[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Studies on the Analytical Chemistry of Tungsten and Molybdenum. II

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In an earlier article[2] the writers described a method for the quantitative separation and determination of tungsten and molybdenum which is applicable to the analysis of a simple mixture of tungstates and molybdates. The use of this method in the analysis of steels and other materials containing these metals as constituents necessitates either the removal of the other metallic components of the sample, or the concentration of the two elements in question in a single group during the early stages of the analysis.

The factors of ionic similitude which render the separation of tungsten and molybdenum a problem of considerable difficulty, favor the application of the latter alternative. In particular, most of the organic reagents which have been proposed for the determination of tungstates or molybdates yield compounds of kindred solubility with both elements.[2] Of these reagents, α-benzoin oxime has been applied successfully to the determination of molybdenum in steels by Knowles[3] and more recently, by Taylor-Austin.[4] Knowles states that any tungsten present in the molybdenum steel is seemingly quantitatively precipitated along with the molybdenum-benzoin oxime complex. Further experiments by the writers revealed that small amounts of tungsten, ranging between 30 to 5 mg. of the metal, are precipitated quantitatively from acid solutions by means of α-benzoin oxime. The method developed for concentrating the tungsten and molybdenum as a unit free from other interfering elements consists essentially in effecting solution of the sample, separating the bulk of the tungsten as tungstic acid along with the silica and precipitating the molybdenum together with the residual tungsten as complex derivatives of α-benzoin oxime. After the ignition of the combined acid insoluble precipitates, the silica is removed from the mixture by means of hydrofluoric acid and the tungstic and molybdic oxides are brought into solution by treatment with sodium hydroxide. The resulting solution then can be analyzed for its tungsten and molybdenum content employing the procedure described in our earlier paper.

In the application of these methods to the analyses of alloy steels difficulty was encountered in the accurate determination of minute amounts of either tungsten or molybdenum owing to the small weight of the resulting purified oxides. In attempts to enhance the weight of the oxides by conversion into salts of high molecular weight and fixed composition, it was discovered that both metals could be determined accurately by precipitating and weighing thallous tungstate or molybdate. Owing to the high atomic weight and the monovalent character of thallium a very marked increase in mass results when the corresponding oxides are converted into the compounds having the composition Tl_2MoO_4 or Tl_2WO_4. By means of this mechanism it was possible to determine the amount of molybdenum present in a 1-g. sample of steel when the element was present only to the extent of 0.1%.

Preparation of Standards.—The experiments leading to the procedure described in the present article were carried out on solutions of the following analyzed alloys obtained from the Bureau of Standards: (a) Nickel-Chromium-Molybdenum Cast Iron No. 107, containing 0.689% Mo; (b) Chrome-Tungsten-Vanadium Steel No. 50a, containing 18.25% W and 0.009% Mo; (c) Ferrotungsten No. 75, containing 75.2% W and 0.23% Mo. The tungsten and molybdenum content of these alloys was varied by addition of weighed amounts of the purified sodium tungstate and molybdate described in our earlier work.

During the course of these investigations new values for the atomic weight of tungsten[5] and molybdenum[6] were published by Hönigschmid and his co-workers. Calculations based on these newer figures alter the theoretical amounts of water and oxides present in the sodium salts employed as standards by less than 0.01%, and as such, it is not found necessary to change the values recorded in the previous paper.

Preparation of Reagents.—The reagents employed in the procedure for the separation of molybdenum sulfide from tungsten in a system buffered by ammonium formate and formic acid are essentially the same as described in our first article.[2] It was found that the time required to prepare a large quantity of water saturated with hydrogen sulfide at 0° could be decreased materially by starting the preparation with a mass of cracked ice containing

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[1] J. T. Baker Chemical Co. Research Fellow in Analytical Chemistry, 1936-37.

[2] H. Yagoda and H. A. Fales, THIS JOURNAL, **58**, 1494 (1936).

[3] H. B. Knowles, *Bur. Standards J. Research*, **9**, 1 (1932).

[4] E. Taylor-Austin, *Analyst*, **62**, 107 (1937).

[5] O. Hönigschmid and W. Menn, *Z. anorg. allgem. Chem.*, **229**, 49 (1936).

[6] O. Hönigschmid and G. Wittmann, *ibid.*, **229**, 65 (1936).

just enough water to permit mechanical stirring of the mixture, and to continue a rapid flow of the gas through the aerator stone until the ice is completely melted. Attempts at storing the saturated solution in glass-stoppered bottles kept in a refrigerator at a temperature of 8° were unsuccessful owing to leakage of the gas and occasional popping of the stopper on account of the pressure developed in the container by the gas liberated from the solution as the liquid assumed the temperature in the refrigerator.

α-Benzoin Oxime.—A solution of this reagent is prepared by dissolving 20 g. of the Eastman Kodak Co. product in a liter of 95% ethyl alcohol. This solution is stable over considerable periods of time, our stock solution showing no evidence of decomposition over a period of one year.

Thallium Acetate.—The reagent employed for the precipitation of thallous tungstate and molybdate is prepared by dissolving 3 g. of thallium acetate in 100 cc. of 95% ethyl alcohol. This solution should be permitted to stand overnight and filtered from any insoluble matter that may separate on standing.

Improved Method of Filtration.—In our studies on the conversion of molybdenum sulfide into the oxide it was shown that the process was facilitated considerably by depositing the sulfide in a layer of uniform depth such as results when the precipitate is filtered through a Gooch or a porous bottom crucible. The use of filter paper pulp as an aid in the filtration of the finely divided sulfide suggested a method of filtration wherein the asbestos fibers are substituted by a thick mat of ashless filter paper (C. S. S. no. 29).[7]

Loss of the ignited oxide through the perforations of the crucible is prevented by means of the platinum disk illustrated in Fig. 1. These guard plates are made from foil, or preferably of thin sheeting about 0.2 mm. thickness of a diameter to fit the standard sized Gooch crucible (approx. 22 mm.), the disk having a multitude of fine pin holes located along the edge about 1 mm. away from its periphery. This device does not interfere materially with the speed of filtration and offers adequate protection against loss of the ignited precipitate. The chief advantages of this procedure are that the mass of the filter pad does not enter into the weighings, with the result that time is saved in preparing the crucible, and that the possible source of error resulting from the loss of fibers during the filtration is entirely eliminated.

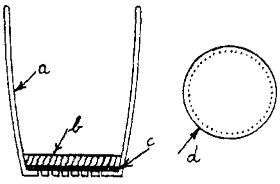

Fig. 1.—Modified Gooch crucible: a, porcelain crucible with perforated bottom; b, filter pad of ashless cellulose; c, perforated platinum disk; d, top view of platinum disk.

This mode of filtration can be applied to substances whose composition remains unaltered during the volatilization of the cellulose mat, and to other compounds that can be ignited subsequently to oxides suitable for the gravimetric determination of the constituent under investigation. This method has been applied successfully in the filtration of calcium oxalate, magnesium ammonium phosphate, barium sulfate, the oxalates of the rare earths, the sulfides of zinc, copper and molybdenum, the tungstic acid–cinchonine complex, small amounts of iron and aluminum hydroxides and in the determination of silicon in steels.

In transferring the precipitate to the crucible it is advantageous to dispense with the rubber tip on the stirring rod and to substitute in its place a roll of ashless filter paper. When emptied of its contents, the vessel in which the reaction took place is rinsed with the washing solution, any particles adhering to the glass rod are wiped off on a sector of filter paper which is then rolled around the rod as illustrated in Fig. 2. The precipitate adhering to the walls of the glass vessel is dislodged by rubbing the prepared rod over the surface, the paper being finally ignited together with the precipitate.

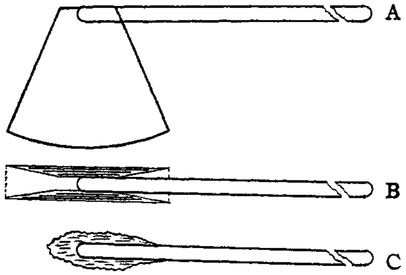

Fig. 2.—Preparation of paper tipped rod: A, glass rod placed on sector of ashless paper; B, paper rolled around rod; C, paper moistened and twisted into shape.

After the ignition of the precipitate it has been our practice to cool the crucible in a desiccator differing in construction from those of classical design. The essential modification consists in the use of aluminum for the construction of both the cover and the crucible support, the glass base remaining unaltered so that it can be filled with any of the common desiccants. The substitution of metal permits the crucible to cool rapidly, the saving in time being most noticeable when several of these are placed in the desiccator. The metal parts of the instrument show no sign of corrosion after being in use for two years. The lid of an aluminum cooking vessel can be made into a satisfactory cover by attaching it to a ring of suitable size having its lower surface ground flat.

Precipitation of Tungsten by α-Benzoin Oxime

The conditions for the quantitative precipitation of tungsten by means of α-benzoin oxime are essentially the same as those found suitable by Knowles for the separation of molybdenum.[8] The results obtained by adding 10 cc. of the reagent to acidified solutions of known tungsten content containing 5% 12 *m*-hydrochloric acid and cooled to 5–10° are represented in Table I.

An inconvenience common to the separation of both molybdenum and tungsten with this reagent is the necessity for conducting the precipitation in chilled solutions in order to avoid the reduction of the metals from their

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[7] These mats are about 2 mm. thick and fit perforated bottom crucibles having an inside diameter of 21 mm. By moistening the paper mat with hot water or cold dilute hydrochloric acid the fibers can be compressed until a tight seal is formed with the inclined walls of the crucible.

TABLE I

SEPARATION OF TUNGSTEN USING α-BENZOIN OXIME

Expt.	Grams of $Na_2WO_4 \cdot 2H_2O$	Weight of tungstic oxide Found	Calcd.	Diff.
1	0.0500	0.0348	0.0352	−0.0004
2	.0250	.0178	.0176	+0.0002
3	.0250	.0170	.0176	− .0006
4	.0100	.0065[8]	.0070	− .0005
5	.0100	.0067[8]	.0070	− .0003

hexavalent condition. The precipitating properties of other oxime compounds were investigated with the hope of finding a reagent that would permit a quantitative recovery of the two metals at room temperatures, but a satisfactory substitute for α-benzoin oxime could not be found.[9] The execution of the work can be facilitated greatly when using α-benzoin oxime as the precipitant by adding two or three ice cubes (approximately 50 g.) to the solution, permitting the ice to melt before the addition of the precipitant.

Determination of Tungsten and Molybdenum as Thallous Tungstate and Molybdate.—The similarity existing between the chemical reactions of the lead and monovalent thallium ions suggested that salts of the latter element might also be suitable for the gravimetric determination of either tungsten or molybdenum. The use of thallium seemed desirable in that two gram atoms of the element are required for the formation of a gram mole of either the tungstate or the molybdate, the resultant compounds containing unusually low percentages of the constituent being determined, as may be seen by inspection of Table II.

TABLE II

PERCENTAGE OF TUNGSTEN AND MOLYBDENUM IN COMPOUNDS USED FOR THEIR DETERMINATION

Compound weighed	Percentage of metal
MoO_3	66.67
$PbMoO_4$	26.14
Ag_2MoO_4[10]	25.55
Tl_2MoO_4	16.88
WO_3	79.31
Tl_2WO_4	28.02

Thallium tungstate and molybdate are sparingly soluble in water, and practically insoluble in solutions containing more than 60% absolute ethyl alcohol by volume. Quantitative precipitation of either the tungstate or the molybdate can be achieved by the addition of a slight excess of thallium acetate to an ammoniacal solution of the metal containing two parts of 95% ethyl alcohol and one part of water by volume. The halogens and large amounts of sulfate ion interfere with the determination, but these substances are not present in the mixture resulting from the solution of the ignited oxides in alkali. The conversion of small amounts of the oxide into the thallium salt has proved particularly useful in the analysis of molybdenum steels after the metal has been separated by means of α-benzoin oxime, the method allowing the use of a gravimetric determination when the alloy contains only a small percentage of molybdenum.

In general, the determination is made after a separation of the two metals has been effected employing the following procedure. Either oxide is dissolved in hot water containing 5 cc. of 5% sodium hydroxide, the solution is filtered into a 150 cc. Erlenmeyer flask and the filtrate is neutralized with 10% acetic acid using phenolphthalein as an indicator. The resulting solution is adjusted to a volume of approximately 30 cc., made ammoniacal by the addition of 1 cc. of 16 *m* ammonium hydroxide, 60 cc. of 95% ethyl alcohol is added and the mixture is heated to approximately 70–80°. The compound is precipitated from the hot solution by slowly adding 10 cc. of 3% thallium acetate dissolved in 95% ethyl alcohol. The mixture is digested at 60–70° for about one hour until the precipitate is completely coagulated. When cool, the thallium salt is transferred to a weighed porous-bottomed crucible, using a mixture of 60 cc. of ethyl alcohol, 30 cc. of water and 1 cc. of 16 *m* ammonium hydroxide as the wash fluid. The weight of the thallium compound is ascertained after the crucible is dried at 110° for one hour. The recovery of small amounts of tungstic and molybdic oxides obtained by following the above process is represented in Tables III and IV.

TABLE III

DETERMINATION OF TUNGSTEN AS THALLIUM TUNGSTATE

Expt.	WO_3, g.	Weight of Tl_2WO_4 Found	Calcd.	Diff.
1	0.0548	0.1550	0.1552	−0.0002
2	.0352	.1000	.0995	+ .0005
3	.0352	.0989	.0995	− .0006
4	.0260	.0734	.0736	− .0002
5	.0197	.0551	.0557	− .0006
6	.0188	.0524	.0531	− .0007
7	.0087	.0245	.0245	.0000
8	.0047	.0130	.0133	− .0003

TABLE IV

DETERMINATION OF MOLYBDENUM AS THALLIUM MOLYBDATE

Expt.	MoO_3, g.	Weight of Tl_2MoO_4 Found	Calcd.	Diff.
1	0.0296	0.1159	0.1168	−0.0009
2	.0260	.1026	.1029	− .0003
3	.0189	.0739	.0745	− .0006
4	.0149	.0584	.0588	− .0004
5	.0149	.0586	.0588	− .0002
6	.0066	.0262	.0259	+ .0003

Estimation of Tungsten and Molybdenum in Steel

The exact method for effecting solution of the sample will depend upon the nature of the steel. In general, the finely divided sample can be decomposed with the aid of concentrated hydrochloric

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[8] Tungstic oxide redissolved after ignition and weighed as Tl_2WO_4.

[9] A 5% alcoholic solution of salicylaldoxime produced a brown flocculent precipitate from 1% solutions of sodium tungstate upon acidification with hydrochloric or sulfuric acids. Under the same conditions a yellow coloration, but no attendant precipitate, was produced by the addition of the reagent to molybdate solutions of varying concentrations. Further studies revealed that the precipitation of the tungsten is incomplete and is further retarded by the presence of large amounts of molybdenum.

[10] LeRoy W. McCay, THIS JOURNAL, 56, 2548 (1934).

and nitric acids, or a mixture of sulfuric and nitric acids. Alloys containing a high percentage of tungsten may require repeated evaporations with hydrofluoric and nitric acid before complete solution is brought about. When the entire sample weighing from 1–2 g. is decomposed completely, the mixture is evaporated to dryness and the silica is dehydrated by the addition and evaporation of two 10-cc. portions of 12 *m* hydrochloric acid. The soluble constituents are brought into solution with the aid of 10 cc. of 12 *m* hydrochloric acid and 100 cc. of hot water. Any chromates or vanadates present in the solution are reduced by the addition of about 200 mg. of ferrous ammonium sulfate crystals to the warm acid solution, and the mixture is chilled to about 5–10° by the addition of three ice cubes. When these are almost entirely melted, 10–20 cc. of 2% α-benzoin oxime is added, followed by a slight excess of saturated bromine water and a further 5-cc. portion of the α-benzoin oxime reagent. The precipitate is allowed to settle over a period not exceeding fifteen minutes and filtered through a coarse textured paper. The precipitate is washed with a solution consisting of 50 cc. of water, 5 cc. of 12 *m* hydrochloric acid, 5 cc. of the benzoin oxime reagent and about 50 g. of cracked ice. The paper is ignited in a platinum crucible at a low temperature not exceeding 550°.

After the incineration, the ash consists of tungstic and molybdic oxides, silica, some graphite and small amounts of iron. The silica is volatilized with the aid of hydrofluoric and sulfuric acids, after which the tungsten and the molybdenum are dissolved from the residue with a small amount of hot water and 5 cc. of 5% sodium hydroxide. The extract is filtered into a 250-cc. flask where it is made approximately neutral with 2 *m* formic acid, treated with an excess of saturated bromine water and finally boiled down to a volume of 10 cc.

At this point the solution contains the two metals in the form of sodium tungstate and molybdate. The two elements can now be separated quantitatively by application of the procedure described in our first communication.[2] When either constituent is present in amounts weighing less than 25 mg. as the oxide, it is advantageous to dissolve the material as previously described and determine the percentage of the metal present from the weight of the thallium compound. The results obtained by following these procedures are illustrated by the analyses of steel samples recorded in Table V.

TABLE V

SEPARATION AND DETERMINATION OF TUNGSTEN AND MOLYBDENUM IN STEELS

Expt.	Material	Percentage of Mo Calcd.	Percentage of Mo Found	Percentage of W Calcd.	Percentage of W Found
1	1 g. No. 107	0.69	0.68	...	...
2	0.5 g, No. 107	.69	.66	...	...
3	1 g. No. 107 plus 0.1 g. of $Na_2WO_4{\cdot}2H_2O$	.69	.70	5.58	5.56
4	1 g. No. 50a	.009	.011	18.25	18.20
5	0.5 g. No. 50a	.009	.000	18.25	18.32
6	1 g. No. 50a plus 0.1 g. of $Na_2MoO_4{\cdot}2H_2O$	4.67	4.71	18.25	18.24
7	0.5 g. No. 75	0.23	0.25	75.2	75.1
8	0.3 g. No. 75	.23	.20	75.2	75.2

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Summary

A method is described for the determination of tungsten and molybdenum in alloy steels which involves (1) separation of tungsten and molybdenum from the other metallic constituents by precipitation with α-benzoin oxime, (2) ignition to obtain the mixed oxides, (3) solution of the oxides and precipitation of molybdenum as sulfide in a buffered formic acid solution, (4) ignition and weighing of molybdic oxide, (5) treatment of the sulfide filtrate and precipitation of tungsten by cinchonine, and (6) ignition and weighing of tungsten oxide. The gravimetric determination of small amounts of tungstic and molybdic oxides is facilitated by the precipitation and weighing of the corresponding thallium salts.

A modification of the Gooch method of filtration is described which eliminates the weighing of the filter medium. A new design of desiccator is proposed which promotes rapid cooling of hot objects placed into it.

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