

THE SIMULTANEOUS DETERMINATION OF
VANADIUM AND MOLYBDENUM

by

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INTRODUCTION:

The increasing importance of steel alloys in modern industry has greatly increased the demand for rapid and more accurate methods of determination for such metals as manganese, chromium, nickel, titanium, vanadium and molybdenum. Inasmuch as several of these elements may be desired as a component of an alloy, the value of methods which determine two or more metals in the same procedure is obvious.

Considerable work has been done in this direction by Willard and Young¹ and also by Koltoff and Sandell² on the simultaneous determination of chromium, vanadium and tungsten. Not since the work of Steffan³ however, in 1902, has any reference been found to an attempt to determine vanadium and molybdenum together. If such a method were possible it would find immediate application in steel and rock analysis, as considerable amounts of both metals are found together in these sources.

To obtain such an analytic method was the object of this research. It was hoped that this could be obtained through the following general operations:

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1. 764, 769, Indus and Eng. Chem. 1928.
 2. 140 Indus and Eng. Chem. Anal. Sec. 1930.
 3. Steffan, Inaug. Dissertation Zurich 1902.

2.

1. Reduction of molybdate and vanadate to definite lower valence states.
2. Quantitative oxidation of both metals to their original states.
3. Reduction of the vanadate alone.
4. Quantitative oxidation of the reduced vanadium.
5. Vanadium and molybdenum concentrations obtained by simple calculation.

Chief difficulties were expected to lie in obtaining reducing agents of proper strengths and in removing their excess. To study these factors preliminary investigations were carried out with vanadium and molybdenum separately.

I. VANADIUM:

Vanadium is reduced to various valence states by such common reducing agents as the metals, sodium thio-sulphate, sulphur dioxide and hydrogen sulphide. Of these several lend themselves fairly well to the proposed plan of analysis. Oxalic acid, citric acid or sulphur dioxide completely reduce vanadium without attacking molybdenum, and the problem of removal of excess is not difficult. Excess oxalate may be precipitated and excess sulphur dioxide may be removed by boiling and bubbling in carbon dioxide. In the course of this investigation two original methods of

determining vanadium were devised.

1. REDUCTION WITH SODIUM SULPHITE:

The acid vanadate solution is heated to boiling and small amounts of solid sodium sulphite are added. Reduction proceeds rapidly to the clear blue solution of the vanadyl salt and excess sulphite is completely removed by boiling with sulphuric acid for about ten minutes. The vanadyl salt may then be titrated with standard potassium permanganate.

This method is essentially Treadwell-Halls⁴ sulphur dioxide method, but it avoids the necessity of gas apparatus and generators, and is much more rapid.

2. REDUCTION WITH ZINC:

The hot acid vanadate solution is treated with metallic zinc until a deep green solution is obtained. The excess zinc is removed and a few cc. of concentrated nitric acid are added until a clear blue color, indicating the formation of vanadyl ion, is obtained. The vanadyl salt is now titrated in the usual manner.

If, on the addition of nitric acid, a green color persists, the original reduction was incomplete. Zinc reduces a vanadate in acid solution to the vanadyl and then to the vanadic salt. A green color is obtained throughout the reaction, but the first is due to a combination of the blue vanadyl and yellow vanadate salts. The vanadic ion is unstable and normally reacts with the vanadate, or is oxidized by air, to form the vanadyl salt. This action, however,

4. P. 538 Treadwell-Halls Analytic Chemistry Vol. II.

4.

is extremely slow, whereas the addition of nitric acid gives the blue vanadyl salt instantly.

Both of the above methods of determination are rapid and accurate and as they involve no special technique offer considerable improvement over present methods.

With these and other standard methods of vanadium analysis, the latter part of the proposed method, i.e. reduction of vanadium with no action on molybdenum, is comparatively simple and the problem reduces itself to an investigation of molybdenum reduction.

II. MOLYBDENUM:

At the present time two methods are commonly employed in laboratory and industrial work for the estimation of molybdenum.⁵

1. PRECIPITATION OF THE LEAD SALT:

Lead molybdate may be quantitatively precipitated and weighed to give an exact determination of molybdenum over a wide range of conditions. Very few substances interfere, a practically pure precipitate is found, and a very accurate value is obtained.

The method, however, has the shortcomings of all gravimetric determinations, in that it is slow, and involves

5. Bureau of Mines Technical Paper No. 230.

5.

tedious filtration and ignition.

2. JONES REDUCTOR METHOD:

This method involves the passing of the acid molybdate solution through a Jones reductor of amalgamated zinc into a standard solution of ferrous ion. The method is reasonably accurate but rather slow, and as air must be excluded special technique is required.

Other methods for estimating molybdenum have been proposed, but they are, on the whole, unsatisfactory due to the interference of other elements.⁶ It is therefore apparent that even apart from the original plan of this research existing analytical methods for molybdenum are by no means completely satisfactory.

On a preliminary survey of the chemistry of molybdenum, several properties suggest themselves as likely means for estimating the element. It exists in several stages of oxidation below the normal six, the lower forms being insoluble in alkaline solution, and also forms a permolybdate in which molybdenum has the valence eight.

We will consider these valence states in order, the methods applied, and the results obtained.

1. REDUCTION OF MOLYBDATE BY A METAL:

Acid molybdate solutions are reduced by metals to

6. P. 221. B. S. Hopkins Chemistry of the Rarer Elements.

form a blue colloidal complex oxide, generally recognized to be of the form $\text{MoO}_2 \cdot 2\text{MoO}_3$. This complex is believed to exist in several different combinations of the oxides but an effort was made to produce the same form continually by maintaining the same conditions, with the idea of investigating the possibility of oxidizing it quantitatively to the molybdate.

This attempt was not successful. It was found that if the lower metals of the electromotive series, e.g. lead or copper, were used, a black deposit forms on the surface of the metal, apparently removing some of the molybdenum from the solution and rendering any quantitative work impossible. On the other hand, if active metals such as magnesium were used, reduction was not consistent and values obtained by titrating the complex with standard permanganate showed no definite relation to the concentration.

2. REDUCING AGENTS OTHER THAN METALS:

Attempts at reduction with other reducing agents in nearly all cases met with failure. The reagents used include ferrous sulphate, sodium sulphite, arsenious acid, oxalic acid, and potassium iodide. In all cases but the last, no reduction could be obtained.

This reduction has been extensively studied by Steffan⁷ and Gooch and Fairbanks⁸. The latter workers

7. Steffan, Inaug. Dissertation Zurich 1902.

8. Z. Anorg. Chem. 13. 101 (1897) and 14, 317.

attempted to use it quantitatively by distilling the iodine vapors and titrating with sodium thiosulphate. They found the reaction hard to control and could not obtain accurate results, as the degree of reduction varied with the time of distillation. Their results were confirmed by Steffan.

Friedheim and Euler⁹ determined vanadic and molybdic acids together in solution by differential reduction with potassium bromide and potassium iodide. It has been proved, however, by Gooch and Fairbanks⁸, that the reaction is not accurate, and may stop at any one of several stages.

The reaction was studied here, by electrometric titration of standard potassium iodide solution into a molybdate solution containing a large excess of hydrochloric acid. No definite break in the curve was observed and continuous fluctuation of the galvanometer needle during the course of the titration indicated a complex reaction. Error is possible from two sources: (a) oxidation of the reduced molybdenum by air, and (b) oxidation of potassium iodide by air. Inasmuch as the titration, to be successful, would have to be carried out electrometrically, elimination of this error is impossible.

It is evident then that to be practical some method of controlling the reaction is necessary. This could best be accomplished by removing the pentavalent molybdenum salt from solution either as a precipitate or a complex ion, or

9. Ber. 28, 2067 (1895).

8. Z. Anorg. Chem. 13. 101 (1897) and 14, 317.

8.

by removal of free iodine by some method other than distillation, in the absence of air.

At this time neither of these has been accomplished but it would appear likely that with some such device the reaction would go to definite stages, depending on the temperature. The solution would seem to lie in an investigation of the pentavalent molybdenum compounds and a study of their properties, with a view to separating the reduced molybdenum salt from the molybdate.

3. PERMOLYBDATES:

If an acid solution of a molybdate is treated with hydrogen peroxide, a compound is formed whose composition corresponds to a permolybdate. The possibility of applying this reaction to a quantitative determination was considered but not attempted for several reasons.

(a) The method would involve use of standard hydrogen peroxide solution which is highly unsatisfactory.

(b) The reaction would require an excess of peroxide to oxidize all of the molybdate to the permolybdate.

(c) An indicator would have to be devised as the color change in the reaction is not great enough to be its own indicator.

SUMMARY:

(1) An investigation with a view to determining molybdenum and vanadium simultaneously has been made. The

effort was unsuccessful due to the fact that molybdenum cannot be quantitatively reduced to its pentavalent state by any known procedure. It may be well to point out here that vanadium and molybdenum can, in all probability, be reduced together in a Jones reductor, both going down to the trivalent state. The reduced solution could be passed into standard ferrous sulphate and the unoxidized ferrous ion determined with permanganate. Vanadium could then be determined by one of the methods earlier mentioned and by calculation the concentration of both metals could be obtained. This method, however, would be merely a combination of existing methods, and offers no improvements.

(2) Two original methods for determining vanadium have been devised.

(a) Reduction of a vanadate, in acid solution, to the vanadyl salt by sodium sulphite, and subsequent titration with permanganate after removing excess sulphite by boiling with sulphuric acid.

(b) Reduction of a vanadate to the vanadic salt by zinc in acid solution, followed by oxidation to the vanadyl form with nitric acid and titration to the vanadate with potassium permanganate.

Both of these methods offer advantages over existing procedures, in that they are rapid, accurate and easily carried out.

(3) In the opinion of this writer, the difficulty encountered in working with molybdenum and vanadium, particularly the former, is directly due to lack of information in the literature on the reactions of these metals in their various valence states in solution. Workers in the field have apparently been more concerned with the preparation and isolation of compounds, in many cases very complex and of doubtful composition, than in a study of their chemical properties and the mechanism and products of their reactions.

A great deal of research could be advantageously applied to a systematic study of the properties of the vanadyl and pentavalent molybdenum compounds. These two series are only one step removed from the stable vanadates and molybdates and a good deal of light could be thrown on the chemistry of the metals by an investigation of the stability, solubility, and reactions of the sulphates, carbonates, hydroxides, oxalates, and other salts considered of value.

COLORIMETRIC RESEARCH

In the course of the foregoing research, several color reactions were observed and investigated to determine their value as possible methods for estimating molybdenum colorimetrically.

Ten standard solutions of sodium molybdate were prepared with the following concentrations of molybdenum:

1. .0001 g Mo/cc.	6. .0032 g Mo/cc
2. .0002	7. .0064
3. .0004	8. .0128
4. .0008	9. .0256
5. .0016	10. .0512

In the following procedures the reactions were investigated over this range for a variety of conditions of temperature and concentrations of reagents.

1. MOLYBDENUM BLUE:

The formation of the complex blue oxide commonly known as molybdenum blue was investigated by reduction with lead, zinc and magnesium, over the range of the ten standard solutions. With both lead and zinc the excess metal must be removed mechanically and removal of molybdenum in some form as a dark coating on the metals cannot be avoided. This can be prevented by using magnesium, as the metal readily goes completely into solution, but the reaction

is not sufficiently sensitive. The blue oxide only forms for concentrations above standard solution No.3, indicating that the sensitivity would be of the order .0005 g per cc. of molybdenum, which is far too large a quantity to be of any value in a quantitative determination.

2. REDUCTION OF PHOSPHO MOLYBDIC ACID:

The micro-estimation of phosphorus by reduction of phosphomolybdic acid is a standard biochemical procedure. The method and conditions necessary for best results were devised by T. Kuttner and H. R. Cohen¹⁰ and were later improved by T. Kuttner and L. Lichtenstein.¹¹

In brief the method is as follows:

To the neutral phosphate solution is added a definite amount of a mixture of 3 normal sulphuric acid and 7.5% sodium molybdate solution. The phosphomolybdic acid forms as a yellow coloration with no precipitate at room temperature. The addition of 1 cc. of a very dilute standard stannous chloride solution gives a deep blue color of great sensitivity. The method is extremely accurate, but the conditions must be closely observed. For these, the original articles should be consulted.

This reaction was here investigated with a view to determining whether or not the conditions could be altered

10. 517 - 75 Journal of Biol. Chem. 1927.

11. 671 - 86 Journal of Biol. Chem. 1930.

so that the estimation of micro amounts of molybdenum could be made.

To test this the following solutions were prepared.

- (1) 3 N. sulphuric acid.
- (2) 10% sodium acid phosphate.
- (3) 10 g. of stannous chloride were dissolved in 25 cc. concentrated hydrochloric acid. For immediate use one part was diluted to 200 cc.

The best concentrations of the above solutions were obtained by holding two fixed, and varying the third. It was found that the amount of stannous chloride must vary proportionately to the amount of molybdenum present.

Five cc. samples of the stock molybdate solutions were treated in all cases. With solution #1, concentration .0001 g Mo/cc, maximum coloration was obtained with .4 cc. sulphuric acid, .25 cc. sodium acid phosphate solution, and .25 cc. of the diluted stannous chloride. With solution #10, concentration .0512 g Mo/cc. maximum coloration was obtained with .4 cc. sulphuric acid, .25 cc. of sodium acid molybdate solution and 1.5 cc. of diluted stannous chloride.

An excess of stannous chloride, i.e. more than .25 cc. at the lower molybdenum concentrations resulted in a green turbidity which coagulated in a short time. This renders the procedure valueless as the depth of color depends on the amount of stannous chloride which must be

adjusted to suit the unknown concentration of molybdenum. The application of a definite procedure which is particularly necessary in colorimetric work is hence impossible. Results with hydrochloric acid and nitric acid were identical with those obtained with sulphuric.

With a view to avoiding this difficulty, reduction of the phosphomolybdate by metallic magnesium was investigated. As before the concentrations of acid, phosphate, and reducing agent were carefully checked over the range by a systematic treatment of solutions No's. 1, 3 and 6. Better results were obtained than with stannous chloride but consistent values could not be obtained. Maximum color was found when 5 cc. of the stock solution were treated with 1.8 cc. of 3 N hydrochloric acid, .8 cc. of 10% sodium acid phosphate solution and 25 - 30 mg. of metallic magnesium. The magnesium dissolved completely in about thirty minutes, and a good gradation of color was obtained. The solutions were examined in a colorimeter and the graph of concentration of molybdenum against the reciprocal depth of solution was very close to a straight line for a series of solutions. If, however, four or five samples of the same solution were treated in the same manner, a good deal of variation in color was noted. No way of overcoming this could be found and the method was abandoned.

This variation in color may be explained in two ways. In most cases with the above concentrations the

magnesium stays at the bottom of the test tube but occasionally particles are carried to the surface where some hydrogen is lost directly to the air. This results in incomplete reduction of molybdenum, and hence, in a paler color than should be obtained. Variation in color may also result from variation of the particle size of the colloid formed in the reaction.

3. PERMOLYBDIC ACID:

If an acid solution of an alkali molybdate is treated with hydrogen peroxide, a yellow permolybdate is formed. As this color is visible in solutions containing as little as .0001 g Mo/cc. it was considered likely that the reaction could be employed in colorimetric analysis.

The reaction was studied for a variety of conditions but it was observed that the concentrations of acid and peroxide had no apparent effect, except for very small amounts of acid. The series of stock solutions were examined using sulphuric acid. A gradation in color intensity was obtained but the sensitivity of the reaction was not great enough. When examined in the visual type and even in the photo-electric colorimeter accurate comparisons could not be made with this pale yellow color.

Various solvents were tested in an effort to find a reagent which would extract the permolybdate in a small volume, giving a more intense color which could better be

compared. Aniline, acetone, carbon tetrachloride, carbon disulphide, ethyl and methyl alcohols were tried with no success.

SUMMARY:

Several color reactions were investigated as possible methods for determining molybdenum colorimetrically.

- (a) Reduction of molybdate by a metal to form molybdenum blue.
- (b) Reduction of phosphomolybdic acid by stannous chloride and by metallic magnesium.
- (c) Oxidation of a molybdate in acid solution to a permolybdate by hydrogen peroxide.

Results obtained in all cases indicate no improvements in these methods over the potassium thiocyanate, stannous chloride method now employed in Bureau of Standards steel analysis.

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