

The analysis of molybdates and tungstates

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Summary. The estimation of molybdenum and tungsten when present together has proved difficult, as is indicated by the large number of methods put forward for their determination.¹ Many of the methods given are for one or other of these elements only, a note often being added that the presence of the other invalidates the method. The estimation of molybdate and tungstate in the mineral powellite has been briefly described by one of the authors (A. A. M.):² molybdate and tungstate were precipitated as oxinates $(\text{Mo,W})\text{O}_2(\text{C}_9\text{H}_8\text{ON})_2$ and the molybdate (MoO_4'') determined by measurement of the optical density at 230 $\text{m}\mu$ of a solution containing molybdate and tungstate. The amount of tungstate present was then estimated by difference. The property of the molybdate ion, MoO_4'' , to absorb strongly in the ultra-violet has been further investigated and it has been found that, if a wave-length of 240 $\text{m}\mu$ is chosen and the proper precautions taken, the MoO_4'' ion can be estimated without significant interference by the WO_4'' ion. Methods are given for the analysis of the common molybdate and tungstate minerals, together with results obtained during the course of this investigation.

THE analysis of molybdates and tungstates resolves itself into three parts: the separation of the anions from the cations, the estimation of the cations, and the estimation of the anions.

The methods used to separate the anions from the cations and to estimate the cations depend on the nature of the mineral but all methods yield a solution of sodium molybdate and sodium tungstate sensibly free from the mineral cations, and the method of analysis of the anions is the same for all minerals.³

Experience has shown that, provided the conditions set out below, under scheelite, are followed, molybdate and tungstate can be precipitated together quantitatively, by means of oxine.

A solution of sodium molybdate containing about 10 ppm MoO_3 shows no appreciable absorption above 275 $\text{m}\mu$. At wave-lengths less than this the absorption increases very rapidly but does not attain a maximum within the limits imposed by the instrument used (Unicam SP 500): with similar concentrations of tungstate the absorption begins at much lower

¹ R. Z. Bachman and C. V. Banks, 1965. *Anal. Chem.*, vol. 37, p. 111R.² M. H. Batty and A. A. Moss, 1962. *Min. Mag.*, vol. 33, p. 160.³ Anthoinite is an exception, see p. 1001.

wave-lengths, viz 240 $m\mu$ (fig. 1). At higher concentrations the absorption curves although similar in shape move to higher wave-lengths, but even at concentrations up to 30 ppm of MoO_3 , similar concentrations of

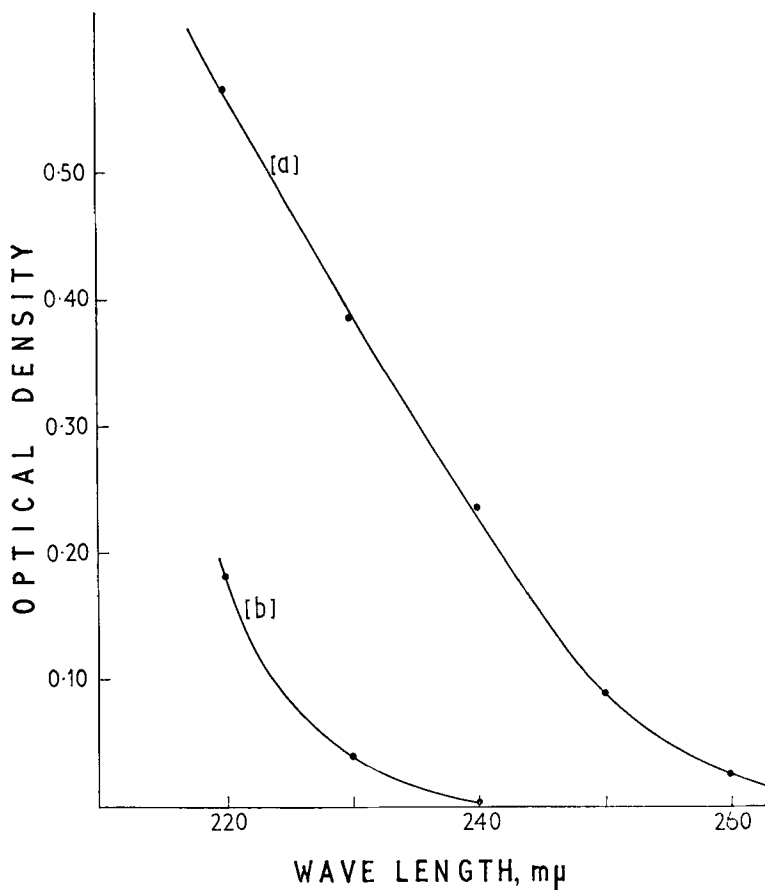


FIG. 1. Absorption curves of aqueous solutions of (a) Na_2MoO_4 , (b) Na_2WO_4 . Concentration of MoO_3 or WO_3 , 10 parts per million; 1 cm cell.

WO_3 have a negligible effect and even ten times these concentrations of WO_3 require corrections that are very small (fig. 2). Furthermore, experiments have shown that the optical densities of the molybdate and tungstate ions when present together are additive. It will be seen, therefore, that by a combination of the oxine precipitation and

absorptiometric methods, molybdates and tungstates can be analysed accurately, but whereas small amounts (down to about 0.1 %) of molybdate can be determined, the method does not make possible the estimation of small amounts of tungstate.

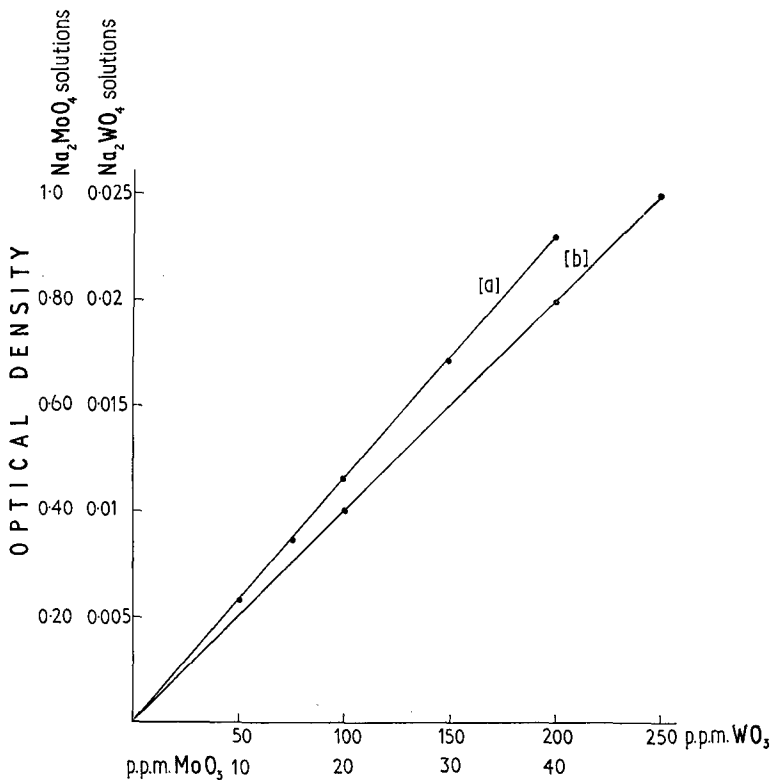


Fig. 2. Optical densities of aqueous solutions of (a) Na_2MoO_4 , (b) Na_2WO_4 , 240 $m\mu$, 1 cm. cell.

The scheelite group

Between 50 and 200 mg of the powdered mineral are fused with 1 g of sodium carbonate in a platinum crucible, the fusion cake leached with hot water,¹ and transferred to a beaker. The contents of the beaker are filtered through a 9-cm 540 Whatman paper² and washed with cold

¹ Distilled water should be stored in glass containers. Water that has been stored in polythene has an appreciable absorption at 240 $m\mu$.

² All filter papers must be washed with distilled water before use in order to remove soluble substances that absorb at 240 $m\mu$.

water. The filtrate, which contains $\text{MoO}_4^{''}$ and $\text{WO}_4^{''}$, is made up to 100 ml in a volumetric flask (solution A). The residues in the crucible and on the filter paper are dissolved in hydrochloric acid, bulked together and the calcium determined by precipitation as calcium oxalate. *A blank is prepared for solution A.*

TABLE I. Analyses of some molybdates and tungstates

	1	2	3	4	5	6	7	8
CaO	—	—	19.7	27.2	0.7	—	—	—
PbO	—	—	—	—	59.5	48.6	—	—
FeO	1.2	18.5	—	—	—	—	—	—
Fe_2O_3	—	—	—	—	—	—	17.0	0.6
Al_2O_3	—	0.5	—	—	—	—	—	14.8
MnO	21.8	5.2	—	—	—	—	—	—
MoO_3	0.4	0.8	0.1	68.0	39.2	0.8	62.6	1.3
WO_3	74.5	75.2	80.5	4.4	—	49.3	—	74.1
H_2O	—	—	—	—	—	—	19.3	9.1
SiO_2	1.0	—	—	—	—	0.3	1.3	—
Total	98.9	100.2	100.2	99.6	99.4	99.0	100.2	99.9
Number of ions on the basis of $\text{Mo} + \text{W} = 1$								
Ca	—	—	1.008	0.987	0.046	—	—	—
Pb	—	—	—	—	0.976	0.991	—	—
Fe^{+2}	0.052	0.780	—	—	—	—	—	—
Fe^{+3}	—	—	—	—	—	—	0.490	0.024
Al	—	0.030	—	—	—	—	—	0.883
Mn	0.948	0.181	—	—	—	—	—	—
Mo	0.008	0.017	0.002	0.961	1.000	0.026	1.000	0.027
W	0.992	0.983	0.998	0.039	—	0.974	—	0.973
$\text{O} + \text{OH}$	4.000	4.008	4.000	3.988	4.020	3.944	6.200	5.897

1. Hübnerite, B.M. 85391. Losquijs Camp, Pima Co., Arizona, U.S.A.
2. Wolframite, Cornwall.
3. Scheelite, B.M. 1961, 133. Cariboo gold mine, Wells, British Columbia.
4. Powellite, B.M. 1921, 59. Black Mountain district, Kern Co., California.
5. Wulfenite, B.M. 47791. Tecomamine, Utah, U.S.A.
6. Stolzite, B.M. 1937, 584. Diko Abuja, N.W. Nassawara Province, Nigeria.
7. Ferrimolybdite, B.M. 1916, 56. Paradox Valley, Colorado, U.S.A.
8. Anthoinite, B.M. 1949, 90. Mount Misoba, Maniema District, Congo.

Solution A. This solution is used to determine MoO_3 , WO_3 , and SiO_2 ¹ if present. An aliquot of the solution is diluted a hundredfold and the optical density at 240 $m\mu$ (1 cm silica cell) is determined. An approximate value for the MoO_3 content of the mineral can then be read off from the curve in fig. 2, and from this another dilution of solution A may be made to give a solution containing about 20 ppm of MoO_3 . The optical density of this solution is then determined accurately using as the reference

¹ Silica is determined colorimetrically.

standard the blank solution similarly diluted. The optical density of this solution is compared with those of suitable diluted standards of sodium molybdate and the percentage of MoO_3 , assuming no correction for WO_3 , calculated. If the sum of the percentages of MoO_3 and cation oxide are deducted from 100, the approximate amount of WO_3 can be estimated. The approximate composition of the mineral having been ascertained the $(\text{MoO}_3 + \text{WO}_3)$ content is next determined by precipitation of the oxinates $(\text{Mo}, \text{W})\text{O}_2(\text{C}_9\text{H}_6\text{ON})_2$. To achieve this an aliquot of solution A containing about 20 mg of $(\text{Mo}, \text{W})\text{O}_3$ is transferred to a 250-ml beaker and nearly neutralized with glacial acetic acid. The solution is diluted to about 120 ml, brought near to boiling and 5 ml of 2% oxine in 2N acetic acid run in, after which glacial acetic acid is added, if necessary, dropwise until a permanent precipitate just forms. A further 5 ml of 2% oxine are run in, the solution boiled gently for a few minutes and the beaker placed on the water-bath to allow the precipitate to coagulate. When the supernatant liquid is clear the beaker is removed from the bath and the solution allowed to cool. When cold the oxinate is filtered on a G4 sintered-silica crucible, washed with cold water, and dried at 120°C . Let mass of oxinate precipitate be M mg.

If there are x mg of MoO_3 and y mg of WO_3 in solution A, then $z(2.890x + 2.174y) = 100M$ where $z =$ volume in ml of aliquot used for the oxinate precipitation.

Since x is known very closely, y can be calculated and this value can be used to give a correction to be applied to the optical density used for the determination of the MoO_3 (fig. 2). In this way a close estimate of the MoO_3 and WO_3 content of solution A is arrived at.

The wulfenite group

About 200 mg of the powdered mineral are warmed with 10 ml of 4N sodium hydroxide solution in a platinum crucible until solution is complete. The solution is transferred to a beaker, diluted with water to about 100 ml, heated to boiling, and hydrogen sulphide passed in until the precipitate starts to settle. The precipitate is allowed to coagulate on the boiling water-bath and filtered on a 9-cm 541 Whatman paper and washed with water. The filtrate is set aside for the estimation of molybdate and tungstate.

The precipitate is transferred to the original beaker by a stream of water. The precipitate remaining on the paper is decomposed by pouring 10 ml of hot 1:1 nitric acid over the paper and the paper is well washed with water. The beaker containing the precipitate and nitric acid is

placed, uncovered, on the water bath and allowed to go dry. 10 ml of hot ammonium acetate solution are poured over the filter paper to dissolve any lead sulphate formed by oxidation of the lead sulphide, after which it is added to the residue in the beaker, warmed, and diluted to a convenient volume. After filtration to remove sulphur, the lead is determined as lead chromate.

To the filtrate from the precipitate of lead sulphide are added 4 ml of sulphuric acid (S.G. 1.84) and the liquid evaporated to low bulk to get rid of most of the hydrogen sulphide, after which 10 ml of nitric acid are added and the solution evaporated to fuming, a few ml of nitric acid being added dropwise to make sure the molybdenum and tungsten oxides are oxidized. About 10 ml of water are added and the solution again taken to fuming to remove the nitric acid. The solution is then neutralized with 2N sodium hydroxide solution using litmus paper as indicator, warmed to clear any opalescence that might be present, after which it is made up to a suitable volume in a volumetric flask (solution A). *A blank is prepared for solution A.* MoO_3 and WO_3 are determined as described on p. 998.

The wolframite group

Between 50 and 200 mg of the powdered mineral are fused with 1 g of sodium carbonate in a platinum crucible, the fusion cake leached with hot water, and transferred to a beaker. About 5 ml of 2N sodium hydroxide solution are added, followed by a few drops of hydrogen peroxide to reduce the permanganate ion, the solution heated to boiling, and then allowed to stand on the water-bath until the precipitate has settled. When the supernatant liquid is water-white it is filtered hot through a 9-cm 541 Whatman paper and the precipitate washed with very dilute sodium hydroxide solution. The filtrate is set aside and the precipitate washed into a beaker, any precipitate remaining on the paper being dissolved off with 10 ml of 4N sulphuric acid containing some hydrogen peroxide and added to the contents of the beaker. The beaker is heated to accelerate the solution of the precipitate, and the iron and manganese hydroxides reprecipitated and filtered off as before. The two filtrates are combined and made up to a suitable volume in a volumetric flask. (Solution A.) *A blank is prepared for solution A.* The iron and manganese hydroxides are dissolved in dilute sulphuric acid containing hydrogen peroxide and the solution made up to 100 ml in a volumetric flask. Iron and manganese are determined in this solution by colorimetric methods.

Solution A. This solution is used to determine the MoO_3 , WO_3 , and impurities such as Al_2O_3 and SiO_2 . Because of the high WO_3 /oxinate ratio, impurities precipitated by oxine must be estimated and allowed for: accordingly a large aliquot of solution A is transferred to a 250 ml beaker, and 0.5 g tartaric acid added; the solution is neutralized with acetic acid, 3 ml of 2 % oxine in 2N acetic acid run in, and the solution heated to boiling and made alkaline with ammonia. The beaker is placed on the water-bath for about an hour and then allowed to cool, any precipitate formed being filtered off on a G4 sintered-silica crucible and weighed. Another aliquot of solution A containing about 20 mg of $(\text{Mo}, \text{W})\text{O}_3$ is used for the estimation of $(\text{Mo}, \text{W})\text{O}_3$ by precipitation as oxinate as described on p. 999. The mass of this precipitate is corrected for the impurities precipitated as oxinate and also for the MoO_3 present, before calculating the WO_3 content of the mineral. MoO_3 is determined on a suitable aliquot of solution A as described on p. 998.

Ferrimolybdite and ferritungstite

Between 50 and 200 mg of the powdered mineral are heated to 250°C in a platinum crucible to determine the water by loss on ignition.¹ The residue is fused with 1 g. of sodium carbonate and the fusion cake leached with hot water. The ferric hydroxide is filtered on a 9-cm 540 Whatman paper and washed with very dilute sodium hydroxide solution. The filtrate is made up to a suitable volume in a volumetric flask. (Solution A.) *A blank is prepared for solution A.* The residue on the filter paper is dissolved in hydrochloric acid, the solution made up to 100 ml in a volumetric flask, and the iron determined colorimetrically. MoO_3 and WO_3 are determined on solution A as described on p. 998.

Anthoinite

Between 50 and 100 mg of the powdered mineral are heated to 450 – 500°C in a platinum crucible to determine water by loss on ignition.² The residue is warmed with 10 ml of 4N sodium hydroxide solution until solution is complete except for a small amount of iron hydroxide. The solution is transferred to a volumetric flask through a 7-cm 541 Whatman paper, the residue well washed with cold water, and bulked to volume. (Solution A.) *A blank is prepared for Solution A.* The residue on the paper is dissolved in hot dilute hydrochloric acid, the solution transferred to

¹ Experiments using a thermobalance confirmed the temperature recommended by E. S. Simpson, 1926. Journ. Roy. Soc. Western Australia, vol. 12, p. 57.

² N. Varlamoff, 1947. Bull. Soc. Géol. Belgique, vol. 70, p. 153.

a volumetric flask, bulked to volume, and the iron determined colorimetrically.

Solution A. This solution is used to determine MoO_3 , WO_3 , Al_2O_3 , and SiO_2 if present. The MoO_3 content is determined on a suitable aliquot of solution A as described on p. 998. An aliquot containing about 10 mg of Al_2O_3 is run into a 250 ml beaker and after adjusting the bulk to about 100 ml, 0.5 g of tartaric acid is added. The solution is neutralized with acetic acid, heated to boiling, and 5 ml of 2% oxine in 2N acetic acid run in, followed by ammonium hydroxide solution until the solution is alkaline, whereupon the beaker is placed on the water-bath and left until the precipitate has coagulated. The aluminium oxinate is filtered on a G4 sintered-silica crucible, and washed with hot water, the filtrate being reserved for the determination of $(\text{Mo,W})\text{O}_3$. The precipitate is dried at 120°C and the weight of Al_2O_3 calculated from the weight of aluminium oxinate.

An aliquot of the filtrate containing about 20 mg of $(\text{Mo,W})\text{O}_3$ is transferred to a silica Kjeldahl flask, 2 ml of sulphuric acid (S.G. 1.84) added and the solution taken down to low bulk over a flame. The heating is continued and the organic matter oxidized by the repeated addition of nitric acid (S.G. 1.42) when the sulphuric acid is near the point of fuming. The silica flask is cooled and the contents neutralized with sodium hydroxide solution. The flask is warmed on the water-bath to ensure complete solution of the $(\text{Mo,W})\text{O}_3$ and the solution transferred to a beaker. The $(\text{Mo,W})\text{O}_3$ content of this solution is determined as described on p. 999.

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