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Gravimetric Determination of Tungsten(VI) in Presence of Other Ions and Its Application to Alloy Steel

By

B. S. Chandravanshi and V. K. Gupta

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Some organic reagents have been used in the gravimetric determination of tungsten¹⁻⁶, but the scope of application of these methods is limited. The use of *N*-phenylbenzohydroxamic acid (PBHA) has also been recommended⁷ but the method is neither selective nor sensitive. According to the data given in the literature⁸ several ions such as Nb, Ta, Ti(IV), Zr, Hf, Sn(IV), Mo(VI) and Ge, would interfere under the conditions used.

It has been found that by suitably substituting an organic reagent the selectivity and sensitivity of the reagent can be modified. It was thought that substitution in the ortho-position of the two phenyl rings of PBHA, might produce more sensitive and selective reagents because of the steric effect of ortho substituents. Hence *N*-*o*-tolyl-*o*-methoxybenzohydroxamic acid, having ortho substituents in both rings has been examined and found to be a highly selective reagent for the gravimetric determination of tungsten(VI).

The present paper describes its use for the gravimetric determination of tungsten(VI) in presence of several foreign ions. Tungsten has been determined in alloy steels with satisfactory results.

Experimental

Reagents

N-*o*-Tolyl-*o*-methoxybenzohydroxamic acid. The reagent was prepared by the reported method⁹, m. p. 102° (reported 100°). A 2% solution of the reagent in ethanol was used.

Tungsten solution. Prepared by dissolving a known amount of analytical grade sodium tungstate in water and standardized by the 8-hydroxyquinoline method.

Foreign ions. Solutions were prepared according to West¹⁰.

Sodium potassium tartrate, 10% solution.

All other chemicals used were of analytical-reagent grade.

General Procedure

A suitable portion of standard tungsten solution was diluted to 200 ml in a 400-ml beaker and heated to 60°; 10 ml of 2% reagent solution were slowly added, with stirring, and the hydrochloric acid concentration was adjusted to between 0.1 and 1.2 M by addition of the concentrated acid. The white crystalline precipitate which separated out was digested on a water-bath at 60° for 30 min with occasional stirring. The precipitate was allowed to settle, collected on a sintered-glass crucible (porosity 3), washed thoroughly with 0.05% reagent solution (50 mg of reagent dissolved in about 10 ml of ethanol and diluted to 100 ml with water) and finally with 0.01% reagent solution. The precipitate was dried at 115° to constant weight. The metal content was determined by using the factor 0.2525.

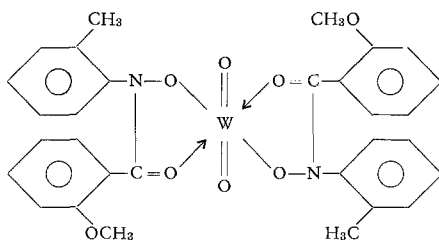
Results and Discussion

Properties and Composition of the Complex

The freshly precipitated complex is white and crystalline, becoming dirty white on drying. It is insoluble in water, dilute acetic acid and aqueous alcohol (10%), and slightly soluble in benzene and carbon tetrachloride. It is highly soluble in chloroform and acetone. The complex decomposes when heated to 210° or when treated with concentrated mineral acid.

The pure dried complex was analysed for tungsten by igniting a known weight of it to tungsten trioxide. The carbon, hydrogen and nitrogen contents were estimated by the usual combustion methods. The tungsten complex was found to have the composition $\text{WO}_2(\text{C}_{15}\text{H}_{14}\text{NO}_3)_2$ (found W, 25.18%; C, 49.0%; H, 4.1%; N, 3.7%; calculated W, 25.25%; C, 49.46%; H, 3.87%; N, 3.84%). The conversion factor to tungsten is 0.2525. The structure of the complex

is presumed to be as under:



Amount of Reagent Needed

Tungsten was precipitated with different amounts of the reagent, the other conditions remaining the same. It was found that the least amount of reagent required for complete precipitation was about thrice the theoretical amount.

Effect of Acidity

Studies on the determination of tungsten(VI) at different acidities, with all other factors kept constant, revealed that the precipitation starts at an acidity of 0.025 *M* hydrochloric acid and is quantitative in the range 0.1–1.2 *M* hydrochloric acid.

In the presence of tartrate the precipitation starts at 0.1 *M* acid and is quantitative at hydrochloric acid concentrations between 0.4 and 1.5 *M*, the maximum error being 0.4%.

Effect of Foreign Ions

An aliquot of tungsten solution was mixed with a known amount of a foreign ion and diluted to 200 ml. The acidity was adjusted to 1 *M* with 10 *M* hydrochloric acid. Tungsten was precipitated and estimated by the general procedure. In 1 *M* hydrochloric acid a considerable number of cations and anions were found not to interfere. In certain cases masking agents were added. Fluoride in acidic media attacks the glass crucibles used and hence in these cases collection of the precipitate on paper and ignition to trioxide at 800–850° is necessary. The results of the studies are given in Table I.

Separation of Tungsten From Molybdenum

Since in the presence of tartrate tungsten(VI) is not precipitated with the reagent at hydrochloric acid concentrations below 0.1 M, tungsten can easily be separated from molybdenum(VI) by prior

Table I. Effect of Foreign Ions
(Acidity = 1.0 M HCl, tungsten taken = 16.20 mg)

Ions added (mg)	Masking agent added (mg)	W found (mg)	Error (mg)
Al(III) (60), Mg(II) (60)	—	16.18	−0.02
Be(II) (60), Bi(III) (60)	—	16.15	−0.05
Cu(II) (80), Co(II) (80)	—	16.17	−0.03
Ni(II) (80), Mn(II) (80)	—	16.19	−0.01
Tl(I) (100), Se(IV) (100)	—	16.15	−0.05
Zn(II) (80), Hg(II) (80)	—	16.18	−0.02
Ga(III) (100), In(III) (100)	—	16.23	+0.03
As(III) (60), Cd(II) (60)	—	16.16	−0.04
Ca(II) (100), Sr(II) (100)	—	16.19	−0.01
Cr(VI) (50), U(VI) (100)	—	16.17	−0.03
La(III) (60), Ce(III) (60)	—	16.19	−0.01
Ce(IV) (60), Th(IV) (60)	—	16.16	−0.04
Fe(III) (80), V(V) (30)	Ascorbic acid (300)	16.22	+0.02
Zr(IV) (50), Hf(IV) (50)	Oxalic acid (300)	16.17	−0.03
Sn(IV) (50), Zr(IV) (50)	NH ₄ HF ₂ (300)	16.24*	+0.04
Ti(IV) (50), Nb(V) (50)	NH ₄ HF ₂ (300)	16.18*	−0.02
EDTA (500)	—	16.16	−0.04
Phosphate (500)	Tartrate (500)	16.15	−0.05
Fluoride (100)	—	16.17*	−0.03
Oxalate, tartrate (500 each)	—	16.21	+0.01
Thiocyanate (50)	Tartrate (500)	16.16	−0.04

* Ignition to WO₃.

precipitation of molybdenum with the reagent at low acidity. Tungsten can be subsequently precipitated from the filtrate after raising the acid concentration.

Aliquots of standard solutions of molybdenum and tungsten were mixed and diluted to 200 ml with water and 10 ml of 10% sodium potassium tartrate solution were added. The solution was heated to 60° and molybdenum precipitated by addition of reagent solution at pH 1.5—2.0. The precipitate was digested at 60°, filtered

off and washed with 0.1% reagent solution. The filtrate and washings were then concentrated to about 200 ml and filtered if any

Table II. Separation of Tungsten From Molybdenum

Mo taken, mg	Mo found*, mg	Error, mg	W taken, mg	W found, mg	Error, mg
8.10	8.11	+0.01	40.80	40.74	-0.06
12.80	12.78	-0.02	28.50	28.53	+0.03
20.70	20.67	-0.03	20.70	20.68	-0.02
23.40	23.42	+0.02	16.80	16.77	-0.03
30.60	30.56	-0.04	11.60	11.59	-0.01

* Conversion factor (molybdenum/molybdenum complex) is 0.1498.

organic matter separated during the concentration. Tungsten was then precipitated and estimated as before. Recovery of molybdenum and tungsten was 99.9% (Table II).

Determination of Tungsten in Steels

About 0.5 g of steel was weighed into a 400-ml beaker and 20 ml of aqua regia were added. The beaker was covered, and after completion of the brisk reaction the beaker was heated gently on a hot-plate, the solution being evaporated to small volume and then cooled. Then 5 ml of concentrated sulphuric acid were added and heated to fumes to drive off nitric acid. To the cooled pasty mass about 100 ml of water were added and heated for a while to take up soluble salts. About 1.5 g of tartaric acid were added and the solution was rendered slightly ammoniacal to dissolve any precipitated MoO_3 or WO_3 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-ml standard flask and made up to the mark. A suitable aliquot of the solution was diluted to 200 ml and the acidity adjusted to 1M with 10M hydrochloric acid, 1 g of ascorbic acid was added and the solution heated to 60°. Tungsten was precipitated and estimated as described above.

Since iron and vanadium cannot be masked with ascorbic acid at an acidity below 0.5N and molybdenum can be separated from tungsten only at pH 1.5—2.0, it was precipitated along with the tungsten. Therefore, the combined tungsten and molybdenum precipitate was

collected on paper, washed well with reagent solution and ignited at 800—850°. The oxides were then dissolved in dilute ammonia solution, 10 ml of 10% sodium potassium tartrate were added and the tungsten was separated from molybdenum and estimated as

Table III. Determination of Tungsten in Steel

	Steel sample B. C. S. No.		W, certified value %	W found* %
1.	64 a	C, 0.80; V, 1.57; Cr, 4.40; Mo, 4.111; W, 5.66%	5.66	5.42
2.	64 b	V, 1.99; Cr, 4.55; Mo, 4.95; W, 7.05%	7.05	6.88
3.	241/1	Cu, 0.1; C, 0.85; Si, 0.33; Sn, 0.025; P, 0.021; S, 0.033; V, 1.57; Cr, 5.03; Mo, 0.52; W, 19.61; Mn, 0.295; Co, 5.67; Ni, 0.075%	19.61	19.47

* Average of 3 analyses.

already described. The results are given in Table III. There is a small negative bias of about 0.2% absolute, irrespective of the amount of tungsten present.

Precision and Accuracy

The relative standard deviation for ten determinations of tungsten (15.4 mg) was 0.2%.

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Summary

Gravimetric Determination of Tungsten(VI) in Presence of Other Ions and Its Application to Alloy Steel

N-o-Tolyl-o-methoxybenzohydroxamic acid has been used for the gravimetric determination of tungsten(VI) by direct weighing of the complex. Tungsten(VI) is quantitative precipitated from 0.1—

1.2 M hydrochloric acid medium. The complex (dried at 110—120°) has the definite composition $\text{WO}_2(\text{C}_{15}\text{H}_{14}\text{NO}_3)_2$. The reagent is sensitive and highly selective. Tungsten(VI) can be estimated in presence of several foreign ions and the method is satisfactory for analysing alloy steels.

Zusammenfassung

N-o-Tolyl-o-methoxybenzohydroxamsäure wurde zur gravimetrischen Bestimmung von Wolfram(VI) durch direkte Wägung der Komplexverbindung verwendet. W(VI) wird aus 0,1 bis 1,2 M Salzsäure quantitativ gefällt. Der bei 110—120° getrocknete Komplex hat die Zusammensetzung $\text{WO}_2(\text{C}_{15}\text{H}_{14}\text{NO}_3)_2$. Das Fällungsreagens ist empfindlich und sehr selektiv. W(VI) kann in Gegenwart anderer Ionen bestimmt werden. Die Methode eignet sich für die Stahlanalyse.

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