ON THE DETERMINATION OF MOLYBDENUM BY POTASSIUM IODATE.

By George S. Jamieson.

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The method in common use for the volumetric estimation of molybdenum is based upon the reduction of the molybdenum in a sulphuric acid solution by means of the Jones reductor and the titration by potassium permanganate. It has been shown by W. A. Noyes and Frohman[1] and later by D. L. Randall[2] that a column of amalgamated zinc can reduce molybdic trioxide to the form of Mo_2O_3. Since Mo_2O_3 is very susceptible to oxidation by the oxygen of the air, Randall passed the molybdenum solution through the reductor, directly into a solution of ferric alum (containing some phosphoric acid to decolorize the ferric salt) then without further precaution the solution was titrated with potassium permanganate. It was conceived that it might be possible to receive the reduced molybdenum solution directly in a hydrochloric acid solution of iodine monochloride, then estimate the molybdenum by titration with potassium iodate according to the general method of L. W. Andrews.[3] It was found that molybdenum could be determined in this way. However, unlike the permanganate titration, the iodate oxidized the molybdenum readily to Mo_2O_5 and further oxidation proceeded so slowly (2–3 days) that it was not practical to wait for it. However, it was found possible to obtain a sharp end point when the pentoxide was completely formed.

In order to test the method, a solution containing 3.567 g. of normal potassium iodate in 1000 cc. was prepared. According to the equations of the expected reactions,

$$KIO_3 + Mo_2O_3 + 2HCl = Mo_2O_5 + ICl + KCl + H_2O$$

$$3KIO_3 + 2Mo_2O_3 + 6HCl = 4MoO_3 + 3ICl + 3KCl + 3H_2O,$$

the equivalents of this solution are, respectively, 1 cc. 0.003200 g. and 0.002133 g. of Mo. For convenience a solution of ammonium molybdate which had been prepared for another purpose, was used. The solution was standardized by precipitating the molybdenum from measured volumes and weighing it as lead molybdate. It was found best to precipitate the molybdenum from a solution made slightly acid with nitric acid, with a solution of lead nitrate. After the solution was thoroughly stirred and the precipitate had settled for a few minutes, 5 cc. of a strong solution of ammonium acetate were added in order to be certain of obtaining a complete precipitation. This procedure gave a course crystalline precipitate, instead of a very finely divided slimy one as is obtained when molyb-

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[1] This Journal, 16, 553; Miller and Frank, *Ibid.*, 25, 919.

[2] *Am. J. Sci.*, [4] 24, 313.

[3] This Journal, 25, 756 (1903).

denum is precipitated (as usually recommended) by lead acetate in the presence of large quantities of acetates. Two analyses were made with the following results: 25.2 cc. of the solution gave 0.0989 g. of $PbMoO_4$ and 25 cc. of the solution gave 0.0973 g. of $PbMoO_4$, giving the value of 1 cc., respectively, 0.001022 and 0.001018 g. of Mo. The average value 0.001020 was used.

The apparatus used for the reduction of the molybdenum consisted of a reductor (20×1.8 cm.) filled to within 3 cm. of the top with 30 mesh amalgamated zinc, which rested on a mat of glass wool about 2 cm. thick which in turn was supported by a perforated platinum disk. The outlet of the reductor extended to within 1 cm. of the bottom of the bottle. The reductor was provided with a stopcock in order to be able to control the rate of reduction. It is recommended that a somewhat longer reduction tube should be used, as it was found that this one would not reduce the molybdenum completely unless the solution was passed through the reductor very slowly. Previous to making a reduction, 5 cc. of iodine monochloride solution, 25 cc. of concentrated hydrochloric acid, 5 cc. of water, and 7 cc. of chloroform were placed in one of the 500 cc. titration bottles.[1] The bottle was placed in a deep pan of cold water in order to cool the reduced solution rapidly. The reductor was set up in another bottle, heated with some dilute hydrochloric acid and about 100 cc. of hot water. When the water had run out, the reductor was transferred at once to the bottle in the cold water. A measured quantity of the ammonium molybdate solution, acidified with 20 cc. of 1 : 1 hydrochloric acid, was heated to about 50°, and passed very slowly through the reductor, using gentle suction, directly into the solution in the bottle. The bottle was frequently agitated gently so as to keep the solution thoroughly cooled and avoid any loss of iodine which separates as the reaction proceeds. After adding all of the solution, the flask was rinsed with 1 : 2 hydrocloric acid several times and the washings were added to the reductor, which was further washed with about 50 cc. more of the acid. The exposure of the zinc during the reduction caused no error in the titration as would be the case with a permanganate titration, because any hydrogen peroxide formed would not react either with iodine monochloride or potassium iodate, as has been found by direct experiments with hydrogen peroxide solutions.[2] When the washings had run through, the reductor was removed and the solution was titrated rapidly at first, then slowly, with thorough shaking with the glass stopper inserted after each

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[1] To prepare iodine monochloride solution, dissolve 10 g. of potassium iodide and 6.44 g. of potassium iodate in 75 cc. of water, add 75 cc. of concentrated hydrochloric acid, then add 5 cc. of chloroform in a glass-stoppered bottle, and adjust exactly to a faint iodine color by violent shaking and adding dilute solutions of iodide or iodate as the solution may require.

[2] "Methods in Chemical Analysis," by F. A. Gooch, p. 430.

addition of potassium iodate, until the chloroform indicator was decolorized, which marked the end point of the titration. If the solution became warm at all during the titration, it was important to cool it under running water. The bottle was placed in cold water for five minutes after the titration. If no more color appeared in the chloroform, the reaction was completed. It should be observed that when more than minute quantities of molybdenum are present, the solution has a rose or red color due to the compound Mo_2O_5. Several blank determinations were made using the same amounts of reagents and carrying out the entire procedure as in the actual experiments. It was found that the blank correction amounted to 0.05 cc. of the potassium iodate solution which has been deducted from each titration given below.

No.	Cc. of Mo sol.	Cc. KIO_3 used.	Mo found.	Mo taken.	Error.
1..............	42.0	13.4	0.04280	0.0428	0.0000
2..............	41.9	13.25	0.0424	0.0427	—0.0003
3..............	29.9	9.55	0.0306	0.0305	+0.0001
4..............	20.05	6.35	0.0203	0.0204	—0.0001
5..............	32.5	10.30	0.0330	0.0332	+0.0002
6..............	46.0	14.70	0.0470	0.0469	+0.0001
7..............	34.9	11.0	0.0352	0.0356	—0.0004

These results show excellent agreement among themselves and the reaction of the titration may be written according to the first equation given above. It is very essential to maintain a long column of zinc in order to obtain complete reduction. When the titrated solutions were allowed to stand the pentoxide was slowly oxidized to the trioxide. The reaction was accelerated by exposing the solution to direct sunlight. This action of direct sunlight has been observed in a number of other iodate reactions. One experiment was made in which the reaction was allowed to proceed until the molybdenum was oxidized to the trioxide. This reaction required 2 days for completion. A solution which contained 0.0181 g. of Mo was reduced and then titrated until no further separation of iodine took place. It required 8.5 cc. of potassium iodate solution, which, multiplied by 0.002133, gave 0.0181 g. of molybdenum, showing that the reaction may be represented according to the second equation given above.

Another molybdenum solution was prepared and standardized as previously described. It was found that 1 cc. of this solution contained 0.001822 g. of Mo. The following results were obtained:

No.	Cc. of Mo sol.	Cc. KIO_3 used.	Mo taken.	Mo found.	Error.
1..............	10.0	5.7	0.0182	0.0181	—0.0001
2..............	15.0	8.6	0.0273	0.0275	+0.0002
3..............	25.0	14.0	0.0455	0.0450	—0.0005
4..............	25.0	14.15	0.0455	0.0453	—0.0002

A third series of experiments was made using weighed portions of molybdenum trioxide which were dissolved in ammonia, then diluted to 20 cc. with water, acidified with 20 cc. of hydrochloric acid, reduced, and titrated as described above. The following results were obtained: 1 cc. of KIO_3 = 0.00480 g. of MoO_3.

No.	MoO_3 taken.	Cc. KIO_3 used.	MoO_3 found.	Error.
1	0.0548	11.45	0.0549	+0.0001
2	0.0627	13.05	0.0626	—0.0001
3	0.0163	3.50	0.0168	+0.0005

The three sets of experiments indicate that molybdenum can be determined with accuracy by the iodate method, observing the precautions already described. It should be observed that it is of importance to maintain not less than 10 per cent. of actual hydrochloric acid in the solution in order to prevent the hydrolysis of the iodine monochloride during the titration, which would cause serious errors. Furthermore, it is important to keep the solution thoroughly cooled and in a shaded place during the titration, especially if much molybdenum is present, in order to obtain a sharp end point.

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ON THE DETERMINATION OF POTASSIUM AS PERCHLORATE.

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One of the chief difficulties met in determining potassium as perchlorate lies in the solubility of this substance in the washing liquid, the main component of which is alcohol. Wense[1] first proposed the addition of perchloric acid to the alcohol used in washing, in order to reduce the solubility of the precipitate, and this recommendation has been adopted by most subsequent workers upon the subject.[2] Even this precaution is not sufficient to prevent loss of material through solution, however, and as a remedy Davis[3] has proposed previously saturating the washing liquid with potassium perchlorate, a suggestion adopted by Thin and Cumming.[4] The reliability of the method has also been discussed by Jarrell[5] and by Hager and Kern.[6]

We have tested further this method for determining potassium and although our experiments were unavoidably interrupted before comple-

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[1] *Z. angew. Chem.*, 5, 691 (1891).

[2] See Scholl, THIS JOURNAL, 36, 2085 (1914).

[3] *J. Agr. Sci.*, 5, 52 (1912).

[4] *J. Chem. Soc.*, 107, 361 (1915).

[5] *J. Assoc. Off. Agr. Chem.*, 1, 29 (1915); *J. Soc. Chem. Ind.*, 34, 1170 (1915).

[6] *Landw. Versuchsstat.*, 87, 365 (1915); *J. Chem. Soc.*, 110, II, 114 (1916).