



Novel Method for Stripping of Molybdenum (VI) after its Extraction with Cyanex 301

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Abstract: Hydrofluoric acid has been used as a novel stripping agent for molybdenum (VI) after its extraction with Cyanex 301. In the extraction steps effects of parameters such as type and initial concentration of acid, type of diluent, extractant concentration, metal concentration and temperature have been studied. In the stripping step, the effects of various stripping agents on stripping efficiency have been investigated. Also, the effects of concentration of hydrofluoric acid, stripping time, volume of hydrofluoric acid and numbers of stages of stripping have been studied. Molybdenum (VI) has been effectively separated from a large number of elements in binary mixtures with very high tolerance limits. Finally, the optimized method has been extended to the analysis of Mo (VI) in spent molybdenum catalysts.

Keywords: *stripping, molybdenum(VI), cyanex 301*

1-Introduction

^{99m}Mo is the parent of ^{99m}Tc which is extensively used in nuclear medicine. High specific activity ^{99m}Mo is prepared by the neutron irradiation of ^{235}U followed by an appropriate physical or chemical extraction step in which the radio-molybdenum is separated from the irradiated uranium matrix. Methods of molybdenum separation include solvent extraction, sublimation, chemical precipitation and chromatography [1]. In this research we have tried some non-radioactive experiments based on solvent extraction of molybdenum (VI). Many investigations have so far been made on the solvent extraction of molybdenum (VI) from aqueous media containing sulfuric acid[2-8], hydrochloric acid[9-11], nitric acid [12-15] and with different extractants such as crown ethers [16], α -benzoinoxime[17-18], organophosphate or organophosphoric acids[3,11,19], especially di (2-ethylhexyl) phosphoric acid [4,12]. Recently, some organophosphines and their sulfur analogues, have been reported due to their considerable resistance to decomposition by hydrolysis [20], as compared to their phosphoro analogues. Radiolytical stability of Cyanex 301 (one of the organodithiophosphines) and its purified form has been studied [21]. In this paper, we present the extraction behavior of molybdenum(VI) in a wide range of acid concentration (10^{-6} –10 M) in

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sulfuric, hydrochloric and nitric acids. To the best of our knowledge, there is no previous report on stripping of Mo(VI) with HF. In this paper, we propose a simple method for extractive separation of molybdenum(VI) using Cyanex 301 and HF as extractant and stripping agent respectively.

2-Experimental

2-1 Materials and Reagents

In the present reasarch kerosene and the sample of Cyanex 301 containing 85% of bis (2, 4, 4-trimethylpentyl) dithiophosphinic acid (Fluka) are used. Cyanex 301 concentrations mentioned throughout the text are actuallydithiophosphinic acid. Kerosene was used as the diluent throughout this work except in diluent effect experiments. All other chemicals including solvents were of analytical grade (Merck). Doubly distilled and deionized water was used throughout the study.

2-2 Experimental procedure

Batch experiments were performed in a 10 ml flask containing equal volumes of aqueous and organic phases. The mixture was agitated at 25°C , (except in temperature effect experiments), by a temperature controlled mechanical shaker at 300 rpm with $\pm 1^{\circ}$ accuracy. Molybdenum was determined in the



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aqueous phase by ICP-AES (Varian, Liberty 150 AX Turbo). Chemical composition of the organic phase was determined using mass balance calculations. Shaking time those of bis (2, 4, 4-trimethylpentyl) for extraction and stripping processes were 20 minutes and one hour respectively.

3-Results and discussion

3-1 Effect of the type and initial concentration of acid

The extraction behavior of molybdenum (VI) from 10^{-6} to 10^{-1} M solutions of sulfuric, hydrochloric and nitric acids using different concentrations of Cyanex 301 is shown in Figures 1, 2 and 3, respectively.

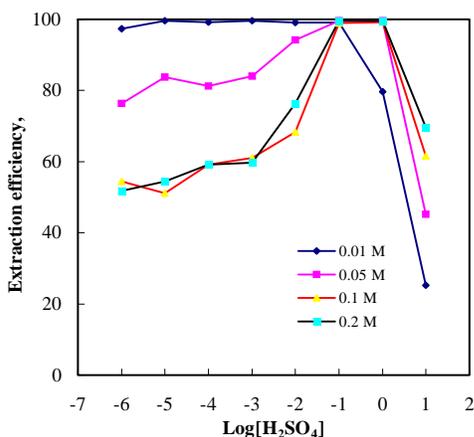


Fig.1 Effect of initial concentration of H_2SO_4 (molar) on extraction efficiency of Mo (VI) [Mo (VI)]= 10^{-4} M, [Cyanex 301] =0.01 & 0.05 & 0.1 & 0.2 M

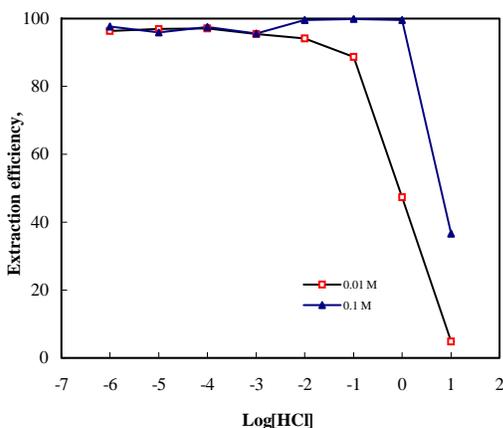


Fig.2 Effect of initial concentration of HCl (molar) on extraction efficiency of Mo (VI) [Mo (VI)]= 10^{-4} M, [Cyanex 301] =0.01 & 0.1 M

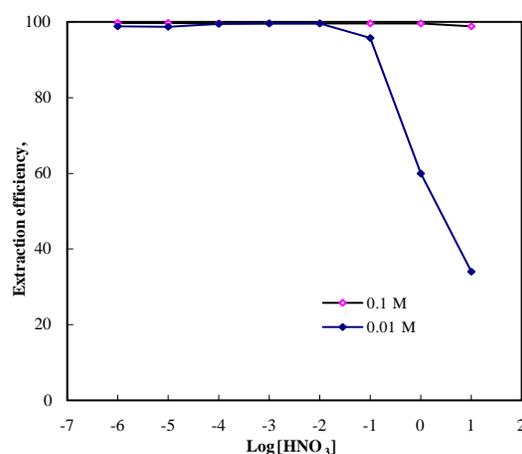


Fig.3 Effect of initial concentration of HNO_3 (molar) on extraction efficiency of Mo (VI) [Mo (VI)]= 10^{-4} M, [Cyanex 301] =0.01 & 0.1 M

3-2 Effect of diluent type

The organic phase diluent can influence the extraction of metals due to both physical and chemical interactions existing between diluent and extractant. The diluent can also affect the economics of a process, thus the suitability of the various diluents for the extraction of Mo(VI) by the proposed method was tested. It was found that the extraction was quantitative with all the chosen diluents. Selection of diluents is also dependent on other parameters such as availability and/or cost. The results obtained and the conditions of extraction are shown in Table 1.

3-3 Effect of extractant concentration

To study the effect of extractant concentration, molybdenum(VI) was extracted

Table 1: Effects of Diluent Type on extraction efficiency

Diluent Type	Dielectric constant	D	E, %
Kerosene	1.8	53.0	98.1
Heptane	1.9	38.1	97.4
Dodecane	2	39.4	97.5
Benzene	2.28	70.3	98.6
Carbon Tetrachloride	2.34	64.7	98.5
Toluene	2.38	54.3	98.1
Chloroform	4.8	34.8	97.2
Dichloro methane	9.08	319.7	99.7
1,2-Dichloro ethane	10.5	508.6	99.8
Nitrobenzene	34.82	118.0	99.2

Extraction conditions: [Mo (VI)]= 10^{-4} M, [HNO₃]=1 M, [Cyanex 301]=0.1 M



from 1 M HNO₃ with varying concentration of Cyanex 301. The Cyanex 301 concentrations were varied from 0.001 to 0.1 M. It was found that the extraction was quantitative at 0.06 M Cyanex 301. The results are shown in Table 2. The log-log plots of distribution ratio versus Cyanex 301 concentrations in 1 M nitric acid gave a slope of 2.3, indicating that the metal to Cyanex 301 ratio in the extracted species is 1:2. Hence, the composition of the extracted species is probably MoO₂R₂.

3-4 Effect of varying metal ion concentration

The effect of metal ion concentration on the extraction of Mo(VI) was investigated from 1 M HNO₃ solution employing 0.06 M Cyanex 301 in kerosene. The results of loading of Cyanex 301 by molybdenum(VI) show that the extraction is quantitative up to 5×10⁻³ M molybdenum(VI). The results obtained are shown in Table 3.

3-5 Effect of temperature

A temperature variation study (25 to 55°C) was carried out on the extraction of molybdenum(VI) at constant acid and Cyanex301 concentrations. It can be seen from Table 4 that the temperature has no significant effect on the extraction efficiency, and hence, it is of no importance at what temperature the extraction is carried out.

3-6 Effect of stripping reagents

Various stripping agents were used in this study. The results Obtained from these experiments are shown in Table 5 and Fig. 4. As can be seen, the results are not very encouraging. Hence further attempts were made to find a novel and effective stripping agent for stripping of Mo(VI). A concentrated HF solution (24.2 M) was found to strip approximately eighty percent of Mo(VI) in a single contact. The results are shown in Table 6. Stripping with ammonia solution (1 to 10 M) and a mixture of ammonium nitrate and ammonia (1 to 10 % NH₄NO₃ in 1:10 NH₄OH) resulted in an emulsion or third phase formation. For expelling HF from stripping solution, 2 ml HClO₄ (71%) was added to the solution and heated at 90°C by successive addition of distilled water. Then the solution

was made up to 10 ml volume. The above procedure was followed wherever necessary.

Table 2: Effect of Cyanex 301 concentration on extraction efficiency

[Cyanex 301], M	D	E, %
0.100	343.2	99.7
0.080	141.5	99.3
0.060	139.2	99.3
0.050	16.4	94.3
0.040	15.2	93.8
0.020	1.3	55.7
0.010	0.5	33.8
0.008	0.4	27.7
0.006	0.3	21.4
0.004	0.2	14.6
0.002	0.1	11.2
0.001	0.1	0.1

[Mo]=10⁻⁴ M, [HNO₃] =1 M

Table 3: Effect of metal ion concentration on extraction efficiency

[Mo]×10 ⁵ , M	D	E, %
10	75.1	98.7
25	47.9	98.0
50	43.4	97.8
75	33.5	97.1
100	37.5	97.4
250	18.3	94.8
500	12.3	92.5
750	5.4	84.3
1000	4.5	82.0

[HNO₃]=1 M, [Cyanex 301] =0.06 M

Table 4: Effect of temperature on extraction efficiency

Temperature, °C	D	E, %
25	87.6	98.9
35	147.4	99.3
45	232.2	99.6
55	232.2	99.6

[Mo (VI)]=10⁻⁴ M, [Cyanex 301] =0.06 M, [HNO₃] =1 M



Table 5: Effect of concentration of various stripping agents on molybdenum (VI) stripping

Stripping agent	Concentration of stripping agent, M	Stripping efficiency, %
HClO ₄	2	0.0
	6	0.0
	10	0.0
Oxalic acid	0.1	1.2
	0.21	2.5
	0.42	2.5
Tartaric acid	0.1	1.8
	2.0	2.5
	0.4	3.0
Cu(NO ₃) ₂ .2H ₂ O	0.1	1.3
	0.2	4.0
	0.5	0.0
FeCl ₃	0.1	0.0
	0.2	1.1
	0.5	0.0
SnCl ₂	0.1	0.0
	0.2	0.0
	0.5	0.0
Sodium Thiosulfate	0.5	0.0
	1	0.0
	2	0.0
Thiourea	0.1	7.1
	0.2	4.4
Methionine	0.1	1.6
	0.2	12.8
Cysteine	0.1	0.6
	0.2	0.4
H ₃ PO ₄	1	0.0
	5	0.0
	9	0.0

Extraction conditions: [Mo (VI)] =10⁻⁴ M, [HNO₃] =1 M, [Cyanex 301] =0.06 M

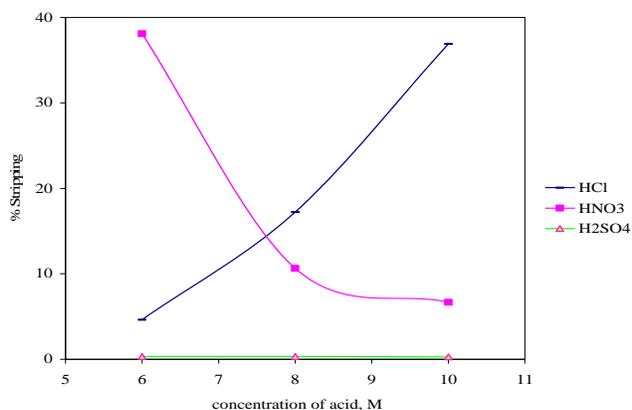


Fig.4 Effect of concentration of acids on stripping efficiency of Mo(VI) Extraction conditions: [Mo (VI)] =10⁻⁴ M, [HNO₃]=1 M, [Cyanex 301] =0.06 M

Table 6: Effect of concentration of HF on molybdenum(VI) stripping

HF, M	Stripping efficiency, %
2.7	16.9
14.5	28.5
16.9	37.5
19.3	48.8
21.7	59.9
24.2	82.6

Extraction conditions: [Mo (VI)] =10⁻⁴ M, [HNO₃] =1 M, [Cyanex 301] =0.06 M

3-7 Effect of NaOH and rate of stripping on stripping efficiency

The effect of NaOH and rate of stripping on molybdenum is shown in table 7. In this experiment, prior to stripping of molybdenum (VI), the organic phase was neutralized with 1 ml of 1 N NaOH (except solutions No.4 and 8). Results show NaOH has an unexpected and an unfavorable effect on the stripping. It is to be expected that free Cyanex 301 in organic phase is neutralized by NaOH and stripping is accomplished easier than before. This table shows that stripping efficiency decreases with increasing stripping time.

3-8 Separation of molybdenum(VI) from binary mixtures

To an aliquot containing a fixed amount of molybdenum (10⁻⁴ M), varying amounts of ions were added to study their interference in the recommended procedure. The tolerance limit was set at the amount of foreign ions required to cause a ±5 percentage error in the recovery of molybdenum(VI). The results are reported in Table 8. in this study, transition metals show

Table 7: Effect of NaOH and stripping time on molybdenum (VI) stripping

Solu. No.	Stripping reagent	Stripping time	Stripping efficiency, %
1	HNO ₃ , 6 M	4 days	1.6
2	HNO ₃ , 6 M	2 days	2.5
3	HNO ₃ , 6 M	1 hour	10.0
4	HNO ₃ ,6M,without NaOH	1 hour	39.4
5	HCl, 6 M	4 days	8.3
6	HCl, 6 M	2 days	38.0
7	HCl, 6 M	1 hour	10.2
8	HCl, 6 M, without NaOH	1 hour	47.0



low tolerance limits compared to other metals. It has to be noted here that Tolerance limits for alkali and alkaline earth metals increases from top to bottom of each group. The organic acid anions were tolerated in lower concentrations compared to inorganic acid anions.

3-9 Recovery of molybdenum(VI) from spent Mo-Co and Mo-Ni catalysts

0.2 gr of the spent catalysts was digested and dissolved. Prior to subjecting the solutions to solvent extraction step, the digested solutions of spent catalysts were diluted forty(A₁) and twenty(B₁) times keeping the acid concentration to 1 M HNO₃. 10 ml aliquots of the solutions A₁ and B₁ were separately equilibrated with 10 ml of 0.1 M Cyanex 301. The raffinate of these solutions were marked as A₂ and B₂. Molybdenum(VI) was subsequently stripped by employing HF (24.2M). The Mo(VI) solutions recovered from the organic phase were marked as A₃ and B₃. The results of analysis are shown in table 9.

4- Conclusions

A novel stripping agent for stripping of Mo(VI) from organic phase is reported in this study. The results reported here show that the extraction efficiency of molybdenum(VI) is dependent on the type and concentration of aqueous phase acid, extractant concentration and metal ion concentration but it is independent on the diluent type and temperature. Molybdenum(VI) can be extracted in the presence of a large number of ions with high tolerance limits, and finally Cyanex 301 is an excellent extractant for molybdenum(VI).

TABLE 8: Separation of molybdenum(VI) from binary mixtures

Ion	Added as	Tolerance limit, mg
NH ₄ ⁺	NH ₄ (NO ₃)	56.22
Na ⁺	Na (NO ₃)	67.60
K ⁺	KCl	52.40
Rb ⁺	RbCl	70.70
Cs ⁺	CsNO ₃	170.48
Mg ²⁺	MgCl ₂ .6H ₂ O	29.89
Ca ²⁺	Ca (NO ₃) ₂ .4H ₂ O	42.43
Sr ²⁺	Sr (NO ₃) ₂	103.51
Ba ²⁺	Ba (NO ₃) ₂	131.40
Y (III)	YCl ₃ .6H ₂ O	73.27
ZrO ²⁺	ZrOCl ₂ .8H ₂ O	1.64
VO ²⁺	VO ₂ SO ₄ .5H ₂ O	15.36
Re (VII)	Re ₂ O ₇	4.92
Fe ³⁺	FeCl ₃	9.06
Os (VIII)	OsO ₄	21.67
Ni ²⁺	NiCl ₂	7.56
Cu ²⁺	Cu (NO ₃) ₂ .3H ₂ O	3.69
Zn ²⁺	ZnCl ₂	5.09
Cd ²⁺	Cd (NO ₃) ₂ .4H ₂ O	5.66
Hg ²⁺	HgCl ₂	8.06
Al ³⁺	Al (NO ₃) ₃ .9H ₂ O	2.08
Sn ²⁺	SnCl ₂ .2H ₂ O	2.00
La (III)	La (NO ₃) ₃ .6H ₂ O	4.31
Ce (III)	Ce (NO ₃) ₂ .6H ₂ O	80.67
Nd (III)	Nd ₂ O ₃	42.90
UO ₂ ²⁺	UO ₂ (NO ₃) ₂ .6H ₂ O	2.25
PO ₄ ³⁻	H ₃ PO ₄	72.49
ClO ₄ ⁻	HClO ₄	98.29
I ⁻	HI	90.99
Br ⁻	HBr	154.66
Cl ⁻	HCl	172.83
SO ₄ ²⁻	H ₂ SO ₄	741.73
C ₂ O ₄ ²⁻	H ₂ C ₂ O ₄ .2H ₂ O	2.78
C ₄ H ₄ O ₆ ²⁻	C ₄ H ₆ O ₆	13.78
C ₆ H ₅ O ₇ ³⁻	C ₆ H ₈ O ₇ .H ₂ O	50.31
CH ₃ COO ⁻	CH ₃ COOH	94.12

[Mo]=10⁻⁴ M, [Cyanex 301]=0.06 M, [HNO₃]=1 M



TABLE 9: Recovery of molybdenum (VI) from spent catalyst

Sample	Metal Ions	Concentration in A ₁ & B ₁ solutions(ppm)	Concentration in A ₂ & B ₂ solutions(ppm)	Concentration in A ₃ & B ₃ solutions(ppm)	Recovery, %	σ*
A	Mo(VI)	10.6	0.0	10.3	97.1	±2%
	Al(III)	90.6	18.9	0.0	0.0	
	B	1.0	0.7	0.3	30.0	
	Co(II)	2.7	0.7	0.0	0.0	
	In	3.1	0.1	0.0	0.0	
	K	6.5	6.4	0.0	0.0	
	Si	48.6	3.1	0.0	0.0	
	Mg	5.1	0.0	0.0	0.0	
	Ca	7.2	0.0	0.0	0.0	
B	Mo(VI)	12.6	0.1	12.0	95.2	±2%
	Al(III)	68.6	67.2	0.0	0.0	
	In**	2.4	0.1	0.0	0.0	
	K	3.4	3.3	0.0	0.0	
	Ni	4.4	4.3	0.0	0.0	
	Si	40.0	4.0	0.0	0.0	
	W [§]	5.5	1.2	0.0	0.0	
	Mg	7.3	6.9	0.0	0.0	

*Standard deviation based on 3 runs.

**Interference was removed by selective stripping with 7 M HCl

§ Masked by Citric acid

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