

Precipitation of molybdenum(VI) with hexamethylenetetramine in presence of phosphate ions

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Hexamethylenetetramine has been employed as a precipitant in acid media for molybdenum determination in presence of phosphate ions. The metal complex is thermally stable and has been assigned the composition $H_3[P^V Mo_{12} O_{40}] \cdot (C_6 H_{12} N_4)_{10} \cdot 3.5 H_2 O$. The method is reproducible with a standard deviation of ~ 0.08 and compares favourably with the existing methods.

Several organic precipitants have been employed for the gravimetric determination of molybdenum, but very few are available for its determination in presence of vanadium and other interfering elements. Though the 8-hydroxyquinoline method is simple and has good reproducibility¹, the non-selective nature of oxine restricts its use. N-Salicylhydroxamic acid² and N-benzoyl-N-phenylhydroxylamine³ also suffer from the same disadvantage. N-Hydroxy-N-p-chlorophenyl-N'-(2-methyl-4-chlorophenyl)benzamidinium hydrochloride has also been used as a chelating agent for molybdenum⁴. Methods based on ignition of Mo-complexes to the oxide of the metal^{5,6} need proper control of temperature because of the appreciable volatility of MoO_3 at higher temperature and are also time consuming.

Though hexamethylenetetramine (hexamine) has earlier been used for analytical purposes⁷, the reagent is being proposed here for the first time as a precipitant for the gravimetric estimation of molybdenum. The method is simple and selective with reasonable accuracy.

Experimental

A stock solution of molybdenum containing 10 mg/ml of the metal ion was prepared by dissolving sodium molybdate dihydrate (E Merck) in distilled water and standardised by 8-hydroxyquinoline method¹. Lower concentrations were prepared by proportionate dilution. A weighed amount of tri-sodium orthophosphate (BDH) was dissolved in distilled water to get a solution containing 1 mg P/ml. For solutions of other cations, their corresponding chlorides and sulphates were used.

A 0.5 M solution of hexamine was prepared in distilled water.

Procedure

To an aliquot of standard molybdenum solution containing ≥ 0.2 mg Mo/ml in a 100 ml beaker was added tri-sodium orthophosphate solution to get Mo/P (w/w) = 20. It was adjusted to contain 0.20-0.26 M HCl (in a final volume of 25 ml), followed by addition of 10-12 ml of hexamine reagent. The solution was stirred for 10 min at room temperature and then cooled at 10-15° for about 15 min. The precipitate was filtered through a sintered glass G-4 crucible and washed with ice-cold water till free from chloride ions. It was dried at 100-120° for one hr and weighed after cooling in the desiccator. The conversion factor to molybdenum is 0.3503.

Results and discussion

Molybdenum, in presence of phosphate ions, forms a white precipitate with hexamine in dilute acid solutions. For different acids, the precipitation decreases in the order: HCl, HNO_3 , H_2SO_4 , CH_3COOH . With hydrochloric acid, it is 85% in the acid range of 0.20-0.26 M and shows a downward trend on further increasing the acidity of the solution containing 0.4 mg Mo/ml, Mo/P = 17 and 0.2 M hexamine. The precipitation of molybdenum has been carried out at varying Mo/P ratios. At Mo/P = 10, 20, 25, the precipitation of molybdenum was found to be 61.5, 92.0 and 86.6% respectively (0.4 mg Mo/ml, 0.25 M HCl, 0.2 M hexamine). Lower results were obtained for higher molybdenum to phosphorus ratios. Other hetero atoms like As, Zr and Ti gave less precipitation in comparison to phosphorus. 0.2-0.24 M hexamine is recommended for effecting complete precipitation. The precipitation starts at 0.12 mg Mo/ml and is maximum if the solution contains ≥ 0.2 mg/ml of the metal ion under the above conditions. Quantitative results are obtained if the temperature is maintained at 10-15° for 15 min after the precipitation has taken place.

It has been concluded on the basis of the above data that ≥ 0.2 mg Mo/ml, Mo/P (w/w) = 20, 0.20-0.26 M HCl, 0.20-0.24 M hexamine in a final volume of 25 ml, stirring for 10 min at room temperature and cooling for 15 min at 10-15°, are the optimum conditions for the quantitative precipitation (99.2%) of molybdenum.

Effect of foreign ions

Cr(VI), U(VI), V(V), Se(IV), Fe(II), Mn(II) and Cu(II) up to 4 mg/ml; Zn(II), 2 mg/ml; As(V), Th(IV), Zr(IV), Ru(III), Cr(III), Fe(III), Co(II), Cd(II), Mg(II) and Be(II), each 0.4 mg/ml; Re(VII), 0.04 mg/ml, and Pd(II), 0.004 mg/ml do not have any influence on the precipitation, W(VI) and Bi(III) interfere. The precipitation is not affected by the presence of sulphate, nitrate and chloride (4 mg/ml of their sodium salts). Acetate (4 mg/ml), fluoride (0.8 mg/ml) and tartrate (0.4 mg/ml) decrease it by 4, 9, 24% respectively. Oxalate and citrate (4 mg/ml) inhibit precipitation.

Composition of the precipitate

The dried complex was analyzed for molybdenum by dissolving a weighed amount in hot dilute hydrochloric acid and estimating the metal ion by oxine method^{7b}. Phosphorus was determined repeatedly by phosphomolybdenum blue⁸ method. The results obtained were found to vary in the range 0.88-0.92% and, therefore, the average value was taken as 0.9%. Carbon, hydrogen were estimated by combustion method and nitrogen by Kjeldahl's method. This elemental analysis is consistent with formula, $H_3(P^V Mo_{12} O_{40}) \cdot (C_6 H_{12} N_4)_{10} \cdot 3.5 H_2 O$ i.e. $[(C_6 H_{12} N_4 H^+)_{10} [P^V Mo_{12} O_{43.5}]]$ [Found: Mo, 36.0%; P, 0.9%; C, 21.0%; H, 3.86%; N, 17%. Required: Mo, 35.03%; P, 0.94%; C, 21.89%; H, 3.95%; N, 17.03%].

The compound was dried at 120°. Hexamine, acting as a weak base, forms a salt with 12-molybdophosphoric acid which is insoluble in water, alcohol, acetone, ether, chloroform, benzene, carbon tetrachloride and acetic acid. It is soluble in conc. H_2SO_4 , NaOH and on heating dissolves in HCl, dilute H_2SO_4 , conc. HNO_3 .

The validity of the method was tested by its application to several synthetic sample mixtures (Table 1). The results under 'Mo found' were obtained by correcting the weight of the precipitate for 99.2% precipitation and multiplying by the factor 0.3503. They are in satisfactory agreement with 'Mo taken'; samples were taken so as to give a concentration of molybdenum ≥ 0.2 mg/ml in the solution for analysis.

This is the first use of phosphomolybdic acid as well as hexamine for the gravimetric determination of molybdenum. The method is very simple and compares favourably with the existing methods^{1,2,7a,9,10} with regard to reproducibility, simplicity and freedom from interference from a large number of other ions. W(VI) interferes, but other equally im-

Table 1—Analysis of samples by the proposed method

Sample No.	Sample composition		Mo found (mg)
	Matrix*	Mo (mg)	
1	Re(1)	40.2	40.2
2	V(10)	15.0	14.60
3	Cd(10), Zn(40)	50.0	49.85
4	V(5), Cr(10)	10.6	10.66
5	Cu(20), Ni(10)	30.3	30.13
6	Cr(20), V(10)	10.5	10.41
7	Fe(10), U(10), Co(5)	18.2	18.01
8	Se(10), Ru(5), Pd(0.1)	70.1	69.65
9	Mn(10), Zn(10), Ni(5)	13.1	13.02
10	Zr(5), As(10), Mg(5), Be(5)	22.5	22.43
11	$[Fe(4), Si(34), S(0.01), Cu(8.42), Al(0.37)]^\dagger$	60.0	59.86
12	$[Fe(6), Ni(50), Cr(100), Co(50), Al(12), Ti(12)]^\dagger$	29.85	29.84

*Figure in brackets represents the amount of metal ion in mg.

†Sample nos 11 and 12 correspond to molybdenum silicide and minonic 80 respectively.

portant elements like chromium and vanadium do not cause interference.

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