

The Titrimetric Determination of Molybdenum in Ammonium Molybdate, Molybdic Acid and Molybdenum Trioxide with Sodium Hydroxide

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Titrimetric methods have been developed for the determination of molybdenum in ammonium molybdate, molybdic acid and molybdenum trioxide, based on their reactions with sodium hydroxide.

ANALYTICAL-GRADE ammonium molybdate, molybdic acid and molybdenum trioxide are usually assayed oxidimetrically¹ after prior reduction with a Jones reductor, or gravimetrically.² The Jones method has recently been critically examined,³ a variety of reductants and oxidants being used.

Previous studies of the effect of sodium hydroxide on ammonium molybdate,⁴ molybdenum trioxide⁵ and molybdic acid⁶ were concerned with physical and chemical aspects of the state of aggregation in polymolybdates.

The present paper describes investigations of the attempts to develop methods of assaying molybdates based on their reactions with sodium hydroxide solution.

EXPERIMENTAL

SAMPLES—

Ammonium molybdate, AnalaR—Samples from two separate batches were used.

Molybdic acid, AnalaR—Samples from four separate batches were used.

Molybdenum trioxide, AnalaR—Samples from two separate batches were used.

REAGENTS—

Standard sodium hydroxide solution, 1.000 N.

Standard hydrochloric acid solution, 1.000 N.

Standard potassium permanganate solution, 0.1000 N.

Phenol red indicator solution—A mixture of 0.1 g of phenol red and 2.8 ml of 0.1 N sodium hydroxide was made up to 100 ml with water.

APPARATUS—

A Pye Dynacap pH meter and Ingold combined electrode were used.

PROCEDURE—

All of the samples were analysed first by permanganate titration, after reduction with a zinc Jones reductor by using the standard method,^{1,7} then by using sodium hydroxide in the following manner.

Ammonium molybdate—Portions of 6 g were accurately weighed and dissolved in 150 ml of water, with heating. The solutions were cooled and titrated with N sodium hydroxide. The pH was recorded after each addition of 0.5 ml in the region of the end-point, which was located by calculating the first and second derivatives of the titration curve.

Molybdic acid—As molybdic acid is almost insoluble in water, it is necessary to dissolve it in sodium hydroxide solution and back-titrate the excess.

Portions of 3 g were accurately weighed, dissolved in 50 ml of *N* sodium hydroxide and boiled until all of the ammonia had been removed. The solution was cooled, diluted to 150 ml with water and back-titrated with *N* hydrochloric acid. A potentiometric titration curve showed that phenol red was a satisfactory indicator, and it was used in these experiments.

Molybdenum trioxide—As molybdenum trioxide, like molybdic acid, is almost insoluble in water, it is also necessary to dissolve it in sodium hydroxide solution and back-titrate the excess.

Portions of 3 g were accurately weighed and dissolved in 50 ml of *N* sodium hydroxide solution and 50 ml of water. The solution was heated to 80° C to aid dissolution, cooled, and back-titrated with *N* hydrochloric acid. A potentiometric titration curve again showed that phenol red was a satisfactory indicator, and it was used in the experiments.

RESULTS

The results given in Table I, which are the means of five determinations, have been calculated for the sodium hydroxide reactions by using the equations given under Discussion. For each sample, the maximum difference from the mean was not greater than ± 0.2 per cent.

TABLE I
COMPARISON OF RESULTS FOR MOLYBDENUM DETERMINATION

Compound	Sample No.	Molybdenum, per cent.	
		Jones method	Sodium hydroxide method
Ammonium molybdate ..	1	54.5	54.5
	2	54.5	54.5
Molybdic acid ..	1	61.2	61.2
	2	60.8	61.1
	3	60.7	60.6
Molybdenum trioxide ..	1	66.9	66.7
	2	66.9	66.7

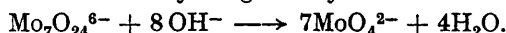
As a further check, an additional sample of molybdic acid was assayed gravimetrically, as the 8-hydroxyquinolate,⁷ and by the sodium hydroxide method.

The mean results by each method of 59.4 per cent. of molybdenum were in agreement.

DISCUSSION

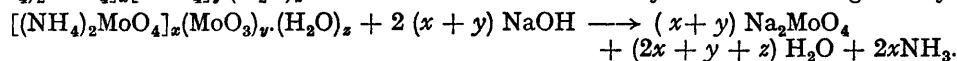
The titration curve of ammonium molybdate shows two inflections; one between pH 5 and 7, corresponding to the conversion of the paramolybdate into the orthomolybdate, and the other between pH 9 and 10, corresponding to the displacement of ammonia.

The first stage of the reaction may be given by—



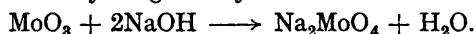
A well defined end-point is obtained at a point corresponding to the above equation. This end-point has to be determined potentiometrically, as the rate of change of pH with addition of titrant is not fast enough to give a sharp change with a pH indicator.

Molybdic acid, which is prepared commercially by the careful addition of nitric acid to a concentrated solution of ammonium molybdate, is a complex mixture of paramolybdates and contains between 4 and 7 per cent. of ammonia. The empirical formula may be written $[(\text{NH}_4)_2\text{MoO}_4]_x[\text{MoO}_4]_y(\text{H}_2\text{O})_z$. Its reaction with sodium hydroxide can be given by—



Thus, provided that all of the ammonia is boiled off, the amount of sodium hydroxide consumed allows the molybdenum content to be calculated, irrespective of the ratio of $(\text{NH}_4)_2\text{MoO}_4$ to MoO_3 in the sample.

The reaction between sodium hydroxide and molybdenum trioxide is a special instance of the previous reaction and may be given by—



The procedures based on the reactions of the compounds with sodium hydroxide possess the advantages of speed and simplicity over the oxidimetric and gravimetric methods.

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