HOMOGENEOUS PRECIPITATION OF MOLYBDENUM OXINATE AND ITS ESTIMATION IN A MULTICOMPONENT SYSTEM

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A homogeneous precipitation method was developed for the estimation of molybdenum as its oxinate from pure solutions or in multicomponent systems. The method uses the slow release of molybdenum from its tartrate complex in the presence of oxine and simultaneous increase of pH by urea hydrolysis. A single step determination of molybdenum in the presence of 16 elements was achieved. EDTA was used to mask the metal ions.

INTRODUCTION

The gaining importance of a multicomponent bismuth-molybdenum catalyst system for the oxidation and ammoxidation of propylene necessitates development of a new analytical procedure for the determination of the principal constituent, i.e., molybdenum, especially in the presence of a number of cations. Even in the present days of sophisticated instrumental analysis, one has to look for a classical titrimetric or gravimetric method for their simplicity as well as for the purpose of standardisation. Molybdenum is normally estimated by gravimetric methods¹⁾ in preference to indirect titrimetric methods²⁾. The available gravimetric methods were discussed by Erdey¹⁾, who observed that though the determination of molybdenum in the form of its oxinate was simpler, the method was not very selective. However, it was also mentioned that unlike many other oxinates molybdenum oxinate was insoluble in organic solvents or in a mixture of organic solvent and mineral acids. The freshly obtained precipitate could only be dissolved in concentrated sulphuric acid or hot alkali. Thus Rao and Tillu³⁾ separated molybdenum from vanadium and tungsten by coprecipitating the metals as their oxinates and selectively removing the vanadium and tungsten oxinates with 2 N hydrochloric acid. Since molybdenum can be precipitated in the presence of EDTA it is possible to mask a number of cations with EDTA⁴⁾ for selective separation. The proposed method can be used for effective separation of molybdenum from a variety of cations and anions for subsequent determination.

In the present investigation an attempt was made to study the precipitation and separation of molybdenum by applying the improved gravimetric technique of homogeneous precipitation. Molybdenum is readily precipitated with oxine at pH=3.3 - 7.6, but in the presence of EDTA or tartaric acid and a lower initial pH, the urea hydrolysis technique gives a precipitate with much superior physical characteristics. Preliminary studies revealed the suitability of this technique for the quantitative determination and effective separation of molybdenum from a number of possible interfering ions.

EXPERIMENTAL

Reagents

All the reagents used were of analytical grade. Aqueous solutions of 0.1 M ammonium heptamolybdate, 20% urea, 10% EDTA (disodium salt), 10% tartaric acid were prepared. Oxine (8-hydroxyquinoline) as a 4% solution was made in 1.5 M acetic acid.

For interference studies 0.1 M solutions of bismuth, iron, aluminium, chromium, uranium, calcium, barium, strontium, lead, copper, nickel, cobalt and beryllium were prepared as their nitrates. Cadmium, zinc and manganese solutions were prepared from their sulphates as 0.1 M solutions in 0.2 M nitric acid. Vanadium, 0.1 M solution, was prepared by dissolving the required amount of vanadium pentoxide in 1 M sodium carbonate.

Method of precipitation

Transfer the solution containing upto 70 mg molybdenum to a 250 ml beaker. Add 10 ml tartaric acid, 20 ml urea and adjust the pH to 2.3. Dilute to 150 ml and heat on a boiling water bath after adding 10 ml oxine. Precipitation starts within a few minutes and is almost complete after about an hour. Heat for a total time of 3 h and filter while hot through a sintered glass crucible of porosity No.4. Wash the precipitate with hot water till the filtrate is free from oxine. Dry the precipitate at 120° C for 1 h and weigh as $\text{MoO}_2(\text{C}_9\text{H}_6\text{ON})_2$. The conversion factor for Mo is 0.2305.

RESULTS AND DISCUSSION

The optimal conditions for complete precipitation of molybdenum oxinate from homogeneous solutions were established as follows:

Effect of pH: To solutions containing about 70 mg molybdenum, 10 ml each of tartaric acid and 20 ml urea were added. The pH was adjusted to values varying from 1.0 to 2.8 using dilute solutions of nitric acid or ammonia. After adding 10 ml oxine, the solutions with different initial pH values were heated on a boiling water bath for 3 hr, the precipitates were filtered through crucibles of porosity No.4, washed with hot water and dried at 120° C for 1 h. When the initial pH was less than 1.5 complete precipitation of molybdenum oxinate was not attained in a reasonable length of time (6 h) while at pH more than or equal to 2.8 precipitation of molybdenum oxinate occurs immediately as in the direct method. For homogeneous precipitation of molybdenum oxinate, the pH range of 1.8 to 2.5 was found to give satisfactory results.

Effect of tartaric acid: The presence of tartaric acid is necessary not only for the homogeneous precipitation of molybdenum oxinate but also to prevent hydrolysis of other cations. Increasing the quantities of tartaric acid strikingly improved the physical characteristics of the precipitate, a dense orange yellow precipitate is obtained at tartaric acid concentration of 3.5 g/70 mg molybdenum as against a bulky light yellow precipitate with 0.25 g/70 mg molybdenum. However, at higher tartaric acid concentration of greater than 1 g/70 mg molybdenum, the initial pH also has to be increased for rapid and quantitative precipitation.

Effect of oxine concentration: It was observed that about 10 ml oxine/70 mg molyb-

denum, which amounts to a slight excess of the stoichiometric quantity is sufficient for quantitative precipitation.

Effect of final volume: It was observed that about 70 mg molybdenum could be precipitated as its oxinate from a total volume of 50, 100, 150, 200 and 300 ml. A volume of 150 ml was chosen by the authors as a matter of convenience.

Filtration and drying: The precipitates obtained were coarse and easily filterable. Sintered glass crucibles of porosity No.4 are recommended. Fairly accurate results were obtained by drying the precipitate at 120° C for 1 h. Minor variations in temperature (110 - 150° C) and prolonged heating of the sample (24 h) did not have any effect on the accuracy of the results.

Molybdenum in pure solutions was estimated by the homogeneous precipitation method and typical results are shown in Table 1. All the results are taken as average of four experiments.

Table 1 Estimation of molybdenum in pure solutions

Molybdenum taken/ mg	Molybdenum found/ mg	Average deviation/ mg
13.4	13.2	0.2
26.9	26.8	0.1
40.3	40.4	0.1
53.8	53.7	0.1
67.2	67.1	0.1

Separation studies

The applicability of the procedure was tested in the presence of possible interfering cations such as monovalent Na, bivalent Sr, Ba, Ca, Cd, Cu, Ni, Mn, Zn, Co, Pb, Be, trivalent Fe, Al, Cr, Bi, pentavalent V, hexavalent U and anions such as Cl^- , SO_4^{2-} and PO_4^{3-} . The following procedures are arrived at after a number of experiments.

In the presence of individual interfering ions: Transfer the solution containing 70 mg molybdenum along with equal amount of the interfering ion to a 250 ml beaker. Add 10 ml tartaric acid, 20 ml urea and 20 ml EDTA solutions and adjust the pH to 2.3. Add 10 ml oxine, dilute to 150 ml and heat on a boiling water bath for 3 h. Filter and dry the precipitate as described above. Addition of EDTA is not required if Ca, Ba, and Sr are present either individually or as a mixture. In the case of copper about 60 ml of EDTA are required to prevent interferences. Vanadium can be masked by EDTA only after reducing the vanadium(V) to vanadium(IV) at pH 1 with sodium sulphite. The results are shown in Table 2.

In the presence of mixture of cations: Transfer the solution containing 70 mg molybdenum along with 10 mg each of Ca, Sr, Ba, Cd, Cu, Ni, Mn, Zn, Co, Pb, Be, Fe, Al, Cr, Bi, and U to a 250 ml beaker. Add 10 ml tartaric acid, 20 ml urea and 30 ml EDTA and adjust the pH to 2.3. Add 10 ml oxine, dilute to 150 ml and heat on a boiling water bath for 3 h. Filter and dry the precipitate as earlier.

Table 2 Estimation of molybdenum in presence of a number of cations and anions*

Co-existing ion	Molybdenum found/ mg	Average deviation/ mg
Na ⁺	67.1	0.1
Ca ²⁺	67.1	0.1
Ba ²⁺	67.0	0.2
Sr ²⁺	66.9	0.3
Cd ²⁺	67.0	0.2
Cu ²⁺	67.1	0.1
Ni ²⁺	67.2	0.0
Mn ²⁺	67.1	0.1
Zn ²⁺	67.3	0.1
Co ²⁺	66.9	0.3
Pb ²⁺	67.0	0.2
Be ²⁺	67.1	0.1
Fe ³⁺	66.9	0.3
Al ³⁺	67.0	0.2
Cr ³⁺	67.0	0.2
Bi ³⁺	67.1	0.1
V ⁵⁺	67.4	0.2
U ⁶⁺	66.9	0.3
Cl ⁻	67.1	0.1
SO ₄ ⁴⁻	67.1	0.1
PO ₄ ³⁻	67.3	0.1
Mixture**	67.3	0.1

* Molybdenum taken = Co-existing ion added = 67.2 mg

** Mixture of cations: 10 mg each of Ca, Sr, Ba, Cd, Cu, Ni, Mn, Zn, Co, Pb, Be, Fe, Al, Cr, Bi, and U

It is well known that molybdenum forms a complex with tartrate⁵⁾. The present studies establish that the slow release of molybdenum from its tartrate complex due to gradual increase in pH caused by urea hydrolysis is good enough for the quantitative and homogeneous precipitation of molybdenum oxinate. The precipitate conforms to the formula reported in literature, i.e. $\text{MoO}_2(\text{C}_9\text{H}_6\text{ON})_2$. The homogeneous precipitation method is particularly advantageous for separation of molybdenum owing to its high accuracy and reproducibility in comparison with the direct addition method. It was reported by Pribil and Malat⁴⁾ that a 6-10 fold excess of EDTA is required to mask the cations. In the present method it was found that a slight excess of EDTA over the stoichiometric ratio is sufficient except in the case of copper where six fold excess is found necessary.

The results from Table 1 indicate that the method gives very accurate re-

sults. Though a starting pH of 2.3 was recommended the method can be applied in the initial pH range of 1.4 - 2.5. At lower pH (less than 2) the solutions are to be heated for longer periods; for pH values less than one quantitative precipitation was not obtained even after 6-7 h heating. Precipitates with superior physical characteristics were obtained with lower initial pH or with higher tartaric acid concentration at higher initial pH. The developed method is a compromise of these two variables so that quantitative precipitation is obtained in a reasonable length of time. Sometimes a white crystalline precipitate gradually separates out when disodium salt of EDTA⁵⁾ is added to a solution containing molybdenum and tartaric acid. This may be due to the induced precipitation of ammonium tartrate by sodium ions from EDTA⁵⁾. This precipitate however, dissolves on heating and does not interfere in the molybdenum estimation. The formation of ammonium tartrate can be prevented by adding EDTA just before pH adjustment. The subsequent steps of addition of oxine and heating are performed immediately thereafter.

From Table 2, the advantage of the method is clearly seen for the determination of molybdenum in the presence of several interfering ions. A single step determination of molybdenum in the presence of 16 cations was also reported. Even though determination of molybdenum was reported upto 70 mg only, the method can also be employed for the determinations in the range of 70-100 mg with the correspondingly increased amounts of tartaric acid, urea and oxine.

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