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Gravimetric Determination of Molybdenum(VI) with *N*-*o*-Tolyl-*o*-methoxybenzohydroxamic Acid by Direct Weighing

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A gravimetric determination of molybdenum(VI) in presence of various foreign ions has been made by precipitation with *N*-*o*-tolyl-*o*-methoxybenzohydroxamic acid. The sample containing 5—20 mg of molybdenum was quantitatively precipitated in 0.025—2.5 mol/dm³ hydrochloric acid medium. The complex having the composition MoO₂(C₁₅H₁₄NO₃)₂ was weighed directly after drying at 120 °C. The method has been applied for the determination of molybdenum in steel.

N-Phenylbenzohydroxamic acid¹ and some of its analogues^{2,3} have been used for the gravimetric determination of molybdenum(VI). Further investigations have been carried out to discover if other reagents with similar atomic groups would be equally useful. It is well known that improvements in selectivity might be brought about by the introduction of a suitable substituent into the hydroxamic acid functional group. In the present investigation *N*-*o*-tolyl-*o*-methoxybenzohydroxamic acid is found to be a suitable reagent for the gravimetric determination of molybdenum(VI).

The present paper describes the gravimetric determination of molybdenum(VI) in presence of several foreign ions. The metal factor is 0.1498. Thus small quantities of molybdenum can be determined rapidly with a good degree of accuracy. The method has been applied for the determination of molybdenum in steel.

EXPERIMENTAL

Reagent Solution. — *N*-*o*-Tolyl-*o*-methoxybenzohydroxamic acid was prepared by the reported method⁴. A 2% (*w/v*) solution of the reagent in ethanol was used for precipitation.

Standard Molybdenum(VI) Solution. — Standard molybdenum(VI) solution was prepared by dissolving a weighed amount of analytical grade ammonium molybdate in water and determining the molybdenum content by the oxine method⁵.

Foreign Ions. — Standard solutions of foreign ions employed were prepared by the method of West⁶.

All other chemicals used were of analytical grade.

Recommended Procedure. — A solution containing 5—20 mg of molybdenum was diluted to 200 cm³ and the acidity was adjusted between 0.1 to 2.0 mol/dm³ with 10 mol/dm³ hydrochloric acid. The solution was heated to 60 °C and the reagent solution (10—15 cm³) was slowly added with constant stirring. The white precipitate of molybdenum complex thus obtained was digested on a water bath at 60 °C for

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30 minutes with occasional stirring. The precipitate was filtered through a sintered glass crucible of porosity G₃ and washed thoroughly with 0.05% reagent solution (prepared by dissolving 50 mg of reagent in about 10 cm³ of ethanol and diluting to 100 cm³ with water containing 1 cm³ of 10 mol/dm³ hydrochloric acid) and finally with 0.01% reagent solution. The precipitate was dried at 120 °C and weighed to a constant weight. The molybdenum content in the complex was determined using the factor 0.1498.

RESULTS AND DISCUSSION

Properties and Composition of the Complex. — The creamy white molybdenum complex is insoluble in water, dilute acetic acid and 20% aqueous alcohol and slightly soluble in benzene and carbon tetrachloride. It is freely soluble in chloroform and acetone. The complex decomposes when treated with concentrated mineral acids or on heating at 220 °C. The pure complex was analysed for molybdenum by igniting a known weight of it to the trioxide (molybdenum found 14.89%; theor. 14.98%) and for nitrogen by Kjeldahl method (nitrogen found 4.56%; theor. 4.37%). These results indicate that its composition is MoO₂(C₁₅H₁₄NO₃)₂.

Effect of Reagent Concentration. — The precipitation of molybdenum was carried out using different amount of the reagent, other conditions remaining the same. It was found that the least amount of reagent required for complete precipitation of metal was about thrice the theoretical amount.

Effect of acidity. — The effect of acidity on the precipitation of molybdenum was studied and it was found that molybdenum (VI) was quantitatively precipitated in the range 0.025 to 2.5 mol/dm³ hydrochloric acid medium (Table I).

TABLE I
Effect of Acidity

HCl mol/dm ³	Mo taken mg	Mo complex mg	Mo found mg	Error mg
0.02	14.90	98.54	14.76	-0.14
0.025	14.90	99.00	14.83	-0.07
0.03	14.90	99.34	14.88	-0.02
0.05	14.90	99.67	14.93	+0.03
0.10	14.90	99.14	14.85	-0.05
0.50	14.90	99.54	14.91	+0.01
1.00	14.90	99.34	14.88	-0.02
1.50	14.90	99.27	14.87	-0.03
2.00	14.90	99.60	14.92	+0.02
2.50	14.90	99.07	14.84	-0.06

Effect of foreign ions. — Interference studies were made by mixing an aliquot of the standard molybdenum solution with a known amount of a desired foreign ion and molybdenum was precipitated and determined by the recommended procedure. A number of foreign ions were found not to interfere in the strong acid medium (1–2 mol/dm³). In certain cases masking agents were employed. Fluoride ion attacks the glass crucibles used in acidic media and hence in these cases collection of the complex on paper and ignition to trioxide at 500–525 °C was necessary. The results of these studies are given in Table II.

TABLE II

Effect of Foreign Ions
(Acidity 1—2 mol/dm³ HCl, Molybdenum taken 14.90 mg)

Ions added mg	Masking agent added/mg	Mo complex mg	Mo found mg	Error mg
Al(III) (50), Mg(II) (50)	—	99.40	14.89	—0.01
Be(II) (50), Bi(III) (50)	—	99.27	14.87	—0.03
Cu(II) (75), Co(II) (75)	—	99.34	14.88	—0.02
Ni(II) (75), Mn(II) (75)	—	99.27	14.87	—0.03
Tl(I) (100), Se(IV) (100)	—	99.60	14.92	+0.02
Zn(II) (80), Hg(II) (80)	—	99.34	14.88	—0.02
Ga(III) (50), In(III) (50)	—	99.20	14.86	—0.04
As(III) (50), Cd(II) (50)	—	99.54	14.91	+0.01
Ca(II) (100), Sr(II) (100)	—	99.27	14.87	—0.03
Cr(III) (50), U(VI) (100)	—	99.40	14.89	—0.01
La(III) (60), Ce(III) (60)	—	99.20	14.86	—0.04
Ce(IV) (60), Th(IV) (60)	—	99.60	14.92	+0.02
Fe(III) (100), V(V) (30)	Ascorbic acid (300)	99.20	14.86	—0.04
Zr(IV) (50), Hf(IV) (50)	Oxalic acid (300)	99.14	14.85	—0.05
Sn(IV) (50), Zr(IV) (50)	NH ₄ HF ₂ (300)	*	14.87	—0.03
Ti(IV) (50), Nb(V) (50)	NH ₄ HF ₂ (300)	*	14.86	—0.04
Thiocyanate (50)	—	99.34	14.88	—0.02
Phosphate (200)	—	99.27	14.87	—0.03
Fluoride (200)	—	*	14.86	—0.04
EDTA (500)	—	99.60	14.92	+0.02
Oxalate (500)	—	99.40	14.89	—0.01
Tartrate (500)	—	99.34	14.88	—0.02

* Ignition to MoO₃.

Separation of Molybdenum from Tungsten. — Molybdenum(VI) has been separated from tungsten(VI) at pH 1.5—2.0 in the presence of tartrate. An aliquot of the standard solution of molybdenum and tungsten were mixed and diluted to 200 cm³ with water and 10 cm³ of 10% sodium potassium tartrate solution was added. The solution was heated to 60 °C after adjusting the pH to 1.5—2.0. Molybdenum was precipitated and determined as described before. Tungsten remained in solution at pH 1.5—2.0 and did not interfere. The recovery of molybdenum was 99.9%.

Determination of Molybdenum in Steel. — About 0.5 mg of a steel sample was accurately weighed into a 400 cm³ beaker and 20 cm³ of aqua-regia was added to it. The beaker was covered with a watch glass. After completion of the brisk reaction the contents were heated gently over a hot plate, evaporated to small volume and cooled. Then 5 cm³ of concentrated sulphuric acid was added and heated to fumes to drive off nitric acid. To the a cold pasty mass about 100 cm³ of water was added and heated for a while to dissolve the soluble salts. About 1.5 mg of tartaric acid was added and the solution rendered slightly ammonical to dissolve any precipitated MoO₃ or WO₃ as their ammonium salts. Any insoluble matter was filtered off and the solution was then rendered neutral by boiling and cooled. The solution was transferred into a 100 cm³ volumetric flask and made upto the mark.

A suitable aliquot of the steel solution was diluted to 200 cm³ and the acidity was adjusted to 1—2 mol/dm³ with 10 mol/dm³ hydrochloric acid. Then 1 mg of ascorbic acid was added and the solution heated to 60 °C. Molybdenum was precipitated and estimated as described before.

Since molybdenum can be separated from tungsten only at pH 1.5—2.0, tungsten will also be precipitated along with molybdenum in 1—2 mol/dm³ hydrochloric acid medium. Therefore for tungsten steels a combined precipitate of molybdenum and tungsten was collected on paper, washed well with 0.05% reagent solution and ignited at 500—525 °C. The mixed oxides were then dissolved in dilute ammonia solution and any insoluble matter was filtered off, then 10 ml of 10% sodium potassium tartrate solution was added and molybdenum was precipitated at pH 1.5—2.0. The results of the analysis are given in Table III.

TABLE III
Determination of Molybdenum in Steel

B.C.S Steel No.	Composition of steel	Mo certified	Mo found*	Standard
		value	%	deviation
		%	%	%
48 bG	Mo, 55.7; Cu, 0.56%	55.7	55.65	±0.060
64 a	V, 1.57; Cr, 4.40; Mo, 4.11; W, 5.66%	4.11	4.02	±0.054
64 b	V, 1.99; Cr, 4.55; Mo, 4.95; W, 7.05%	4.95	4.88	±0.065

* Average of 5 analysis.

Precision and Accuracy. — The standard and relative standard deviations for ten determination of molybdenum (containing 14.9 mg of metal) with *N*-*o*-tolyl-*o*-methoxybenzohydroxamic acid were found to be ± 0.018 mg and ± 0.12% respectively.

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SAŽETAK

Gravimetrijsko određivanje molibdena(VI) s *N*-*o*-tolil-*o*-metoksibenzohidroksamskom kiselinom i njegova primjena na čelik

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Molibden(VI) u prisutnosti različitih iona određen je gravimetrijski, taloženjem s *N*-*o*-tolil-*o*-metoksibenzohidroksamskom kiselinom. Uzorci sadržaja 5—20 mg molibdena kvantitativno su taloženi u 0,025—2,5 mol/dm³ HCl. Kompleks sastava MoO₂(C₁₅H₁₄NO₃)₂ vagan je nakon sušenja pri 120 °C. Metoda je primijenjena za određivanje molibdena u čeliku.

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