ammonium oxalate to precipitate a portion of the uranium. The precipitate was ignited, dissolved in nitric acid and again precipitated with oxalate. A precipitate consisting chiefly of bismuth oxalate was obtained, but no thorium could be detected with the peroxynitrate test after removal of the bismuth as sulfide.

TABLE II

LEAD–URANIUM ANALYSES OF ST. JOAQUIMSTHAL PITCHBLENDE

Pb = 206.50

Sample	Sample, g.	$PbSO_4$, g.	% Pb	$PbCrO_4$, g.	% Pb	U_3O_8, g.	% U
1	2.4310	0.1137	3.192	0.1214	3.197	lost	...
2	2.4583	.1175	3.262	.1248	3.251	1.7453	60.21
3	2.0904	.1000	3.265	.1053	3.225	1.4867	60.31
4	2.2388	.1055	3.216	.1125	3.217	1.5896	60.21
		Average	3.234		3.223		60.24

Pb/U = 0.0536

Since 41.3% of the lead in this mineral appears to be common lead, the percentage of uranium lead in the pitchblende is 1.892 and the corrected Pb/U ratio 0.0314. The approximate age on this basis is 239 million years. With the logarithmic formula the age is 234 million years. Lead–uranium ratios from this pitchblende range from 0.10 to 0.02.[5] Specimens with the low ratios may be freer from common lead than this one.

Summary

1. The atomic weight of a specimen of lead from St. Joaquimsthal pitchblende has been found to be 206.50.
2. The percentage of common lead calculated from the atomic weight is 41.3. This agrees with the percentage found by Dr. A. O. Nier from isotopic analysis.
3. The percentages of lead and uranium in the mineral are found to be 3.22 and 60.24, respectively.
4. The percentage of uranium lead is calculated to be 1.89 and the Pb/U ratio 0.0314.
5. The approximate age of the mineral appears to be 239 million years, and the age by the logarithmic formula 234 million years.

(5) Bull. Nat. Res. Coun. No. 80.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Determination of Molybdenum with the Silver Reductor[1]

BY NATHAN BIRNBAUM AND GEORGE H. WALDEN, JR.

A number of oxidimetric methods for the volumetric determination of molybdenum involving reduction to both the quinquivalent and trivalent states have been developed.[2] In the method involving reduction to the trivalent state the reduced solution must be protected from air oxidation by an atmosphere of an inert gas or by collecting the reduced solution in a flask containing excess of an oxidizing agent. No such protection is necessary when the molybdenum is reduced to the quinquivalent state.

Walden, Hammett and Edmonds[3] observed that molybdenum is reduced by the silver reductor to the quinquivalent state and that the reduced solution can be titrated with ceric sulfate using the *o*-phenanthroline ferrous complex indicator. They failed, however, to obtain reproducible results with the method they used.

Furman and Murray[4] recently have developed a method for the determination of molybdenum by reduction with mercury and titration with ceric sulfate. They have shown that quinquivalent molybdenum solutions are stable at room temperature for several hours.

We have found that molybdenum is quantitatively reduced by the silver reductor when the solution is 2 *M* in hydrochloric acid and the temperature of the solution 60–80° during passage through the reductor. The method is precise and the use of a reductor column makes it rapid and convenient.

Apparatus and Reagents.—The silver used was prepared according to the directions of Walden, Hammett and Edmonds.[3] The reductor column was similar to the one they describe except that the length of the glass column was 17 cm. and the length of the silver column 12 cm. About 25 g. of silver was required. Calibrated glassware was used throughout the investigation.

An aqueous ammonium molybdate solution, approximately 0.1 *M* with respect to molybdenum, was prepared from Merck ammonium heptamolybdate (blue label reagent grade). The amount of molybdenum in the solution

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(1) From a dissertation submitted by Nathan Birnbaum in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

(2) (a) Bonardi and Barrett, Tech. Paper 230, Bureau of Mines, 1920; (b) Stehlik, *Coll. Czechoslov. Chem. Comm.*, **4**, 418 (1932); (c) Lang and Gottlieb, *Z. anal. Chem.*, **104** (1936).

(3) Walden, Hammett and Edmonds, THIS JOURNAL, **56**, 350 (1934).

(4) Furman and Murray, *ibid.*, **58**, 1689 (1936).

was determined by the silver molybdate method of McCay[5] and the lead molybdate method described by Weiser.[6] The ceric sulfate solution was standardized against Bureau of Standards sodium oxalate by the method of Walden, Hammett and Chapman.[7]

Reduction of Molybdate

The reduction of molybdate in acid solution has been investigated by Foerster, Fricke and Hausswald.[8] They found that the reaction may be represented by the equation

$$\mathrm{MoO_2^{++}} + 2\mathrm{H^+} + e \rightleftarrows \mathrm{MoO^{+++}} + \mathrm{H_2O}$$

and measured the molal oxidation potential in 2, 4 and 8 *M* hydrochloric acid. By extrapolation of their data the potential in 1 *M* hydrochloric acid is found to be 0.530 v. referred to the normal hydrogen electrode. The oxidation potential of the silver reductor in 1 *M* hydrochloric acid is 0.213 v.,[9] amply below that necessary for quantitative reduction of molybdenum to the quinquivalent state. We have found, however, that in the cold and in 1 *M* hydrochloric acid the reduction is incomplete, but at 60–80° and in 2 *M* hydrochloric acid it is complete and rapid. In 4 and 6 *M* hydrochloric acid reduction is rapid even at room temperature and the titers are higher than corresponds to reduction to the quinquivalent state and vary erratically. The data of Foerster, Fricke and Hausswald[8] show that in this environment partial reduction to the trivalent state is possible.

Solutions reduced at 60–80° in 2 *M* hydrochloric acid may be fairly satisfactorily titrated in the cold with ceric sulfate using the *o*-phenanthroline ferrous ion indicator although the reaction is somewhat sluggish. We have found that the presence of phosphoric acid in no way interferes with the completeness and rapidity of reduction and considerably improves the end-point by increasing the velocity of the oxidation reaction.

We have made potentiometric titrations of quinquivalent molybdenum solutions with and without addition of phosphoric acid. In spite of the well-known formation of phosphomolybdates we have found no significant difference between the two titration curves, nor do they show the small secondary break reported by Furman and Schoonover[10] and Furman and Murray[4] and which is attributed by them to the presence of iron in the ceric sulfate reagent. Tests on the ceric sulfate we used showed iron to be absent.

Procedure

Fifty cc. of solution containing the molybdate was made 2 *M* with respect to hydrochloric acid, 3 cc. of phosphoric acid of sp. gr. 1.689 added and the solution heated to 60–80°. It was then passed through the silver reductor, which had been preheated with hot 2 *M* hydrochloric acid, at the rate of about 10 cc. per minute. The reduced solution was caught in a 400-cc. beaker and the reductor column washed with 150 cc. of 2 *M* hydrochloric acid. The first few washings were made with hot acid and the rate of passage through the reductor of the last 100 cc. of wash liquid was increased. The solution was cooled, one drop of 0.025 *M* *o*-phenanthroline ferrous complex indicator solution was added and the solution titrated with 0.1 *M* ceric sulfate.

In the titration of the quinquivalent molybdenum solutions the last 0.3–0.4 cc. should be added dropwise with vigorous stirring. As the ceric sulfate is added a precipitate of ceric phosphate forms which dissolves on stirring. At the end-point a fraction of a drop of the oxidant bleaches the indicator sharply.

Determinations of molybdate were made at varying speeds of flow through the reductor and it was found that a flow of 5 to 15 cc. per minute gave consistent results; at 25 cc. per minute and above the results were low.

Blank determinations on all materials used were made. Corrections varying between 0.02 and 0.10 cc. of the ceric sulfate were required. We found that these blanks were caused by iron mainly in the hydrochloric and phosphoric acids used.

Effect of Small Amounts of Nitrate.—Although the presence of moderate quantities of nitrate does not interfere with the reduction of iron or vanadium in the silver reductor[3] even as little as 0.2 mg. of nitrate causes low results with molybdenum and adversely affects the sharpness of the end-point. With larger amounts of nitrate, oxides of nitrogen are formed in the reductor and the results for molybdenum are low by several per cent. This effect is probably due to the catalytic effect of molybdate on the reduction of nitrate.[11]

Experimental Results

Comparative results obtained by the silver reductor method and the two precipitation methods previously referred to are given in Table I. In each case mean values of two or more determinations are given; the precision in each case is within a part per thousand.

TABLE I

COMPARISON OF MOLARITY OF AMMONIUM MOLYBDATE SOLUTIONS AS FOUND BY DIFFERENT METHODS

Method	Solution 1	Solution 2	Solution 3	Solution 4
Silver reductor	0.05259	0.1045	0.0934	0.0982
Lead molybdate	.05254	.1042	.0931	
Silver molybdate			.0934	.0982

As a further check on the method, four samples of Merck ammonium heptamolybdate ranging between 0.4004 and 0.7024 g. were analyzed by the silver reductor method and gave an average value of 54.40% molybdenum, with an average deviation of 0.02% and an extreme deviation of 0.04%. Calculation of the molybdenum content gives 54.46%; found by the ignition method, 54.44%.

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(5) McCay, THIS JOURNAL, **56**, 2548 (1934).

(6) Weiser, *J. Phys. Chem.*, **20**, 640 (1916).

(7) Walden, Hammett and Chapman, THIS JOURNAL, **55**, 2649 (1933).

(8) Foerster, Fricke and Hausswald, *Z. physik. Chem.*, **146**, 81 (1930).

(9) Scatchard, THIS JOURNAL, **47**, 641 (1925).

(10) Furman and Schoonover, *ibid.*, **53**, 2561 (1931).

(11) Kolthoff, Sandell and Moskovitz, *ibid.*, **55**, 1454 (1933).

Precipitation of Molybdenum with Silver Nitrate, Barium Chloride and Hexammine Cobaltic Chloride

It is evident from a consideration of the oxidation potentials involved that iron will interfere in the above method for the determination of molybdenum. Application to the determination of molybdenum in the presence of large amounts of iron is practicable only if a method can be found to separate molybdenum from iron in a form readily dissolved in hydrochloric acid. We have therefore studied the separation of molybdate from iron by precipitation in the presence of acetic acid–acetate buffers with silver nitrate[5] and hexammine cobaltic chloride.[12] It was found, however, that neither reagent gave a precipitate free from iron at a *p*H high enough to allow complete precipitation of the molybdate. We have also studied the precipitation of barium molybdate from alkaline tartrate and citrate solutions. Although quantitative precipitation is obtained in the absence of citrates and tartrates, the presence of sufficient amounts of these substances to prevent precipitation of iron also prevents the quantitative precipitation of molybdate. Moderate amounts of iron may, of course, be separated from molybdate by double precipitation with ammonia.

Summary

1. In 2 *M* hydrochloric acid solution and at a temperature of 60–80°, molybdenum is reduced quantitatively by the silver reductor to the quinquivalent state.
2. The reduced solution may be titrated with ceric sulfate using the *o*-phenanthroline ferrous complex indicator.
3. It is shown that these reactions lead to a precise and rapid method for the determination of molybdenum in the absence of other reducible substances.

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[12] Parks, Dissertation, Columbia University, 1930.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Coprecipitation of Ammonium Silicomolybdate and Ammonium Phosphomolybdate. An Improved Volumetric Method for the Determination of Phosphorus[1]

BY NATHAN BIRNBAUM AND GEORGE H. WALDEN, JR.

The development of rapid and precise methods[2] for the determination of molybdenum has led us to investigate the determination of phosphorus by analysis of the ammonium phosphomolybdate precipitate. There are several methods based upon the composition of the yellow precipitate which depend upon empirical mole ratios of molybdenum to phosphorus.[3] This ratio has received much attention and values ranging widely from the theoretical 12.00:1 have been reported.[4] We have found that an important factor affecting the composition of the precipitate is the presence of small amounts of silica. The interference of silicates has been reported previously,[5] but the extent of the interference is not generally recognized. As little as 0.25 mg. of silica in the presence of 6 mg. of phosphorus causes a measurable excess of molybdenum to be retained by the ammonium phosphomolybdate precipitate. Alkaline solutions of ammonium molybdate become significantly contaminated with silicate in about four weeks when stored at room temperature in Pyrex bottles. We have not investigated the solubility of glass in acid molybdate solutions but the yellow color which they rapidly develop suggests that they also attack the glass.

Reagent grade ammonium molybdate free from detectable traces of silicate is obtainable. By precipitating with freshly prepared solutions of this reagent precipitates containing the correct mole ratio of molybdenum to phosphorus can be obtained consistently. Alkaline ammonium

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[1] From a dissertation submitted by Nathan Birnbaum in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] (a) Furman and Murray, THIS JOURNAL, **58**, 1689 (1936); (b) Birnbaum and Walden, *ibid.*, **60**, 64 (1938).

[3] (a) Lundell and Hoffman, *Ind. Eng. Chem.*, **25**, 44 (1933); (b) Baxter, *Am. Chem. J.*, **28**, 298 (1902); (c) Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," John Wiley and Sons, Inc., New York, 1931, p. 224.

[4] For bibliographies on this subject see: (a) Hibbard, *Ind. Eng. Chem.*, **5**, 998 (1913); (b) Johann, Dissertation, Columbia University, 1921.

[5] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 562.