

Ferron as an Analytical Reagent for Extractive Separation of Molybdenum

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Molybdenum forms an yellow coloured complex with ferron. This coloured complex is extractable in 1% tribenzylamine-chloroform mixture from aqueous acidic solution containing ascorbic acid. This forms the basis of the selective method for the separation of molybdenum. The method overcomes the interference due to Re(VII), W(VI), U(VI), Cr(III), VI, V(V), Ce(IV), Th(IV), Ru(III), Co(II), Ni(II), Fe(II), Mn(II), Mg(II), Cd(II), Pb(II), SO_4^{2-} , Cl^- , NO_3^- , PO_4^{3-} and $\text{C}_2\text{O}_4^{2-}$ Zr(IV) and Pd(II) interfere. The ratio of molybdenum : ferron : tribenzylamine in the extracted species is found to be 1 : 1 : 3.

Molybdenum, both in the pentavalent and hexavalent states, is extractable into chloroform as 8-hydroxyquinoline¹ and 8-hydroxy-2-methylquinoline² chelates. 8-Mercaptoquinoline³ has also been used for the extraction of molybdenum. All these methods suffer from several interferences and, therefore, have serious limitations in their applications to various technical samples.

In the present work, a highly selective method of separation of molybdenum is proposed. This involves extraction of an yellow coloured complex formed by molybdenum with 7-iodo-8-hydroxyquinoline-5-sulphonic acid (ferron) into tribenzylamine-chloroform.

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 gravimetrically by the oxine method⁴. Solutions of lower concentrations are prepared by suitable dilution. Stock solution (5 or 10 mg/ml) of other elements were prepared by dissolving their commonly available salts (CP grade). A 0.5% solution of ferron (Riedel) was prepared in 1 : 1 water-acetone mixture. Tribenzylamine (TBA) (Fluka) was dissolved in chloroform to give 1% (w/v) solution. Ascorbic acid (S. Merck) was used as such.

Procedure—To a sample solution containing \leq 0.5 mg Mo/ml were added 0.5% ferron solution (10 ml) and 5M sulphuric acid (4ml). The volume was made upto 20 ml with distilled water and to this was added ascorbic acid (100 mg) and the solution shaken for 1 min. The coloured species thus obtained was extracted once by an equal volume of 1% TBA in chloroform if the content of molybdenum was \leq 0.25 mg/ml and twice if the molybdenum content was

$>$ 0.25 mg/ml, each time for 3 min. The organic phase was separated and the metal ion back extracted by shaking twice with an equal volume of water made just alkaline with sodium hydroxide. To the combined aqueous extracts, 4-5 drops of 30% H_2O_2 was added and boiled for 2-3 min. The solution was rendered just acidic with HCl, excess H_2O_2 boiled off and the solution cooled. Milligram amounts of molybdenum in the solution were determined gravimetrically by the oxine method⁴ and micro amounts colourimetrically by the thiocyanate method⁵.

It is observed that under the optimum conditions, viz. an aqueous solution (20 ml) containing 0.5 mg Mo/ml, 10 ml ferron solution and 2N acid, the extraction of the metal ion in different acids decreases in the order H_2SO_4 (99%), CH_3COOH (55%), HCl (40%) H_3PO_4 (35%), HNO_3 (18%). There is practically no extraction from the neutral media. The extraction is 72% at 0.25M and 80% at 0.5-1.25M H_2SO_4 and thereafter decreases with increase in acid concentration (5 ml ferron reagent per 20 ml aqueous volume). With 2, 8 and 10-15 ml of ferron (0.5%), the extraction is 58, 94 and 99% respectively. Upto 0.25 mg Mo/ml, the extraction of molybdenum is 100% and at 0.5 mg/ml it is 99%. At higher concentrations, turbidity results.

Ascorbic acid keeps Cr(VI), V(V) and Fe(III) in solution, while the extraction of molybdenum remains unaffected by its presence even upto 200mg in the aqueous solution.

The extraction is 95% if the equilibration time is 1 min and is 99% for equilibration for 3 min or more.

It is clear from the above observations that for \leq 0.5 mg Mo/ml, 1M H_2SO_4 , 10 ml 0.5% ferron reagent in 1 : 1 water-acetone mixture equilibrating once (twice when $>$ 0.25 mg Mo/ml are present in aqueous solution) for 3 min with an equal volume of 1% tribenzylamine in chloroform (w/v), are the optimal conditions for the quantitative extraction of molybdenum.

The effect of diverse ions on the extraction of Mo(VI)-ferron complex has been studied. W(VI), U(VI), V(V), Th(IV), Ru(III), Cr(III), Co(II), Ni(II), Fe(II), Mn(II), Mg(II), Cd(II), 2.5 mg/ml each; Ce(IV) 1 mg/ml; Pb(II), 0.5 mg/ml; Cr(VI) 0.05 mg/ml; Re(VII) 0.005 mg/ml; are not at all extracted. Zr(IV) (0.5 mg/ml) and Pd(II) (0.05 mg/ml) interfere. Sulphate, chloride, nitrate, phosphate (0.5 g/20 ml as sodium salts) and oxalate (0.1 g/20 ml) do not interfere. EDTA, acetate, tartrate, citrate and fluoride (0.1 g/20 ml) lower the extraction by 0.5, 1, 1.5 and 3% respectively.

The wide scope of the method is tested by the analysis of several synthetic and technical sample mixtures (Table 1) and the results obtained are quite satisfactory. The proposed method compares favourably with the existing methods^{1-3,8-10} of extractive separation of molybdenum.

Table 1—Analysis of Molybdenum in Technical Samples by the Proposed Method

Sample No.	Sample Composition		Mo found
	Matrix*	Mo(mg)	(mg)
1.	Re (0.1)	0.1	0.1
2.	W(1), V(1)	1.5	1.49
3.	Co(10), Ni(5)	1.0	1.05
4.	Th(5), Zr(5)	2.2	2.23
5.	Fe(2), Cr(1)	6.3	6.4
6.	U(10), Ru(5)	10.0	10.10
7.	Mn(5), Mg(10), Zn(5)	5.0	4.95
8.	[Fe(2.9), Ni(0.75), Cr(1), Co(0.005), Mn(0.1), Si(0.05), P(0.0025)]†	0.2	0.198
9.	[Fe(7), Cu(0.1), Ni(0.9), Cr(1.9), C(0.02)]†	0.1	0.099

*Figures in brackets indicate the amount of metal ion in mg;

†Sample Nos. 8 and 9 correspond to stainless steel and stainless U respectively.

Composition of the extracted species—The ratio of molybdenum : ferron : TBA in the extracted species was determined as 1 : 1 : 3 by Job's method⁶ of continuous variations and mole ratio method⁷.

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