used; if rape, colza or sperm oils are present, of course, it will be necessary to separate the total free fatty acids, and from this calculate the amount of saponifiable fats present.

FRANKLIN, PA.,
February 1, 1904.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 96.]

THE DETERMINATION OF MOLYBDENUM IN STEEL AND IN STEEL-MAKING ALLOYS.[1]

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INTRODUCTION.

As THERE is difficulty in obtaining an accurate and rapid estimation of molybdenum in steel and in steel-making alloys, the following work was undertaken in order to compare the best methods now in use. It was also the object of the investigators to point out the reasons for the discrepancies in the several methods, and, if possible, to devise a rapid and accurate method which will not be affected by the impurities in molybdenum steel, or by the other metals which are sometimes added, or may in future be added. The impurities are silicon, phosphorus, sulphur, manganese and copper; metals added are molybdenum, tungsten, chromium, and those which may in future be added are uranium and vanadium.

PART I.

In making a determination of molybdenum in steel and in steel-making alloys the main difficulty is the separation of molybdenum from iron.

There are two general methods for this separation. The first, and most commonly used, is to separate the iron from the molybdenum as ferric hydroxide, and the second is to separate the molybdenum from the iron as sulphide of molybdenum.

After the separation of the iron the molybdenum may be determined by three different methods. First, by reduction and titration with potassium permanganate; second, precipitation of

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[1] Read at the meeting of the New York Section of the American Chemical Society, January 8, 1904.

the molybdenum as lead molybdate; third, by weighing molybdenum as molybdenum disulphide. There are several oth means of estimating molybdenum, but they do not seem to merit extensive consideration; therefore, in comparing the different methods now used for analyzing steel for the molybdenum content the separation of molybdenum and iron will first be considered, and then the estimation of the molybdenum.

In order to test the efficiency of these two separations it was thought advisable to conduct a large number of experiments on solutions of pure salts, made up with varying proportions of iron and molybdenum. In beginning the work, two burettes were standardized against a standard 2-cc pipette; 7 liters of potassium permanganate solution were made up approximately N/10, filtered and standardized against pure iron ammonium sulphate, and against pure oxalic acid, the results agreeing. About 1 gram of iron ammonium sulphate was used for the titration, and 0.3 gram of oxalic acid, the titrations being made in duplicate. A solution of ferric chloride was made up, containing approximately 50 mg. of iron per cubic centimeter. This solution was standardized against the standard potassium permanganate solution. Four liters of a solution of ammonium molybdate were then made up, containing approximately 5 mg. of molybdenum per cubic centimeter and the strength of the solution determined.

As the accuracy of all the subsequent results depended upon the accuracy of the molybdenum content in this solution, it was necessary to standardize by different methods, and to have them check.

Conditions for Precipitating Molybdenum as Lead Molybdate.[1]—A number of determinations of the molybdenum were made, precipitating the molybdenum as lead molybdate under the following conditions:

To 30 cc. of the molybdate solution (containing about 150 mg. of molybdenum) a few drops of ammonia were added, and then 2 to 3 cc. of acetic acid (33 per cent.) in excess. The solution was diluted to a volume of from 200 to 250 cc. and 4 to 5 grams of ammonium chloride added; the solution was heated to boiling, and while boiling 45 to 50 cc. of a lead acetate solution (40 grams of crystallized lead acetate per liter) were added, then boiled for from two to four minutes, with vigorous stirring. The pre-

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[1] Ibbotson and Brearley: "Analysis of Steel Works Materials," p. 278.

cipitate was allowed to settle, filtered through asbestos in a Gooch crucible, using suction, and washed by decantation with boiling water containing about 5 grams of ammonium chloride in 200 cc. and a few drops of acetic acid, until free from lead, the wash-water being tested with hydrogen sulphide. In washing by decantation, the washing solution was kept as hot as possible, and the solution stirred thoroughly before allowing the precipitate to settle. When free from lead, the precipitate was washed once or twice with boiling water. The Gooch crucible was heated on an asbestos plate until dry, then with the free flame, allowed to cool in a desiccator, and weighed.

RESULTS.

Molybdate solution taken. cc.	Weight of lead molybdate found. Gram.	Weight of molybdenum found. Gram.	Molybdenum per cubic centimeter. Gram.
30	0.5644	0.14765	0.004915
30	0.5655	0.14793	0.004931
35	0.6614	0.17302	0.004943
35	0.6579	0.17211	0.004917
40	0.7514	0.19657	0.004914

Not more than 3 cc. of acetic acid should be added, as a large excess of acetic acid has a solvent effect upon the lead molybdate. Under these conditions the precipitate was granular, settled quickly, and filtered easily.

In order to check the results obtained by this method several others were employed·

First, precipitation of the molybdenum in an acid solution by hydrogen sulphide, at a temperature of 80° C. After an hour the solution was filtered and the filtrate re-treated as before. This was repeated four or five times, and a little more sulphide was obtained each time. The precipitation under these conditions is incomplete unless repeated several times, as stated by Rose,[1] although used by Döhler[2] in his method for analyzing steel. The molybdenum was then precipitated as molybdenum trisulphide in a sulphuric acid solution with hydrogen sulphide under pressure. The precipitation was complete, as stated by Treadwell,[3] and was carried out as follows: 200 cc. of water at the room temperature, containing 10 cc. of concentrated sulphuric acid, were saturated

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[1] "Traité Complet de Chimie Analytique Analyse Quantitative," 1862, p. 490.

[2] *Chem. News*, **82**, 294. 1900.

[3] "Kurzes Lehrbuch der Analytischen Chemie." Vol. II, p. 183.

with hydrogen sulphide, and added to the molybdate solution in a pressure bottle. The pressure bottles used were the ordinary citrate of magnesia bottles, of about 350 cc. capacity. After adding the solution, hydrogen sulphide was passed through until the precipitate collected; the bottles were then closed, placed in a water-bath and heated at 100° C. for from one to two hours; after cooling, the sulphide was filtered on a Gooch crucible, and washed by decantation with water containing sulphuric acid (1 : 50) saturated with hydrogen sulphide. The sulphide was then converted into oxide, as described by Treadwell.[1] The results were low, 0.004733 to 0.004776 gram molybdenum per cubic centimeter. Converting the molybdenum trisulphide to molybdenum disulphide, as used by Blair,[2] was attempted, with no uniform results. Evaporating the molybdate solution with dilute nitric acid in a platinum dish was then tried, adding more nitric acid, and evaporating to dryness several times, to obtain molybdenum trioxide. This gave high results, 0.005064 to 0.005095 gram per cubic centimeter.

As these high results might be due to small traces of alkali in the ammonium molybdate, or other impurities, it was thought that the best method to separate them would be to use the electrolytic method, as given by Kollock and Smith.[3] Accordingly, different amounts of the molybdate solution were electrolyzed according to their conditions of precipitation, using a platinum dish as a cathode. After the deposition was complete (on testing the solution by adding hydrochloric acid, tin and potassium thiocyanate, no red color was obtained) the sesquioxide was dissolved in nitric acid, evaporated to dryness and heated to constant weight. The results checked those of the lead molybdate precipitation, *i. e.*, 0.004908 gram per cubic centimeter.

Having determined the strength of the molybdate solution, the potassium permanganate solution was standardized against it, under the following conditions: Volume, 200 cc.; acidity, 6 cc. of concentrated sulphuric acid; temperature, 21° C. A reductor 45 cm. long and 1.5 cm. in diameter was used, filled with granulated zinc. The solution was poured into the reductor, and then suction applied. The solution was run through the reductor twice,

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[1] "Kurzes Lehrbuch der Analytischen Chemie," Vol. II. p. 184.

[2] "Chemical Analysis of Iron." 4th edition, pp. 199-200.

[3] This Journal, **23**, 669 (1901).

followed by 200 cc. of water, not allowing air to be sucked through during the pouring, and titrated immediately with potassium permanganate. A "blank" consisting of 200 cc. of water and 6 cc. concentrated sulphuric acid was run and the permanganate required was subtracted.

Separation of Molybdenum from Iron by Precipitation as Molybdenum Trisulphide by Hydrogen Sulphide under Pressure and Titration with Potassium Permanganate.—Different proportions of molybdenum and iron were taken and treated in the following manner: The molybdate and iron solutions were run into a pressure bottle (as previously described) and a drop or two of dilute sulphuric acid added to prevent the formation of a precipitate of ferric molybdate. Two hundred cc. of sulphuric acid (1 : 20) were then saturated with hydrogen sulphide and added to the pressure bottle, at the room temperature. Then a very rapid stream of hydrogen sulphide was passed through the solution in the bottle, which prevented the sulphide from adhering to the glass tube. The bottle was closed and placed in a boiling water-bath and heated for from one to two hours, then allowed to cool, emptied into a beaker, the bottle washed out with water, and the precipitate allowed to settle. The solution was filtered through a Gooch crucible by decantation, using suction, and washed with about 300 cc. of dilute sulphuric acid (1 : 50) saturated with hydrogen sulphide. The precipitate was transferred to the Gooch crucible, and washed two or three times with water. The precipitate and filter were transferred to a casserole, 10 cc. concentrated sulphuric acid, 10 cc. concentrated hydrochloric acid and 5 cc. concentrated nitric acid were added, and the contents evaporated to fumes of sulphur trioxide. Dissolving the precipitate directly through the filter by different acids was tried, but without success. In evaporating to fumes of sulphur trioxide, great trouble was experienced at first by the bumping of the solution. This was finally overcome by blowing air through the solution during the evaporation. After evaporation, the solution was allowed to cool, diluted with water, and washed into a beaker. A slight excess of ammonia was added, and the solution filtered to remove the asbestos and a small quantity of ferric hydroxide. The precipitate was washed with hot water until the filtrate had a volume of 200 cc., neutralized with sulphuric acid, 6 cc. concentrated sulphuric acid added and allowed to cool.

When at room temperature, the solution was reduced and titrated under exactly the same conditions as used in standardizing. The results obtained are given below:

Iron taken. Gram.	Molybdenum taken. Gram.	Molybdenum found. Gram.
0.10760	0.00197	0.00189
0.10760	0.00197	0.00220
0.10760	0.00492	0.00487
0.10760	0.00984	0.01163
0.10760	0.02460	0.02374
0.10760	0.04921	0.04953
0.05380	0.04921	0.04937
0.02690	0.04921	0.05095
0.00538	0.04921	0.04875
0.00215	0.04921	0.04969

In each case it was observed that there was iron present after dissolving the molybdenum trisulphide in the mixture of acids and adding ammonium hydroxide. Therefore, it was thought advisable to determine whether the iron was carried down with the molybdenum sulphide, either mechanically or chemically, or whether it came from some outside source.

Two solutions containing 0.1076 gram iron and 0.04921 gram molybdenum were precipitated with hydrogen sulphide under pressure, and treated as already described. Having dissolved the molybdenum trisulphide, ammonia was added to the solution in excess, and the solution filtered. The precipitate remaining on the filter had the characteristics of ferric hydroxide and, when dissolved in hydrochloric acid, gave a deep red color with potassium thiocyanate. A blank consisting of asbestos, water and the same amounts of acids was run under the same conditions, and gave only a trace of iron. This showed that the iron present came from the precipitation with hydrogen sulphide under pressure, and proved that it is necessary to remove it by adding ammonium hydroxide. In order to determine whether it was possible to obtain any precipitation of iron by hydrogen sulphide under pressure, two similar solutions were precipitated under the same conditions, except that no molybdenum was added, and no iron was found. In order to determine the amounts of iron present, several tests were made upon varying proportions of molybdenum and iron. The operation was conducted according to previous conditions, and the iron weighed as ferric oxide in a platinum crucible.

Molybdenum taken. Gram.	Iron taken. Gram.	Ferric oxide obtained. Gram.	Iron obtained. Gram.
0.00492	0.10760	0.00010	0.00007
0.00984	0.10760	0.00020	0.00014
0.02460	0.10760	0.00030	0.00021
0.04921	0.10760	0.00050	0.00035

Each ignited precipitate was red, and when dissolved in hydrochloric acid gave a deep red color with potassium thiocyanate. These results indicate that the contamination is mechanical.

Separation of Iron from Molybdenum by Precipitating the Iron as Ferric Hydroxide by Sodium Hydroxide and Titrating the Molybdenum with Potassium Permanganate.—As there seemed to be some difference of opinion[1] in regard to the use of sodium hydroxide or ammonium hydroxide in precipitating iron from a molybdate solution, it was thought advisable to determine which precipitant gives the best results.

Varying proportions of molybdenum and iron were taken and precipitated by adding 70 cc. of sodium hydroxide solution (1 : 10) to the mixture of molybdenum and iron in a bulk of 50 to 60 cc., acid with 2 cc. sulphuric acid. The solution was stirred, the precipitate allowed to settle, and then filtered and washed with hot water until the filtrate had a volume of 200 cc. The precipitates of ferric hydroxide were dissolved in dilute sulphuric acid, and reprecipitated and washed as before. The filtrates obtained were neutralized with sulphuric acid, then 6 cc. concentrated sulphuric acid added to each, allowed to cool, reduced and titrated, as usual.

Iron taken. Gram.	Potassium permanganate required for first filtrate. cc.	Potassium permanganate required for second filtrate. cc.	Molybdenum found. Gram.	Molybdenum taken. Gram.
0.00215	16.15	0.05	0.05041	0.04921
0.00538	16.2	0.00	0.05041	0.04921
0.02690	16.2	0.05	0.05057	0.04921
0.05380	16.2	0.05	0.05057	0.04921
0.10760	16.1	2.00	0.05072	0.04921
0.10760	7.9	0.00	0.02458	0.02460
0.10760	3.3	0.00	0.01027	0.00984
0.10760	1.7	0.00	0.00529	0.00492
0.10760	0.75	0.00	0.00233	0.00197

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[1] F. T. Kopp: This Journal, **24**, 186 (1902); J. Brakes: *J. Soc. Chem. Ind.*, **21**, 832 (1902); G. Auchy: This Journal, **24**, 273 (1902); G. Auchy: This Journal, **25**, 215 (1903).

All but one of the results are slightly high. In order to determine whether this might be overcome by increasing the strength of the sodium hydroxide solution used for precipitation, 0.04921 gram of molybdenum and 0.1076 gram of iron were precipitated in 50 cc. bulk with 70 cc. of sodium hydroxide solution (1 : 5). The amount of molybdenum found in the two filtrates was 0.05088 gram. Then 0.04921 gram molybdenum and 0.1076 gram iron were taken and precipitated as before, using 105 to 110 cc. sodium hydroxide solution (1 : 5). The amount of molybdenum found was 0.05057 gram. This showed that the discrepancy cannot be eliminated by the addition of more of the precipitant. In order to find out whether these high results were due to impurities in the iron solution used, 0.1076 gram of iron was taken and 2 cc. sulphuric acid added as before and precipitated in 50 cc. bulk with an excess of sodium hydroxide, and treated as before. The number of cubic centimeters of potassium permanganate required was the same as for the blank.

Separation of Iron from Molybdenum by Ammonium Hydroxide, without Boiling out the Excess of Ammonium Hydroxide, and Titration with Potassium Permanganate.—This series of experiments was carried out under the same conditions as when precipitating with sodium hydroxide, 30 cc. ammonium hydroxide (sp. gr. 0.9) being added in excess.

Iron taken. Gram.	Potassium permanganate required for first filtrate. cc.	Potassium permanganate required for second filtrate. cc.	Molybdenum found. Gram.	Molybdenum taken. Gram.
0.00215	16.5	0.00	0.05134	0.04921
0.00538	16.65	0.00	0.05184	0.04921
0.02690	16.75	0.00	0.05212	0.04921
0.05380	15.9	0.5	0.05103	0.04921
0.10760	16.3	0.4	0.05197	0.04921

These results show conclusively that sodium hydroxide gives a more accurate separation of iron from molybdenum than ammonium hydroxide.

In order to determine whether the excess of ammonium hydroxide caused this increased discrepancy, ammonia was added as before and then boiled out completely with the following results, the other conditions being maintained as given:

Iron taken. Gram.	Potassium permanganate required by first filtrate. cc.	Potassium permanganate required by second filtrate. cc.	Molybdenum found. Gram.	Molybdenum taken. Gram.
0.00215	16.1	0.05	0.05010	0.04921
0.00538	15.2	0.35	0.04839	0.04921
0.02690	15.15	0.5	0.04870	0.04921
0.05380	13.15	1.35	0.04512	0.04921
0.10760	11.20	0.8	0.03734	0.04921
0.10760	1.80	2.25	0.01260	0.02460
0.10760	0.35	0.2	0.00171	0.00984
0.10760	0.3	0.00	0.00093	0.00492
0.10760	0.05	0.00	0.00015	0.00197

These results show that boiling the ammonia out of the solution renders the results worthless. As the molybdenum solution, when treated alone, gave no precipitate, the error is due to the formation of an iron molybdate which is precipitated in a neutral solution.

This fact led to the belief that the high results obtained in the sodium hydroxide and ammonium hydroxide separations were due to the formation of a ferric molybdate, which was slightly soluble in excess of sodium or ammonium hydroxide, and thus caused high results by the iron being reduced and titrated together with the molybdenum.

Ibbotson and Brearley state[1] that when an alkali is added to an acidified mixture of ferric chloride and molybdic acid, a point is reached at which an insoluble basic ferric molybdate is formed and no perfect separation of the two metals is possible until sufficient alkali has been added to decompose this compound. Also that similar bodies are formed during the separation of chromic, tungstic, or vanadic acid from iron.

It was then undertaken to find iron in the filtrate after separation of the iron by the ammonium hydroxide. Two portions containing 0.04921 gram of molybdenum and 0.1076 gram of iron each were taken, and precipitated by ammonia, as described. The solutions were filtered, washed with water, and the filtrates (200 cc.) were neutralized with sulphuric acid, and 10 cc. of concentrated sulphuric acid added in excess. Then the molybdenum was precipitated from this solution by hydrogen sulphide under pressure. The solutions were allowed to cool, and filtered. The filtrates were evaporated to small bulk, ammonia added, and

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[1] "Analysis of Steel-works Materials," p. 81.

the solution filtered. The precipitates were washed and dissolved in hydrochloric acid. The filtrate from one was divided into two equal portions: To one-half, potassium thiocyanate was added, and a red color obtained; the other half was reprecipitated with ammonia, and redissolved in hydrochloric acid, potassium thiocyanate added, and a red color obtained. The filtrate from the other was precipitated twice with ammonia, and finally dissolved in hydrochloric acid, potassium thiocyanate added, and a deep red color obtained. The precipitate of ferric hydroxide was plainly visible. A blank consisting of 200 cc. of water and 10 cc. of sulphuric acid was run under the same conditions, and only a trace of color was obtained and no precipitate of ferric hydroxide could be seen. The precipitates of molybdenum trisulphide were dissolved in nitric, hydrochloric and sulphuric acids, and evaporated to fumes of sulphur trioxide. The solution was allowed to cool, diluted a little, ammonia added and filtered. The precipitates were dissolved in hydrochloric acid, and potassium thiocyanate added, and red colors were obtained. The experiment was repeated, using 0.24605 gram of molybdenum and 0.538 gram of iron. In precipitating with hydrogen sulphide, the hydrogen sulphide gas was passed through two plugs of asbestos, and through two wash-bottles, in order to prevent any iron from being carried over from the generating flask. The iron was precipitated twice with ammonia, ignited and weighed as ferric oxide. The weight of ferric oxide found was 0.0005 gram. This was dissolved in hydrochloric acid, potassium thiocyanate added, and a deep red color obtained.

These experiments show that the high results obtained are due to the formation of a ferric molybdate in small amount, which is soluble in the excess of the precipitant.

The reason that we can find the iron by the foregoing method is probably because the relative concentration of molybdenum and iron is changed, and therefore not as much ferric molybdate is formed as in the initial precipitation, thus allowing some of the iron to be precipitated by ammonium hydroxide.

Separation of Iron from Molybdenum by Sodium Hydroxide, and Precipitation of the Molybdenum as Lead Molybdate.[1]—

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[1] Brearley: *Chem. News*, **78**, 203-5 (1898); Abs. *J. Chem. Soc.*, **76**, 129 (1899); Chatard: *Chem. News*, **24**, 175; Brearley: *Chem News*, **79**, 2-4, 14-15 (1899); Abs. *J. Chem. Soc.*, **76**, 336 (1899); Ibbotson and Brearley: *Chem. News*, **79**, 3; Ibbotson and Brearley: *Chem. News*, **81**, 269.

In order to test the accuracy of the lead molybdate precipitation compared with the titration by potassium permanganate, a series of experiments were undertaken, using the same concentrations of molybdenum and iron as before. The details are as follows: Two cc. of hydrochloric acid (sulphuric acid could not be used on account of the subsequent precipitation by lead acetate) were added to each solution, and they were then diluted to from 50 to 60 cc., 70 cc. of sodium hydroxide (1 : 10) were added, and the solution filtered and washed until the filtrate was about 150 cc. in volume. The precipitate of ferric hydroxide was redissolved by hydrochloric acid and reprecipitated as above. The filtrates were combined and boiled down to 200 cc. An excess of ammonium hydroxide was added, then 2 to 3 cc. excess of acetic acid (33 per cent.) and 5 to 6 grams of ammonium chloride. The solution was heated to boiling, 20 to 50 cc. lead acetate solution (40 grams per liter of lead acetate) added, depending on the amount of molybdenum present, and the solution stirred vigorously for from two to four minutes, and then treated as under the conditions already given for standardizing the molybdate solution.

In measuring the *small* amounts of molybdenum for the test, 5 cc. of the standard molybdate solution were diluted to 100 cc. and the proportional amount used.

Iron taken. Gram.	Molybdenum taken. Gram.	Lead molybdate found. Gram.	Molybdenum found. Gram.
0.00215	0.04921	0.1920	0.05022
0.00538	0.04921	0.1915	0.05010
0.02690	0.04921	0.1932	0.05054
0.05380	0.04921	0.1927	0.05040
0.10760	0.04921	0.1909	0.04994
0.10760	0.02460	0.0958	0.02506
0.10760	0.00964	0.0403	0.01054
0.10760	0.00492	0.0204	0.00534
0.10760	0.00197	0.0084	0.00220

From these results we see that the estimation of molybdenum, after the separation of the iron as ferric hydroxide, by titration and by precipitation with lead acetate is about equally accurate. The molybdate precipitation has a slight advantage in accuracy, but as it takes very much longer, the titration method is to be preferred. Two of the precipitates of lead molybdate were dissolved in concentrated hydrochloric acid, diluted with an equal volume of water, and extracted with 50 cc. of ether, the ether solution drawn off, diluted with water, the ether evaporated off, hydrochloric acid and then ammonium hydroxide added. The solution was filtered, and the precipitate was dissolved in hydrochloric acid, and the presence of iron shown by potassium thiocyanate. This experiment was made in order to corroborate the theory that ferric molybdate is formed, and is slightly soluble in excess of alkali.

EFFECT OF CERTAIN METALS ON THE VARIOUS METHODS.

In order to test the different methods when the metals commonly added are present, and also those which in future may be added, experiments were made with mixtures of the molybdenum and iron solutions, adding vanadium, tungsten, uranium and chromium.

Separation of Iron by Sodium Hydroxide and Titration of the Molybdenum by Potassium Permanganate.—In making the following experiments, the operation was conducted under exactly the same conditions as used for the estimation of molybdenum, separating the iron by sodium hydroxide and titrating the reduced molybdenum by potassium permanganate, with the exception that the iron was not reprecipitated. The relative amounts of iron and molybdenum taken were those corresponding to the usual molybdenum steel. This relation was kept constant, and the amount of other metals varied.

Iron taken. Gram.	Molybdenum taken. Gram.	Molybdenum found. Gram.	Gram.	
0.1076	0.00492	0.00856	0.00169	Amount of vanadium added.
0.1076	0.00492	0.01867	0.00843	
0.1076	0.00492	0.00716	0.00242	Amount of tungsten added.
0.1076	0.00492	0.01074	0.01210	
0.1076	0.00492	0.00545	0.00190	Amount of uranium added.
0.1076	0.00492	0.00749	0.00951	
0.1076	0.00492	0.00560	0.00210	Amount of chromium added.
0.1076	0.00492	0.00560	0.01048	

The vanadium added was pure V_2O_5 (containing 56.22 per cent. of vanadium). The uranium salt was uranium nitrate, C. P., Kahlbaum (containing 47.57 per cent. uranium). The tungsten was added in the form of sodium tungstate. The amount of tungsten in the salt was determined by converting the sodium tungstate into tungsten trioxide, and weighing the ignited tungstic oxide in a porcelain Gooch crucible. The amount of tungsten present in the salt was found to be 60.49 per cent. The chromium was added as sulphate, obtained from pure chromic acid.

From the results obtained we see that vanadium, tungsten and uranium all interfere with the method, chromium giving slightly higher results than those obtained where iron only is present.

The vanadium goes partly into solution, some being precipitated as a ferric vanadate with the iron, as shown by Pope,[1] and thus gives high results, being reduced with the molybdenum, and oxidized by the potassium permanganate during the titration of the molybdenum.

The uranium probably forms a uranyl molybdate, which is soluble in excess of alkali, and this is reduced to UO_2 and oxidized again to UO_3, and gives high results. The filtrates from the ferric hydroxide, after adding sodium hydroxide, were yellow in color.

Tungstates and tungstic acid are soluble in alkali, and, of course, are present with the molybdenum in the filtrate.

Separation of Molybdenum from Iron as Molybdenum Trisulphide by Hydrogen Sulphide under Pressure, and Titration with Potassium Permanganate.—In order to determine the effect of these metals upon the precipitation method by hydrogen sulphide under pressure, a series of experiments, similar to the last, were conducted. The experiments were pursued under the same conditions as for the determination of molybdenum in the absence of these metals, and the results obtained showed that neither vanadium, tungsten, uranium, or chromium interfered, even when the quantities were increased. In the case of tungsten 3 to 4 grams of tartaric acid were added in order to keep the tungsten in solution, as in the method for the separation of tungsten from molybdenum by H. Rose.[2]

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[1] Pope: "Investigations of Magnetic Iron Ores from Eastern Ontario," *Trans. A. I. M. E.*, **29**, 372 (Oct., 1899).

[2] Treadwell: "Kurzes Lehrbuch der Analytischen Chemie." Vol. II, p. 187, 1902.

Iron taken. Gram.	Molybdenum taken. Gram.	Molybdenum found. Gram.		
0.1076	0.00492	0.00529	0.00169	Amount of vanadium added.
0.1076	0.00492	0.00498	0.00169	
0.1076	0.00492	0.00498	0.00843	
0.1076	0.00492	0.00529	0.00843	
0.1076	0.00492	0.00498	0.01687	
0.1076	0.00492	0.00482	0.00190	Amount of uranium added.
0.1076	0.00492	0.00529	0.00190	
0.1076	0.00492	0.00513	0.00951	
0.1076	0.00402	0.00544	0.01902	
0.1076	0.00492	0.00560	0.00242	Amount of tungsten added.
0.1076	0.00492	0.00498	0.00242	
0.1076	0.00492	0.00529	0.01210	
0.1076	0.00492	0.00513	0.01210	
0.1076	0.00492	0.00498	0.00210	Amount of chromium added.
0.1076	0.00492	0.00482	0.01048	

PART II.

A new method for the determination of molybdenum in steel and steel-making alloys was then devised, founded upon the foregoing results, and then tested by the analysis of a set of samples of molybdenum steels and alloys, and compared with a typical sodium hydroxide separation method, followed by titration with potassium permanganate, and the precipitation method as lead molybdate.

After considerable experimenting the following method was used for analysis:

For Molybdenum Steel.—Dissolve about 1 gram of drillings in 80 cc. of "silicon mixture" (500 cc. concentrated nitric acid, 50 cc. concentrated sulphuric acid and 1500 cc. of water[1]) in a porcelain casserole, adding a little at first, as the action is violent. Evaporate to fumes of sulphur trioxide. Allow to cool, and add 50 cc. of hot water and heat to boiling in order to get the salts into solution. Pour the solution into a pressure bottle, and add 6 cc. concentrated sulphuric acid. Dilute until the bulk of the solution is about 200 cc. and pass a very rapid stream of hydrogen sulphide through the solution until the precipitate collects. Then close the bottle and heat in a water-bath at 100° C. for from one to two hours. Allow to cool, empty the contents into a beaker and wash out the bottle. Filter on a Gooch crucible, using suc-

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[1] Phillips' "Methods of Iron Analysis," p. 116.

tion, and wash with dilute sulphuric acid (1 : 50) saturated with hydrogen sulphide. Remove the precipitate and asbestos with a glass rod, and place in a small casserole, washing out the Gooch crucible with water. Add 10 cc. concentrated hydrochloric acid, 5 cc. concentrated nitric acid and 10 cc. concentrated sulphuric acid, and evaporate to very copious fumes of sulphur trioxide, blowing air through the solution. Allow to cool, add 50 cc. of water, then ammonia in excess, and filter out the asbestos and a little ferric hydroxide. Wash thoroughly with hot water. The filtrate is then acidified, run through a reductor, and titrated with potassium permanganate, using the same conditions as for standardizing the permanganate solution.

For Ferromolybdenum.—Dissolve 4 to 5 grams of ferromolybdenum in 180 to 200 cc. "silicon mixture," pour the solution into a standard liter flask, and dilute to the mark when cold. Take out portions of 50 cc. or 100 cc. and evaporate to fumes of sulphur trioxide, and proceed as in the case of molybdenum steel.

For Molybdenum Metal.—Dissolve 2 to 3 grams of metal in "silicon mixture," add concentrated hydrochloric acid and heat for some time. Dilute with water, and filter into a liter flask. Burn the filter, moistened with nitric acid in a platinum crucible, using as low a heat as possible and fuse the residue with potassium pyrosulphate. Dissolve the melt in hot water, and add it to the solution in the flask. Allow to cool and dilute to the mark. Take out portions of 50 cc. and proceed as in the case of molybdenum steel.

Tungsten, if present, separates out partially as tungstic oxide when the solution is evaporated to fumes of sulphur trioxide. This may be tested for by dissolving it in ammonia, making strongly acid with hydrochloric acid, adding a saturated hydrochloric acid solution of stannous chloride, and then ammonium or potassium thiocyanate. A deep green color shows tungsten. Molybdenum, under similar conditions, gives a deep red color.

It is very important to note that tungsten trioxide is quite soluble in acids, although otherwise stated by most authorities.[1]

When tungsten is present, after dissolving the steel in the "silicon mixture," and evaporating to fumes of sulphuric trioxide, allow to cool, add 50 cc. hot water, 5 grams of tartaric acid, and

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[1] Comey's "Dictionary of Solubilities," p. 438 ; Storer's "Dictionary of Solubilities"; Watts' "Dictionary of Chemistry."

heat to boiling. Filter into the pressure bottle, and wash the residue with hot water. Then wash the residue back into the casserole, and repeat the treatment with "silicon mixture" and tartaric acid as before. Filter again into the pressure bottle, and when washed proceed as already described.

"Silicon mixture" was found to be the best solvent for molybdenum steels and ferromolybdenums, and was also used because it is a common reagent at the steel works. When tungsten was present it was found necessary to re-treat the residue, as it contains a little molybdenum.

In titrating with potassium permanganate, the conditions used were those given by Miller and Frank.[1] Length of column of unamalgamated zinc (20 to 30 mesh), 15 inches; time of passage, six minutes; temperature, 70°-75° C.; volume of solution, 200 to 250 cc.; acidity, 10 cc. concentrated sulphuric acid; and titrated immediately. The following percentages of molybdenum were obtained by these methods:

Molybdenum steel.	Molybdenum, chromium steel.	Molybdenum, vanadium steel.	Molybdenum, chromium, tungsten steel.	Ferromolybdenum.	Ferromolybdenum, high in sulphur.	Molybdenum metal.
3.63	4.02	9.11	3.47	44.50	34.18	83.84
3.62	4.11	9.12	3.51	44.57	34.24	84.00
3.595	4.09	9.26	...	44.72	34.42	84.00
...	...	...	...	...	34.49	84.16

In analyzing the molybdenum, chromium, tungsten steel the residue was not filtered out at first, and the results obtained for percentages of molybdenum were 4.06 per cent., 4.04 per cent. and 3.97 per cent., due to small amounts of tungsten which were dissolved by the acids when making the final evaporation with sulphuric acid. The solution was filtered and washed before the addition of ammonia.

In order to compare this method with those now in general use, the same samples were next analyzed by the latest modification[2] of the method of Kopp, Brakes, and Auchy, which is in brief as follows: Dissolve 0.8 gram of drillings in a mixture of 15 cc. dilute nitric acid, 10 cc. concentrated hydrochloric acid, and

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[1] This Journal. **25**, 919 (1903).

[2] *Iron Age*, Nov. 20, 1902; This Journal, **25**, 215 (1903).

3 cc. concentrated sulphuric acid. Keep covered. Evaporate to fumes, which must be very dense, being careful that no nitric acid remains on the cover. Boil the residue with 50 cc. water. Allow to cool, and pour by degrees with shaking into 100 cc. of caustic soda solution (1 pound of caustic soda in 2000 to 2100 cc. water). Dilute up to 200 cc. (by 200 cc. graduated Erlenmeyer flask), mix well by shaking, and allow to settle. Filter through a dry filter into a 100 cc. measuring flask, till mark is reached, add 15 cc. of concentrated sulphuric acid, reduce and titrate.

The percentages of molybdenum obtained were as follows:

Molybdenum steel.	Molybdenum, chromium steel.	Molybdenum, vanadium steel.	Molybdenum, chromium, tungsten steel.	Ferro molybdenum.	Ferro molybdenum high in sulphur.	Molybdenum metal.
3.91	4.28	11.72	6.21	46.78	36.21	86.58
3.92	4.37	11.63	6.26	46.93	36.26	86.58
4.08	4.43	11.96	6.30	47.01	36.32	86.88

In reducing and titrating the molybdenum in the foregoing samples, the conditions just described for reducing and titrating were followed.

From the results we see that when molybdenum, or molybdenum and chromium are present, the results are high, due to the formation of a ferric molybdate, which is slightly soluble in the large excess of alkali. The method has the advantage of being very rapid. Three cc. of concentrated sulphuric acid is too small an amount when evaporated to fumes of sulphur trioxide in order to get rid of all other acids. Eight to ten cc. are preferable. A defect in the method is the addition of 15 cc. of concentrated sulphuric acid to the alkaline filtrate, containing molybdenum for reduction and titration. No correct results can be obtained in reducing and titrating molybdenum, unless the same conditions are followed in analyzing the steel as are used for standardizing the permanganate solution. The amount of free acid should be kept constant. The solution should be made neutral, and then a definite quantity of concentrated sulphuric acid added in excess.

If tungsten, vanadium, or uranium be present, the method is worthless, as they will be obtained in the filtrate with the molybdenum, and will be reduced and reoxidized by the permanganate.

The next method used was that of Ibbotson and Brearley, as given in their "Analysis of Steel Works Materials," p. 84, slightly modified to obtain more correct results, by statements made previously by them in the *Chemical News*,[1] *i. e.*, reprecipitating the lead molybdate to get rid of silica and any other impurity. The method used was as follows:

Dissolve 2 grams of the sample in hydrochloric acid and oxidize by nitric acid or potassium chlorate. Add sodium carbonate, taking care to stop the addition short of the production of a red color or precipitate. Pass through a small pulp filter and place the filter in a flask containing 30 to 40 cc. more of double normal caustic soda than is necessary to precipitate the whole of the iron. After disintegrating the added filter, which may possibly contain a little tungstic or molybdic oxide, heat the contents of the flask to boiling, and add the hot solution, shaking constantly. Make up to 500 cc., filter off 250 cc., add a drop of methyl orange and a decided excess of hydrochloric acid, then an excess of lead acetate solution (40 grams of crystallized lead acetate per liter), and more than enough ammonium acetate to destroy the free hydrochloric acid. Heat the solution to boiling, allow to settle, filter, wash with hot water, ignite and weigh the lead molybdate.

In carrying out this method, difficulty was first encountered in dissolving the steels, as hydrochloric and nitric acids are not the best solvent for a molybdenum steel, and in the case of the samples of ferromolybdenum it was found impossible to get them into solution completely by the use of hydrochloric and nitric acids. In adding sodium carbonate, it is difficult to get the solution at the right point of acidity. If left too acid, there will not be enough sodium hydroxide to separate the iron and the molybdenum, as only a small excess is used.

Great difficulty was encountered at this point, on account of the reddish color of the steel solution. By increasing the strength or amount of sodium hydroxide added, this could be remedied. This would also obviate the necessity of filtering the solution of the steel, and treating the residue separately.

In precipitating the molybdenum as lead molybdate, a decided excess of hydrochloric acid is first added, and then this excess of hydrochloric acid is destroyed by the addition of ammonium acetate. If there is a large excess of hydrochloric acid present,

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[1] *Chem. News*, 81, 269 (1900).

there will be a large excess of acetic acid present, and this affects the precipitation of lead molybdate.[1] By first neutralizing the acid with ammonia and then adding 2 to 3 cc. of acetic acid (33 per cent.) in excess, the best conditions for precipitation are obtained.

In analyzing the molybdenum, chromium, tungsten steel, the following modification of the method was used:[1] Dissolve the ignited lead salts in hydrochloric acid, add a few drops of nitric acid, and evaporate nearly to dryness. Add 100 to 200 cc. of dilute hydrochloric acid (1 : 4), boil, and filter off the tungstic oxide. The molybdenum is reprecipitated from the filtrate with lead acetate, etc.

It is claimed that an accurate separation of the two oxides from their lead salts can be made in this manner, no matter in what proportion they exist. The results obtained were as follows:

Molybdenum steel. Per cent.	Molybdenum, chromium, tungsten steel. Per cent.
3.84	4.31
3.68	4.43
...	4.44

The precipitates of ferric hydroxide from the molybdenum steel were dissolved in acid after thorough washing, and the iron precipitated again by a large excess of sodium hydroxide (200 cc. of 5½ normal sodium hydroxide), and the filtrates precipitated with lead acetate as before. The results were 3.93 and 3.90 per cent. of molybdenum, showing that the molybdenum had not been completely separated from the iron.

In analyzing the molybdenum, chromium, tungsten steel, the results are about 0.9 per cent. high, due to tungsten, as tungstic acid is not precipitated completely by boiling to a small volume with acid.

The results obtained on the molybdenum, chromium steel were very low, the molybdenum not being completely separated by the small amount of alkali used.

Vanadium interferes with the lead molybdate precipitation, as stated by Ibbotson and Brearley.

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[1] Brearley: *Chem. News*, **78**, 203 (1898).

[2] Ibbotson and Brearley's "Analysis of Steel Works Materials," p. 85.

The other methods[1] for the determination of molybdenum were not investigated, as they did not seem applicable to steel analysis.

We believe that the following conclusions are warranted by the experiments described:

(1) That molybdenum can be precipitated completely from an acid solution containing iron, using hydrogen sulphide under pressure, the precipitate being slightly contaminated by iron, which is probably held mechanically, and cannot be washed out and that it is necessary to remove this iron subsequently by ammonium hydroxide. That this method of separation of molybdenum from iron is more accurate than the use of either sodium or ammonium hydroxide.

(2) Both sodium and ammonium hydroxide give high results in the determination of molybdenum, due to the formation of a ferric molybdate, which is soluble to a slight extent in excess of alkali.

(3) The separation of iron from molybdenum is more accurate when sodium hydroxide is used than with ammonia.

(4) If the ammonia is boiled out, in separating iron from molybdenum, the precipitation of the molybdenum as ferric molybdate increases with the increase in ratio of iron to molybdenum and when the ratio is 50 : 1, the molybdenum is practically all precipitated with the iron.

(5) The estimation of molybdenum by precipitating with lead acetate, and weighing as lead molybdate, is as accurate as the method of reducing and then titrating with potassium permanganate, but it takes much longer, and, therefore, the titration method is to be preferred.

(6) When vanadium, uranium, or tungsten are also present with molybdenum and iron, they are not separated from molybdenum by sodium or ammonium hydroxide, and therefore these methods of separation are worthless.

(7) In separating molybdenum from iron by hydrogen sulphide in an acid solution, under pressure, vanadium and uranium do not interfere, remaining in solution. Tungsten may be held in solution by the addition of 3 to 4 grams of tartaric acid.

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[1] Gooch and Fairbanks: Abs. *J. Chem. Soc.*, 76 (1897); Gooch and Norton: *Am. J. Sci.*, **6**, 168 (1898); Abs. *J. Chem. Soc.*, 1898, p. 648; Gooch and Pulman: *Am. J. Sci.*, **12**, 449-451 (1901); Abs. *J. Chem. Soc.*, **82**, 230 (1902); Friedheim and Hoffman: *Ber. d. chem. Ges.*, **35**, 791-795; de Benneville: *J. Iron and Steel Inst.*, 1, 202 (1895).

(8) Chromium does not interfere with either method, but more accurate results are obtainable by the hydrogen sulphide method, using pressure.

(9) The sulphide precipitation, followed by reduction and titration with potassium permanganate, not only gives accurate results, but has the great advantage that nothing which is present in steels, ferromolybdenum, or molybdenum metal, interferes with the accuracy of the results.

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March 4, 1904.

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SOME METHODS FOR THE DETECTION OF COBALT AND NICKEL.[1]

BY STANLEY R. BENEDICT.

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BECAUSE of the great similarity of chemical behavior between cobalt and nickel, the detection of these two elements in the presence of each other, particularly of small amounts of either, is a problem which presents peculiar difficulties. Many solutions of this problem have been proposed.

For comparison with the methods I wish to propose, I mention what are, so far as I have been able to learn, the most delicate methods yet offered for the detection of cobalt and nickel when both are present in one solution. The one for the detection of cobalt was proposed by Vögel.[2] A saturated solution of ammonium sulphocyanide is added, then a mixture of amyl alcohol and ether added and the solution shaken. If cobalt be present, the alcohol-ether layer has a blue color. This method is very sensitive, and will detect 0.5 per cent. of cobalt in nickel solutions.

The detection of traces of nickel in an excess of cobalt is a more difficult problem. The most delicate method, up to the present time, is probably the one suggested by Parr,[3] which de-

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[1] Read before the Cincinnati Section of the American Chemical Society, February 10, 1904.

[2] *Ber. d. chem. Ges.*, **12**, 2314 (1879).

[3] This Journal, **19**, 341 (1897).