot water, then 6 to 8 times with dilute (1/3) ammonia, and finally with hot water.

The siliceous residue (which contains a great deal of the lead) is burned at a low heat in a porcelain crucible, cooled, transferred to a platinum crucible. It is then treated with 2 to 3 drops of conc. sulfuric acid and several cc. of hydrofluoric acid and evaporated until the sulfuric acid has been completely expelled. Any small residue is fusea with Na_2CO_3 , dissolved in H_2O and added to the main solution.

Method of Analysis.

To the solution containing all or practically all of the molybdenum, there is added sufficient ferric sulfate, (10 times as much Fe as there is As present); from 0.3 to 0.4 gr. is usually ample. The acid solution is then nearly neutralized with ammonia (addition of a sufficient amount to impart a red tint to the clear yellow solution is avoided), heated nearly to boiling and poured very slowly, and with vigorous stirring into 75 cc. of nearly boiling 15% NH₄OH contained in a 250 cc. beaker. When it has settled, the ferric hydroxide (which will carry down quantitatively all As. in the ore) is filtered and washed thoroughly with hot H_2O ; it is then dissolved in a slight excess

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of hot dilute (1/4) H₂SO₄ and the resulting solution is again heated to boiling and poured into 75 cc. of boiling 75% NH₄OH. The two filtrates which will contain all of the molybdenum are collected in a 500 cc. beaker.

To the ammoniacal filtrates are added 3 grams of tartaric acid and when the acid has dissolved the warm liquid is thoroughly saturated with hydrogen sulphide. The tartaric acid prevents the precipitation of vanadium and tungsten along with the molybdenum. Under these conditions, the molybdenum remains in solution as ammonium thio-molybdate $(NH_4)_2 MoS_4$ which imparts a deep red color to the solution. If a small precipitate of insoluble sulphides separates out, it is filtered off and washed with hydrogen sulphide water; if the solution remains clear this step is omitted. Copper, in the amounts usually present, remains entirely in solution at this point and is reprecipitated with the molybdenum when the solution is The thio molybdate solution is then made slightacidified. ly acid with sulfuric acid (1/1). This results in the precipitation of the molybdenum as a trisulphide.

The cessation of effervescence on addition of more acid, the absence of the odor of ammonium sulphide, and the disappearance of the red color of the $(NH_4)_2MoS_4$, mark the point where sufficient acid has been added to complete the reactions.

After heating for a short time, the precipitate is allowed to settle and is filtered on an ll cm. paper, then washed thoroughly with hydrogen sulphide water containing a small amount of sulfuric acid.

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The filtrate from the MoS3 sometimes contains appreciable amounts of molybdenum. Addition is made to it of 15 cc. of $HNO_3(1.42)$ and the solution is evaporated to fumes of SO3, more sulfuric acid is added if sufficient is not already present. After allowing it to cool, 5 cc. of conc. HNO_3 are added and the solution is again evaporated to white fumes. The addition of nitric acid and evaporation to strong fumes is repeated once more to insure the destruction of all organic compounds. After allowing to cool, sufficient water is added to dissolve all salts, 2 grams of tartaric acid are added and after additions of an excess of NH_3 (.90), the warm liquid is thoroughly saturated with hydrogen sulphide and filtered. The filtrate is acidified with sulfuric acid (1/1) and if, after standing for 15 to 30 minutes in a warm place, any MoS₃ has separated out it is filtered and washed well with hydrogen sulphide water containing a small amount of $\mathrm{H}_2\mathrm{SO}_4$ and combined with The precipitation of the molybdenum the main precipitate. as sulphide, when carried out as described, effects the separation and removal of tungsten, vanadium, chromium and all other interfering elements likely to be present.

The MoS_3 precipitates and paper are put into a 250 cc. beaker and treated with 6 cc. of H_2SO_4 and 10 cc. of conc. HNO_3 and the liquid is cautiously boiled until dense fumes of SO3 are evolved. After cooling, 5cc. of HNO_3 are added and the evaporation repeated. The evaporation with 5 cc. portions of strong HNO_3 is repeated several times until the filter paper has been completely destroyed and

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every trace of yellow color due to carbonaceous matter has disappeared. When this has been accomplished, the solution is fumed strongly for a short while, cooled, 5cc. of water added and the liquid is again taken to white fumes of SO_3 in order to insure the expulsion of every trace of HNO_3 The solution is then cooled and 75 cc. of H_2O added. It is then boiled, which should give a clear solution. Five grams of pure shot zinc (0.002%Fe) are added and the solution boiled until most of it has been dissolved. This results in partial reduction of molybdenum and complete precipitation of the copper which is usually present. The liquid is then filtered off on an asbestos or alundum filter to remove the undissolved zinc and copper.

The solution is then passed through the reductor after first passing 100 cc. $H_2SO_4(2.5\%)$ and followed by 200 cc. $H_2SO_4(2.5\%)$ and 50 cc. of H_2O . The reduced solution is caught in a flask containing 35 cc. of ferric phosphate solution.

The molybdenum solution is green when it reaches the lower part of the reductor, but turns red when it hits the ferric phosphate solution. These reactions may be represented by the following equations.

> $2 \text{MoO}_{3} + 3 \text{Ln} + 6 \text{H}_{2} \text{SO}_{4} \longrightarrow \text{Mo}_{2} (\text{SO}_{4})_{3} + 3 \text{ZnSO}_{4} + 6 \text{H}_{2} \text{O}$ $5 \text{Mo}_{2} (\text{SO}_{4})_{3} + 6 \text{KMnO}_{4} + 24 \text{H}_{2} \text{SO}_{4} \longrightarrow 10 \text{Mo} (\text{SO}_{4})_{3} + 3 \text{K}_{2} \text{SO}_{4} + 6 \text{MnSO}_{4} + 24 \text{H}_{2} \text{O}$

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Results Obtained by Above Procedure:

l)	3.518%	Mo	5)	3.847%	Mo
2)	3.790 %	Мо	6)	2.713%	Mo
3)	2.720	Мо	7)	2.990%	Mo
4)	2.740%	Мб	8)	7.90%	Mo

These results were higher than expected and showed excessive variation, so a study of the separate steps in the procedure was undertaken in order to discover the cause of the variations.

Since the hydrogen sulphide precipitation is known to be very often the cause of discrepancy, it was studied using a standard solution of molybdate to which was added a known amount of tungstate. The procedure was as follows:

A solution containing a known amount of molybdenum as ammonium molybdate was taken to which was added a solution of approximately 0.1 gr. of tungsten as sodium tungstate. The solution was made alkaline with ammonium hydroxide and 2 gr. of tartaric acid added. It was then saturated with hydrogen sulphide. After the solution was saturated with hydrogen sulphide (indicated by the blood red color), sulfuric acid (1/1) was added until effervescence ceased. The molybdenum trisulphide was then filtered off and washed with hydrogen sulphide water containing a few cc's of sulphuric acid.

The filtrate was treated with 5 cc. of H_2SO_4 and 5 cc. HNO_3 , and evaporated down to white fumes. Portions of 5 cc. HNO_3 were added after each evaporation to SO_3 fumes until all the organic matter was removed.

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After the organic matter was entirely eliminated, the solution was diluted up to 100 cc., boiled and 2 gr. of tartaric acid added. It was then made alkaline with ammonium hydroxide and the precipitation with hydrogen sulphide repeated as before.

The combined precipitates of molybdenum trisulphide were then transferred to a beaker and fumed with nitric and sulphuric acid as above to dissolve the precipitate and destroy the filter paper.

After all organic matter from the filter paper was eliminated, the solution was diluted up to 200 cc., boiled in preparation for the Jones reductor. The prepared solutions were passed through the reductor as **described** in the Bureau of Mines procedure.

Results:

Grams of Mo Present	Grams of Mo Found	Gram Deviation	Per cent Deviation
•05736	.05711	00025	43%
• 057 36	•0 57 25	00011	19%
.05736	.05720	00016	27%
.05736	.05804	+.00068	+1. 20%
•05736	.05716	00020	34%
•03 7 36	.05720	00016	27%
•05 7 36	.05ô77	00059	-1.20%

Since these results were all low, they did not account for the high results previously obtained. The iron separation was then investigated.

An aliquot portion of the standard ammonium molybdate solution to which was added approximately 0.1 gram of FeSO4

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was treated with 5 cc. of sulphuric acid and 10 drops of HNO₃. The solution was then evaporated down to the evolution of white fumes. This solution mixture was fumed strongly for 15 minutes to remove nitrates. Fifty cc. of distilled H₂O was then added and the solution boiled until all the salts had dissolved.

The ferric iron was then precipitated with 50 cc. of 20% NaOH and the resulting Fe(OH)₃ filtered off. The precipitate was washed thoroughly with hot water.

The filtrate was neutralized with $H_2SO_4(1/1)$ and 5 cc. of H_2SO_4 added in excess and the solution diluted up to 200 cc.

The prepared solution was then passed through the Jones reductor as previously described and titrated with a standard potassium permanganate solution.

Results:

Grams of Mo Present	Grams of Mo Found	Gram Deviation	Deviation Per cent
.05762	.06296	+.00534	+9.43%
•05762	•06659	+.00897	+15.57 %
•05 7 62	•06589	+.00827	+14.3 5%
.05762	•06589	+.00827	+14. 35,0

It was here thought that the iron had not been entirely removed. The procedure was repeated adding varying amounts of nitric acid and also using varying amounts of **sodium** hydroxide. The same high variation of results were obtained as may be seen by the following:

Grams of Mo Present	cc. of HNO ₃ Added	cc. of 10% NaOH Added	Gms. of <u>Mo Found</u>	Gram Deviation	Percentage De v iation
•05736	5.0	50	.05860	4.00124	↓2.1 6%
• 057 36	5.0	50	•05762	+.00026	+. 45%
• 0 5 7 36	5.0	50	.05831	00095	-1.66%
.05736	5.0	50	•05746	+.00010	+.17%
•05736	0.5	50	•05 7 33	00003	05%
•05736	0.5	50	•0 70 45	+.01309	+22.8 2%
• 057 36	0.5	50	• 0572 3	00013	23 [#]
•05 7 36	0.5	50	•05734	00002	04%

Further experiments were made using a double precipitation of the iron with ammonia instead of the single precipitation with NaOH.

Results:

Grams of Mo Present	Grams of <u>Mo Found</u>	Gram Deviation	Percentage Deviation
• 057 36	•06313	+. 00577	+10.05%
•05736	•083 99	↓. 02563	+44.67%
•05 73 6	•05340	00496	-8.67%
•05736	.05751	+.00015	+. 26%

It was then realized that the error might be due to incomplete removal of nitric acid in the evaporation with H_2SO_4 .

A portion of the ammonium molybdate solution containing approximately 0.1 gr. of FeSO₄ was treated directly with 50 cc. of 40% NaOH and the procedure carried out as before. Results:

.05641	.05617	00024	43%
•05641	.05635	00006	11%

Sodium peroxide was then substituted for nitric acid and sodium hydroxide and the solution treated as before, after eliminating the excess peroxide by boiling. <u>Results</u>:

•056 97	•05688	00009	16%
•056 97	•05 706	+.00009	+.16%

These results confirmed the suggestion of the presence of nitrates, which had not been completely removed by fuming with the sulphuric acid.

It was here noted that the presence of 0.05 cc. of nitric acid required an excess of approximately 30 cc. of standard permanganate for an end point.

With these difficulties in mind, an analysis of the ore was undertaken by a short procedure eliminating the hydrogen sulphide precipitation as tungsten was known to be absent. The procedure was as follows:

l gr. sample of the finely pulverized ore was treated with 7 cc. of sulphuric acid (sp. gr. 1.84) and 20 cc. of nitric acid (sp. gr. 1.42) in a 250 cc. beaker provided with a watch-glass cover. It was then digested at a temperature somewhat below the boiling point until all of the MoS₃ appeared to have been decomposed and then evaporated to white fumes. The solution was cooled and the sides of the beaker washed down twice with 5 cc. portions of distilled water, followed by subsequent heating to white fumes. The solution was cooled down again and 50 cc. of water added to it and then boiled briskly for a few minutes until all of salts had dissolved. The residue was then filtered and washed with hot water, then 6 to 8 times with dilute (1/3) ammonia, and finally with hot water.

To the filtrate containing all of the molybdenum was added 75 cc. of 40% NaOH, very slowly and with vigorous stirring. When the Fe(OH)₃ had settled, it was filtered and washed thoroughly with hot water.

The filtrate was diluted up to 200 cc., neutralized with $H_2SO_4(1/1)$ and 5 cc. of H_2SO_4 added in excess. The solution was then passed through the Jones reductor as previously described in the Bureau of Mines procedure. Results:

1)	3.172	3)	2.557%
•			

2) 2.558	4)	2.491%
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These results were still not altogether consistent. It was thought possible that the molybdenum might not have been brought completely into solution by the acid treatment used for the decomposition of the ore.

The silicious residue of these samples was then tested for the presence of molybdenum. They were treated with 3 drops of conc. H_2SO_4 and 3 cc. of HF and evaporated to white fumes. The residue was then fused with Na_2CO_3 and the mixture dissolved in hot water. The solutions were then tested for molybdenum by the KCNS method as described by Feigl.(59) As no vermillion fleck due to the presence of $K_3(Mo(CNS)_6)$ appeared in all four solutions. it was concluded that the molybdenum was thoroughly decompposed by the acid treatment.

Due to the flaky structure of molybdenite, some variation in results was to be expected by the uneven distribution of the element in samples. This sampling error should be decreased by using a larger sample. Two 5 gram samples were taken to test this. They were decomposed in the usual manner and the silicious residue filtered off. The solutions were then diluted up to exactly 250 cc. Aliquot portions of these solutions were taken and the analyses carried out as previously described.

Results:

With 1 Gram Sample	With 5 Gr	am Sample
(Mean of Previous	<u>#1.</u>	#2.
	2.64%	2.62 %
2.69%	2.66%	2.59%

It is evidently desirable in the case of a molybdenite ore to carry out the analysis on an aliquot portion of the solution obtained from a relatively large sample of the ore.

2. Precipitation of Molybdenum with Alpha Benzoin Oxime.

The procedure recommended by the U. S. Bureau of Mines for the analysis of molybdenum ores is long and tedious. The method of H. B. Knowles (10) of precipitation of the molybdenum with alpha benzoin oxime is much shorter and more convenient since it provides in one operation an accurate separation from all interfering elements except tungsten, sexivalent chromium, pentavalent vanadium, palladium and tantalum. Since sexivalent chromium and pentavalent vanadium can easily be reduced by sulfurous acid before the precipitation of the molybdenum, and palladium and tantalum only rarely occur, the only interfering element that is likely to cause trouble is tungsten.

However, this procedure has one serious disadvantage. In the ignition of the oxime precipitate to MoO_3 , the temperature has to be controlled between $500^{\circ}-525^{\circ}C$. If this temperature is exceeded, the molybdenum is volatilized to some extent; if the precipitate is heated below this temperature, there is a possibility that all the organic matter may not be exidized. Another factor which may lead to erroneous results is the presence of silica in the ignited precipitate, which is very often the case in ore analysis.

Sterling and Spuhr (28) modified the alpha benzoin oxime method by dissolving the precipitate in ammonium hydroxide and reprecipitating the molybdenum as lead molybdate. This eliminated the necessity for controlled ignition to MoO₃ and for correcting for impurities in the MoO₃.

It was considered that a more rapid and convenient method could be achieved by combining the obvious advantages of the alpha benzoin oxime separation with a volumetric instead of a gravimetric determination of the molybdenum. The alpha benzoin oxime precipitate can be dissolved in alkali without difficulty, but before the molybdenum can be reduced and titrated in the usual way with permanganate or ceric sulfate, the organic matter must be eliminated.

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An attempt was first made to oxidize the organic matter by evaporation with nitric and sulphuric acid. It was found to be possible to destroy the organic matter, but the excess nitric acid, of course, had to be completely eliminated by evaporating to fumes of sulphuric acid. It was found to be very difficult to avoid "bumping" and after several analyses were ruined by losses during the evaporation, this procedure was abandoned in favor of oxidation with $30^{\frac{1}{12}}_{\frac{1}{12}}$ hydrogen peroxide which was found to proceed rapidly and smoothly.

The following procedure was adopted. The precipitation of the molybdenum was made as recommended by H. B. Knowles.(10)

The filter paper containing the washed precipitate was transferred to a 250 cc. beaker and treated with 10 cc. of NH₄OH and 10 cc. of $30^{c'}_{12}$ H₂O₂. The solution was heated until all the oxime precipitate containing the molybdenum had dissolved and then the insoluble matter along with the filter paper was filtered off and washed with $NH_4OH(1/1)$. The filtrate was acidified with H_2SO_4 until 7 cc. in excess, 10 cc. of 30% H_2O_2 was added and the solution was evaporated down to white fumes. More of the 30% hydrogen peroxide was added in 5 cc. portions until the organic matter was completely destroyed. Some care was necessary to avoid excessive frothing when the peroxide was added to the hot solution. When the dark color due to organic matter had completely disappeared the solution was cooled, diluted to 200 cc. and boiled until all solid salts had dissolved.

A 100 cc. portion of H_2SO_4 (2.5%) was first passed through the reductor, followed by the molybdenum solution. The reductor was washed free of the molybdenum solution with 200 cc. of H_2SO_4 (2.5%) and 50 cc. of distilled water. The delivery tube of the reductor extended below the surface of 30 cc. of 10% ferric alum and 4 cc. of phosphoric acid in a one liter suction flask. The solution was then titrated with standard ceric sulphate (60) (61) using o-phenanthroline (62) as indicator or with standard potassium permanganate.

The method was tested by making a series of determinations on aliquot portions of an ammonium molybdate solution using the above procedure. The ammonium molybdate content of the solution was determined by a direct determination on an aliquot portion by reduction in the Jones reductor and titration with the standard solution available. The following results were obtained:

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	Grams of of Mo <u>Present</u>	Gms. of <u>Mo Found</u>	.1053N. KMn04 Required	.1037N. Ce(SO ₄)2 Required	Gram Deviation	Percentage Deviation
#1	.01417	.01417		4.27	.0000	sui,
	•01417	.01410		4.25	00007	49%
	•01417	.01407		4.24	0001	71%
	.01417	.01417		4.27	.0000	
#2	• 028 34	.02831		8.23	00003	11%
	.02834	.0284 0		8.26	+.00006	+.21%
	•02834	.02834		8.24	•0000	
	•02834	.02831		8.23	00003	11%
#3	•05603	•05 590	16.59		00013	23%
	. 05603	.05570	16.53		00033	60%
	•056 0 3	.05590	16.59		00013	23%
	.05603	•05563	16.51		00040	71%
	•05603	•0558 0	16.56		00023	41%
	.05603	•05560	16.50		00043	77%
] 7 77 4	.1133	•1133		34.15	0000	
	•1133	.1132		34.10	00010	08%
	.1133	•1134		34.16	+.00010	+.08%
	•1133	•1132		34.11	00010	08%
<i>∄</i> 5	•14 17	.1414		42.65	0003	21%
	.1417	.1413		42.60	0004	28%
	•1 417	.1417		42.69	0000	
	.1417	.1416		42.67	0001	07%

Using 0.1 N permanganate or ceric sulphate, the sample taken for analysis should contain about 0.1 gm. molybdenum. This requires a reasonable volume of the standard reagent in the titration while at the same time alpha benzoin oxime precipitate does not require unduly prolonged treatment with the hydrogen peroxide. It was found that with samples containing more than 0.15 gm. molybdenum, the time required for complete destruction of organic matter by the hydrogen peroxide treatment was so greatly increased that it was difficult to obtain satisfactory results.

Some further determinations were then made on portions of the ammonium molybdate solution to each of which approximately 0.1 gm. ferrous sulphate was added. Results were as follows:

Grams of Mo Present	Grams of Mo Found	cc. of .1053 <u>KMnO4</u>	Gram Deviation	Percentage Deviation
•05603	.05573	16.54	0003	54%
•05603	.05563	16.51	0004	71%
•05603	•05583	16.57	0002	36%
•05603	.05560	16.50	0004	54%

Comparison with the previous table shows that the iron caused absolutely no interference in this procedure.

The procedure was then applied to the same molybdenum ore that had previously been analyzed.

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Analysis of Molybdenite Ore.

Percentage of Mo by U. S. Bureau of Mines Procedure.	Percentage of Mo by Described Procedure.		Deviation of Percentage.
	#1	2.569%	058%
2.627% (Mean)	#2	2.575%	052%
	#3	2.550%	077%
	#4	2.573%	054%

It was only after the above procedure had been devised that Arrington and Rice's paper (17) came to hand. They had also investigated the alpha benzoin oxime method and had also devised a procedure essentially similar to that just described except that perchloric acid (HClO₄) was used to oxidize the organic matter instead of 30% hydrogen peroxide.

For comparison a few determinations were made on the standard ammonium molybdate solution using their procedure. It was noted that in treatment with perchloric acid, no frothing resulted, and the results showed no appreciable difference from those obtained using 30% hydrogen peroxide.

R	lesu	Lts	Using	; Per	chloric	Acid:

Grams of <u>Mo Present</u>	Grams of <u>Mo Found</u>	cc. of .1053 <u>KMn04</u>	Gram Deviation	Percentage Deviation
•05603	•05590	16.59	00013	23%
•05603	• 0557 3	16.54	00030	53%
•05603	•05563	16.51	00040	71%
.05603	.05570	16.53	00033	59%

The only objection that could be offered to the use of perchloric acid is that the chlorides have to be completely removed as they interfere in the permanganate titration.

3. Determination of Molybdenum in the Presence of Tungsten.

Since precipitation with alpha benzoin oxime provides a method for the separation of molybdenum from practically all other elements except tungsten, it seemed desirable to investigate the problem of determining molybdenum in the presence of tungsten. There are two general methods available for the separation of these elements. The tungsten may be precipitated in an acid solution by the addition of cinchonine, or the molybdenum may be precipitated with hydrogen sulphide in the presence of tartaric acid which keeps the tungsten in solution. The precipitation of the tungsten with cinchonine tends to give low results for molybdenum since some molybdenum is carried down with the cinchonine tungstate. Arrington and Rice (17) in their very thorough review of the determination of molybdenum, recommended Yagoda and Fales' (8) modification of the hydrogen sulphide method in the case of materials containing tungsten.

Yagoda and Fales' procedure is scarcely adapted for rapid routine analysis. Since a rapid volumetric method of treating the alpha benzoin oxime precipitate had been successfully applied in the absence of tungsten, it was thought worth while to attempt to modify the procedure to make it applicable with tungsten present.

(a) Cinchonine Separation.

An attempt was first made to remove the tungsten with cinchonine after dissolving the alpha benzoin oxime precipitate. About .05 gm. of tungsten in the form of a solution of sodium tungstate was added to a portion of the standard ammonium molybdate solution. Precipitation was made with alpha benzoin oxime and the precipitate dissolved in ammonia and hydrogen peroxide exactly as before. Insoluble matter was filtered off, the solution acidified with hydrochloric acid, excess peroxide destroyed by boiling and cinchonine solution added. The solution was then digested for one hour. After filtering off the cinchonine tungstate, 5 cc. of H_2SO_4 was added and the solution evaporated with the addition of 30% H₂O₂ to destroy the organic matter. However, the oxidation of the large excess of cinchonine required for quantitative precipitation of the tungsten proved to be impracticable, so the procedure was dropped.

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(b) Reduction of Molybdenum to the Pentavalent State.

The possibility of determining molybdenum in the presence of tungsten by a method involving reduction of the molybdenum to the pentavalent state was next considered. As a preliminary, Furman and Murray's (43) method of reduction with metallic mercury in a 2NHCl solution was investigated. A portion of the standard ammonium molybdate solution was made acid with HCl, shaken for fifteen minutes with 25 cc. mercury, separated from the mercury and titrated. Owing to the presence of HCl in the solution, the titration was made with standard ceric sulphate solution rather than with permanganate. The following results were obtained:

Grams of <u>Mo Present</u>	Grams of <u>Mo Found</u>	Gram Deviation	Percentage Deviation
•05649	.05731	00082	-1.45%
•05649	.05661	+.00012	+0.21%
•05649	•05041	00008	-0.14%
•05649	•05632	00017	-0.30%
•05649	.05651	00002	-0.03%

A silver amalgam was also prepared and compared with the mercury reduction method.

The silver amalgam was prepared by reducing a solution of silver nitrate and mercuric chloride with zinc. The solution was stirred until all of the metallic silver and mercury had deposited out. The zinc was then removed by acidifying the mixture with hydrochloric acid and boiling. The silver amalgam was then filtered off and washed with distilled water.

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The silver amalgam was transferred to a 2 M. hydrochloric acid solution containing a known quantity of molybdenum and stirred vigorously for ten minutes. The reduced molybdenum was then filtered off and titrated with a standard solution of ceric sulphate.

Results:

Grams of <u>Mo Present</u>	Grams of <u>Mo Found</u>	Gram Deviation	Percentage Deviation
.05649	.05681	+.00032	+0.57%
•056 49	.05661	+.00012	+0.21%

Since these results were less satisfactory and the procedure less convenient than the mercury reduction method, the latter was subsequently used.

A portion of the standard ammonium molybdate solution to which approximately 0.05 gm. of tungsten in the form of sodium tungstate solution had been added, was then acidified to 2 N. HCl, treated with memoury and titrated as above described.

It was noted that the tungsten separated out of solution in the form of a blue precipitate (WCl₅). (63) This evidently carried down some of the molybdenum along with it, as may be seen from the following results:

Grams of Mo Present	Grams of Mo Found	Gram De vi ation	Percentage De v iation
•0 5649	.05314	00335	-5.93%
.05649	•0476 7	00982	-17.38%
•05649	.04966	00168	-2.97%
•05649	•05175	00474	-8.39%

Portions of 0.1000 to .3000 gr. of the sodium tungstate solution were treated alone by the above procedure. The tungsten was entirely precipitated out of solution as two drops of ceric sulfate solution was sufficient to establish an end point in all cases in the filtrate.

Attempts were then made to separate the tungsten quantitatively from the molybdenum by redissolving the blue tungsten precipitate with (1/1) ammonium hydroxide; acidifying and reducing as before. The two filtrate were combined and titrated with ceric sulphate.

Results.

Grams of <u>Mo present</u>	Grams of <u>Mo Found</u>	Gram Deviation	Percentage Deviation
.05661	•05552	00119	-2.10%
•05661	•05542	00129	-2.28%

It was evidently necessary to keep the tungsten in solution. Tartaric accomplishes this, but interferes with the titration. Some attempts were made to convert the precipitated tungsten to the soluble sodium meta-tungstate, (63) without much success.

The procedure used by Gottlieb and Lang (18) of adding sodium fluoride was then tried. This keeps the tungsten in solution as a soluble fluo-tungstate. This was found to be effective in keeping the tungsten in solution during the reduction with mercury and the subsequent titration. Fluoride is known to interfere seriously in titrations with ceric sulphate owing to the formation of complexes with ceric ion. Nevertheless, an end point was obtained in the titration, but the high results suggested that some of the tungsten as well as the molybdenum was being reduced.

Results:

Grams of <u>Mo Present</u>	Grams of Mo Found	Gram De v iation	Percentage Deviation
.05661	•08268	↓. 03407	+60.18
•05661	. 06 5 70	+.00911	+16. 09
.05661	•06645	+. 00984	+17.22

The Rueginberg and Smith (12) procedure for the separation of the two elements was then carried out before the mercury reduction. The procedure was as follows:

A solution of standard ammonium molybdate containing sodium tungstate was acidified with H_2SO_4 and evaporated down to white fumes. The fuming was continued for one half hour with occasional addition of a few drops of HNO₃ when a green color was obtained. The solution was diluted up with water and the tungstic acid precipitate filtered off. The filtrates were then acidified to 2 N. HCl and reduced by the mercury reduction procedure and titrated with a standard ceric sulphate solution. Results.

Grams of Mo Present	Grams of Mo Found	Gram Deviation	Percentage Deviation
.05612	•05314	00398	-7.09
.05612	•04766	00846	-15.07
.05612	•04966	00646	-11.51
.05612	•051 7 5	00437	-7.79
•05612	•04966	00646	-11.51
•05612	•04073	01539	-27.41

Evidently the tungstic acid precipitate retained a considerable amount of molybdenum.

(c) Titration of Molybdenum with Vanadate Solution.

Gottlieb and Lang (18) described a selective oxidation procedure whereby molybdenum might be determined in the presence of tungsten. The tungsten is kept in solution by adding sodium fluoride and the molybdenum reduced to the pentavalent state by means of stannous chloride, which also partially reduces the tungsten. Bromine is added which reoxidizes the tungsten but not the molybdenum. The excess bromine, which would otherwise destroy the indicator, is reduced with sodium arsenite and the molybdenum is titrated with standard ammonium vanadate solution using barium diphenylamine sulphonate as indicator. Under the conditions specified, the vanadate does not react with either bromide or arsenite. The procedure recommended by Gottlieb and Lang is as follows:

The solution of alkali molybdate and tungstate is

treated with 2 gr. of NaF, 20 cc. conc. HCl and diluted up to 120 cc. After the solution becomes clear, 15 to 20 cc. of 2 N. SnCl₂ solution is added at once. The solution is let stand according to the quantity, 0.1 gr. of molybdenum up to fifteen minutes and 0.2 gr. up to 25 minutes. Then 2 to 3 drops of approximately 0.5 M. CuSO₄ solution and 20 to 25 cc. of 0.2 N. bromine solution (16 gr. of bromine and 120 gr. of KBr per liter) are added. After stirring for a short time, the excess bromine is removed by adding sodium arsenite solution. 2 gr. of NaF, 10 cc. of conc. HCl, then 2 to 3 drops of barium diphenylamine sulphonate are added. The titration is made with standard ammonium vanadate solution which is added in excess and back-titrated with standard ferrous sulphonate solution.

No ammonium vanadate was at hand and the only vanadium compound available for the preparation of a standard vanadate solution was some vanadium pentoxide (Eimer and Amend). This was a grey powder which was not appreciably soluble in either ammonia or sodium hydroxide. It was dissolved to some extent on heating with sulphuric acid (1/25) to give a dark green solution which could not be successfully titrated with ferrous sulphate. A portion of the V_2O_5 was then fused with sodium carbonate and treated with hot water and sulphuric acid. A reddish brown precipitate of vanadic acid was obtained which was filtered out and dissolved readily in sodium hydroxide. The resulting solution was diluted and acidified with sulphuric acid (1/25), giving a light yellowish green solution.

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This was standardized against a standard solution of ferrous sulphate, using barium diphenylamine sulphonate as indicator. Results.

Grams of Mo Present	Grams of <u>Mo Found</u>	Gram Deviation	Percentage Deviation
•1134	.1152	+.0018	+1.59
•1134	•1132	0002	-0.18

(d) <u>Titration of Molybdenum with Standard Potassium</u> Bichromate.

It was thought possible that potassium bichromate might be substituted for ammonium vanadate solution since the oxidation potentials of bichromate and vanadate are not very different. Potassium bichromate would be distinctly preferable since it is a more generally available and a standard solution may be readily made up by direct weighing.

A number of experiments were made with this end in view, in all of which the reduction of the molybdenum was effected with mercury rather than with stannous chloride. Previous experiments had shown that tungsten could be kept in solution with sodium fluoride, but was at least partly reduced by the mercury. Hence it would be necessary to reoxidize the tungsten with bromine as in Gottlieb and Lang's procedure and to eliminate the excess bromine if diphenylamine sulphonic acid was to be used as indicator. Consequently experiments were made on ammonium molybdate solutions containing no tungsten to test the possibility of titrating the molybdenum with potassium bichromate in the presence of bromide and arsenite. Blank titrations on solutions containing bromide and arsenite were satisfactory, but with molybdenum present, high results were obtained. The titration in this case was made by adding an excess of potassium bichromate and back-titrating with standard ferrous sulphate solution. Apparently there was some reaction of the excess potassium bichromate with either bromide or arsenite. High results were still obtained after adding sufficient silver nitrate to precipitate all the bromide in solution as silver bromide, so attempts were made to avoid the presence of excess arsenite.

One method that was tried was to add just sufficient arsenite to reduce the free bromine. After reduction of the molybdenum with mercury and addition of bromine solution, three cc. of chloroform was added to the solution and it was then titrated with sodium arsenite until the chloroform layer was colorless. It was found difficult to obtain a definite end-point and the subsequent titration with bichromate failed to give consistent results.

An effort was made to avoid the use of arsenite altogether by eliminating the excess bromine in some other way. The usual method of simply boiling the solution was not applicable here because of the comparative instability of the pentavalent molybdenum. Bubbling air through the solution at room temperature was found to be inadequate. Extraction with carbon tetrachloride or chloroform effectively removed the bromine, but it was difficult to make a

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satisfactory separation of the two layers and titration gave low results due either to loss in the separation from the carbon tetrachloride layer or possibly to some of the molybdenum having been extracted. Reduction of the bromine with NaNO₂, and removal of the excess nitrate with urea proved useless as no satisfactory end-point could be obtained in the titration.

Attempts were then made to remove the bromine by means of organic reagents of which phenol seemed the most promising. Solutions containing phenol gave a satisfactory blank so that it seemed worthy of further investigation.

The solution of alkali molybdate was reduced by mercury as previously described. Bromine solution was added and then a few cc. of phenol solution until all of the free bromine had precipitated. Silver nitrate was then added to precipitate the bromides. The bromide precipitate and the brom-phenol derivative were filtered off and washed thoroughly with 2 N. HCl.

The titration was then made with standard bichromate solution which was added in excess and back-titrated with standard ferrous sulphate solution. The results varied considerably which was probably due to the oxidation of the phenol.

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Results:

Grams of Mo Present	Grams of Mo Found	Gram Deviation	Percentage Deviation
•1134	•1164	+.0030	+2.65%
•1134	.1157	+.0023	+2.03%
•1134	.1120	0014	-1.23%
•1134	•1242	+.0108	+9. 52%
.1134	•1083	0051	-4.50 ² /2

Chapter IV

Summary

1. A sample of a molybdenite ore was analyzed by the standard volumetric method of the U. S. Bureau of Mines and by a shortened procedure in which the molybdenum was titrated directly using the Jones reductor and potassium permanganate, after precipitation of the iron with sodium or ammonium hydroxide. For an ore of this character, the latter method was found entirely satisfactory.

Sodium hydroxide was found more convenient than ammonium hydroxide for the precipitation of the iron. A single precipitation with sodium hydroxide was found to give a satisfactory separation, whether the iron was present in the ferric or ferrous state.

It was found to be necessary, after bringing the sample into solution, to use great care to eliminate nitric acid completely by evaporating to fumes of sulphuric acid several times, washing down the sides of the casserole thoroughly between successive evaporations.

The flaky nature of molybdenite makes sampling difficult and variations in the results of analysis are apt to result from uneven distribution of the molybdenite in the sample. It was found that such variations could be largely avoided by performing the analysis on an aliquot portion of the solution prepared from a large (five-gram) portion of the sample.

(2) A volumetric modification of Knowles' alpha benzoin oxime method was independently developed.

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The molybdenum oxime precipitate was dissolved in ammonia and 30% hydrogen peroxide without difficulty. The resulting solution was acidified with 5 cc. of conc. sulphuric acid in excess, and the organic matter eliminated by oxidation with 30% hydrogen peroxide. It was then diluted up to 200 cc., passed through the Jones reductor, and titrated with standard potassium permanganate or ceric sulphate in the usual way. This is a convenient and accurate procedure when samples used contain not more than 0.15 gm. of molybdenum.

(3) The above method is inapplicable to materials containing tungsten since tungsten is precipitated along with molybdenum by alpha benzoin oxime. An attempt was made to apply the method after dissolving the alpha benzoin oxime precipitate and precipitating the tungsten with cinchonine, but it failed owing to the impracticability of destroying the large excess of cinchonine in the solution by oxidation with hydrogen peroxide.

A search was made for a selective oxidation method by which molybdenum might be titrated in the presence of tungsten after the above treatment of the alpha benzoin oxime precipitate. The reduction of molybdenum to the pentavalent state by metallic mercury followed by titration with ceric sulphate was tried and found to give satisfactory results with molybdenum alone, but tungsten if present, is precipitated and carries down with it appreciable amounts of molybdenum. The tungsten may be kept in solution by adding sodium fluoride, but it is then partially reduced

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by the mercury. It may be re-oxidized by bromine, but attempts to titrate the molybdenum with potassium dichromate with diphenylamine sulphonic acid as indicator proved unsuccessful as excess bromine destroys the indicator, and no satisfactory method was found of eliminating the excess bromine.

A trial was made of Gottlieb and Lang's method by which sodium fluoride is added to keep the tungsten in solution; the molybdenum is reduced with stannous chloride; bromine is added to re-oxidize any reduced tungsten; excess bromine is removed by adding sodium arsenite, and the molybdenum is titrated with standard ammonium vanadate. Reasonably satisfactory results were obtained and it is suggested that the application of Gottlieb and Lang's procedure to the solution obtained by treating the alpha benzoin oxime precipitate with hydrogen peroxide as recommended in the second part of this thesis, will provide a rapid volumetric method for the estimation of molybdenum in materials containing tungsten.

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