

Solvent extraction separation of molybdenum(VI) with dibenzo 18-Crown-6 from chloride solutions

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Molybdenum(VI) was quantitatively extracted with 0.01 M dibenzo 18-Crown-6 (DB18C6) in dichloroethane from 3-8 M hydrochloric acid, and was stripped with 0.05 M hydrochloric acid. After dryashing it was determined spectrophotometrically as its complex with Tiron at 390 nm. Other crown ethers such as 15C5, DC18C6 and DB24C8 were ineffective for extraction but with DB18C6 the extraction was quantitative. Amongst diluents only dichloroethane was effective. The stripping was complete with dilute solutions (0.05 M) of hydrochloric acid. Molybdenum(VI) was separated from large number of elements with which it is generally associated in minerals. The method was extended for analysis of molybdenum in real samples. The relative standard deviation was $\pm 1.2\%$.

Molybdenum(VI) in hexavalent state is usually stable, but in other states its hydrolysis leads to complicated behaviour in solvent extraction processes. From 8 M hydrochloric acid, it was quantitatively extracted with methylisobutyl ketone¹ as well as tributyl phosphate², but such extraction decreases with the increase in metal concentration³. Molybdenum(V) was also extracted from thiocyanate media in the presence of reducing agents⁴. The high molecular weight amines such as Aliquat 336 was used for its extraction from ascorbate solutions but such extraction was dependent on the amine concentration⁵. Bis(2-ethyl-hexyl)-phosphoric acid was used for its extraction where stripping of molybdenum was possible with hydrogen peroxide⁶. When toluene 3-4 dithiol⁷ was used, extraction was slow and time-consuming.

So far, no systematic efforts were made to extract molybdenum(VI) with macrocyclic polyethers. Dicyclo-18-Crown-6 (DC18C6) in ethylene chloride was used for the extraction of molybdophosphoric acid from 0.1-0.6 M hydrochloric acid⁸, but several metals showed interference. Therefore, this paper presents a method for solvent extraction of molybdenum(VI) from 3-8 M hydrochloric acid with 0.01 M dibenzo 18-crown-6 in ethylene chloride. Molybdenum from the organic phase was stripped with 0.05 M hydrochloric acid and it was determined spectrophotometrically at 390 nm as its complex with tiron⁹. The proposed method permits separation of

molybdenum from large number of elements associated with it. The method was extended for the analysis of molybdenum in the real samples such as stainless steel and soil sample.

Experimental Procedure

Perkin Elemer Lambda UV visible spectrometer with 10 mm quartz cuvettes, pH meter Elico model with glass and calomel as the reference electrodes.

The stock solution of molybdenum(VI) was prepared by dissolving 2.30 g of ammonium molybdate tetrahydrate (BDH, AnalR) in 250 mL of distilled water. The solution was standardised gravimetrically with 8-hydroxyquinoline¹⁰. It contained 5 mg/mL of molybdenum. A diluted solution containing 40 $\mu\text{g/mL}$ molybdenum was prepared by appropriate dilution.

15 Crown 5 (15C5), dibenzo-18 crown-6 (DB18C6), dicyclohexyl 18-Crown-6 (DC18C6) and dibenzo 24-Crown-8 (DB24C8) (Merck) were used without further purification. Aqueous 0.5% tiron (1,2-dihydroxybenzene 3-5 disulphonic acid disodium salts) was used as the chromogenic reagent for molybdenum(VI).

An aliquot of solution containing molybdenum(VI) (40 μg) was taken. To this solution concentrated hydrochloric acid was added so as to have its concentration as 3-8 M in a total volume of 10 mL. It was then transferred into a separator funnel and 10 mL of 0.01M DB18C6 in ethylene chloride was added to it. It was then shaken

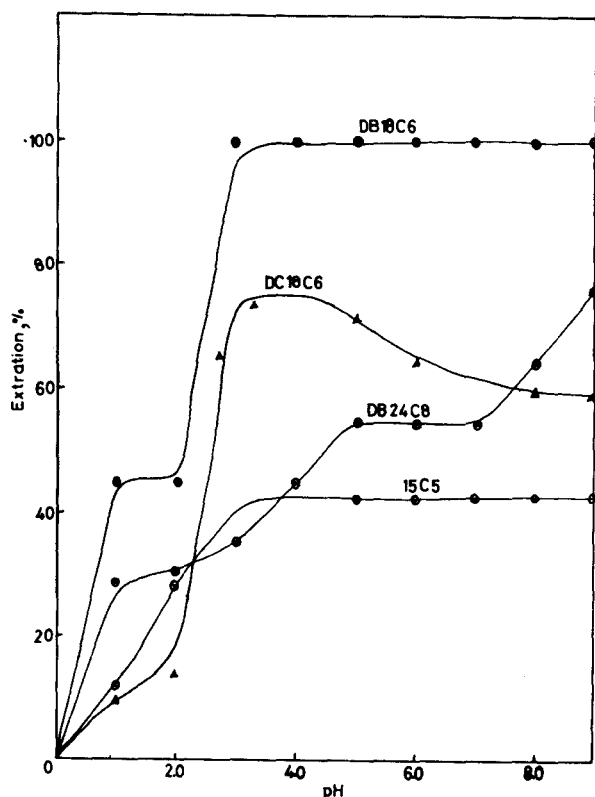


Fig. 1 — Extraction as function of pH with various crown ethers

for about 10 min. The two phases were allowed to settle and separate. The organic phase was carefully withdrawn and once again shaken with equal volume of 0.05 M hydrochloric acid to strip out molybdenum. The aqueous solution was evaporated to dryness to expel acid and the residue was dissolved in water to which 5 mL of buffer solution of pH 7.0 and 2 mL of 0.5% tiron were added. The solution was made up to 25 mL. The orange coloured complex was measured spectrophotometrically at 390 nm against the reagent blank. The amount of molybdenum was calculated from the calibration curve⁹ (Fig. 1).

Results and Discussion

Effect of hydrochloric acid concentration — Molybdenum(VI) was extracted with 0.01 M each of DC18C6, 15C5, DB18C6 and DB24C8 in ethylene chloride from varying concentrations of hydrochloric acid. From 10 M hydrochloric acid solution the extraction was 42.85% with 15C5. It was 59% with DC18C6 and 76.2% with DB24C8. Only with DB18C6 the extraction was quantitative. Therefore, all the extractions were carried out from 3–8 M of hydrochloric acid with 0.01 M DB18C6 in ethylene chloride (Table 1).

Effect of varying concentration of DB18C6 — Molybdenum(VI) was extracted from 3 M hy-

Table 1 — Extraction of molybdenum(VI) as function of hydrochloric acid concentration with various crown ethers

HCl, M	15C5 % E	DC18C6 % E	DB18C6 % E	DB24C8 % E
0.5	6.0	4.72	45.2	20.1
1.0	11.9	9.53	46.7	28.6
2.0	28.6	14.3	46.7	30.9
3.0	40.5	76.2	99.9	35.7
4.0	40.5	76.2	99.9	45.2
5.0	42.8	71.4	99.8	54.8
6.0	42.8	64.3	99.7	54.8
7.0	42.8	64.3	99.8	54.8
8.0	42.8	59.5	99.8	64.3
9.0	42.8	59.5	99.9	76.2
10.0	42.8	59.5	99.9	76.2

Table 2 — Extraction of molybdenum(VI) as a function of DB18C6 concentration

DB18C6 1×10^{-3} M	Extraction % E	Distribution ratio (<i>D</i>)
0.1	59.5	1.47
1.0	60.0	1.47
2.5	66.7	1.94
4.0	76.0	3.20
5.0	78.0	3.50
6.0	80.0	4.00
7.0	85.0	5.60
8.0	88.0	7.40
9.0	96.0	24.0
10.0	99.9	999

drochloric acid with varying concentration of DB18C6 in ethylene chloride. The extraction was 60% with 0.001 M of DB18C6 80% with 0.006 M of DB18C6 while with 0.01 M DB18C6 it was quantitative. Hence all the extractions were carried out with 10 mL of 0.01 M DB18C6 in ethylene chloride (Table 2).

Effect of diluents — Molybdenum(VI) was extracted with 0.01 M DB18C6 in various diluents. Generally the diluents with high dielectric constant favoured extraction with crown ethers. In these studies the nonpolar diluents like benzenes, toluene, xylene and carbon tetrachloride exhibit a poor extraction. The extraction was also incomplete (< 61.9%) even with nitrobenzene and chloroform. However, with ethylene chloride the extraction was quantitative. Therefore, ethylene chloride was preferred as the diluent. This difference in extraction behaviour in the presence of ethylene chloride may be attributed to the exist-

Table 3 — Extractions of molybdenum(VI) with various diluents

Diluent	Dielectric constant	Extraction % E	Distribution ratio (<i>D</i>)
Benzene	2.28	9.5	0.10
Toluene	2.30	7.1	0.08
Xylene	2.38	9.5	0.10
Carbon tetra-chloride	2.24	4.8	0.05
Chloroform	4.80	61.9	1.62
Nitrobenzene	34.80	61.9	1.62
Dichloromethane	9.08	76.2	3.20
Dichloro ethane	10.50	99.9	99.9

Table 4 — Effect of stripping agents

Molarity M	HCl	HNO ₃	H ₂ SO ₄	HClO ₄
0.01	99.9	80.0	94.0	97.0
0.05	99.9	80.0	94.0	97.0
0.1	89.7	79.3	93.1	95.7
0.5	77.7	65.5	89.7	92.9
1.0	65.5	55.8	72.4	85.7
2.0	58.6	51.7	65.5	57.1
3.0	41.6	44.8	58.7	42.9
4.0	18.6	41.4	48.3	40.4

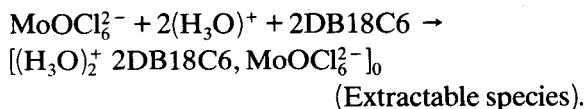
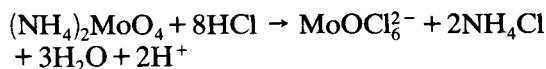
ence of strong interactive forces between oxygen atoms of crownether and hydrogen atoms of the ethylene chloride (Table 3).

Effect of stripping agents—After extraction from 3 M hydrochloric acid with 0.01 M DB18C6 in ethylene chloride molybdenum(VI) was stripped with various mineral acids in the varying concentration from 0.01 to 8 M. With 0.01 M nitric acid stripping was 80%, while with same concentration of sulphuric acid it was 94% but with 0.01-0.05 M hydrochloric acid, the stripping was quantitative. Therefore, for routine work, 0.05 M hydrochloric acid was used as the stripping agent. This also facilitated the colorimetric determination of molybdenum(VI) after dry-ashing (Table 4).

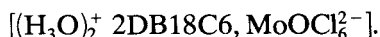
Nature of extracted species—In order to ascertain the composition of the extracted species, graphs of $\log D$ against $\log [\text{DB18C6}]$ at fixed acidity as well as $\log D$ against $\log [\text{HCl}]$ at fixed DB18C6 were plotted. The corresponding slopes were 2 and 5.9 respectively. The possible mechanism of extraction is

Table 5 — Effect of diverse ions, Mo(VI) = 40 μg

Foreign ion	Amt. taken μg	Tolerance ratio
Na^+ , Pd^{2+} , Te^{4+} , Cd^{2+} , SCN^-	0	strongly interfere
Sb^{3+} , Cs^+ , Sn^{2+}	40	1 : 1
Cu^{2+} , Zr^{4+}	80	1 : 2
Th^{4+} , IO_3^-	200	1 : 5
UO_2^{2+} , Bi^{3+} , I^- , Cl^- , ClO_4^-	400	1 : 10
Ti^{3+} , In^{3+} , NO_3^- , Cit^{3-} , CH_3COO^-	800	1 : 20



Thus the probable nature of extracted species is



This finding is in agreement with that of earlier workers^{11,12}.

Effect of counter anions—An attempt was made to extract molybdenum(VI) with 0.01 M DB18C6 in ethylene chloride in the presence of 0.01 M of bulky counter anions like picric acid, eosine, erythrosine, Rose Bengal, Tropelion and metanil yellow. In no case extraction was more than > 10%. Further these anions posed serious problem for colorimetric determination of molybdenum(VI) with tiron after extraction and subsequent stripping into aqueous phase. Hence the extraction from 3 M hydrochloric acid was preferred.

Effect of diverse ions—Molybdenum(VI) was extracted with 0.01 M DB18C6 in dichloroethane at 3-5 M HCl in the presence of a wide variety of ions. The tolerance limit was set as the amount of foreign ion causing an error of $\pm 1.2\%$ in recovery of molybdenum(VI). Several elements from main group were tolerated in ratios of > 1 : 10 while transition metals like copper, zirconium and thorium were tolerated in ratio of > 1 : 2. Antimony, tin and caesium were tolerated in small ratio of 1 : 1. The common anions were also tolerated in higher ratios (Table 5). The elements like sodium, palladium, cadmium, tellurium and anions like thiocyanate, oxalate showed strong interferences during extraction of molybdenum. The interference of some of the ions can be eliminated by selective extractions.

Table 6 — Analysis of steel and soil samples

Element	Extractant	Diluent	pH(H ⁺)	% Recovery (standard)
<i>Steel sample</i>				
Mo(VI)	DB18C6	Ethylene chloride	3M HCl	99.9(100)
Fe(III)	Diethylether	Ether	8M HCl	69(70)
Cr(VI)	Symm. diphenyl carbazide	Chloroform	0.2 M H ₂ SO ₄	17(17.6)
Mn(II)	8-Hydroxyquinoline	Chloroform	pH 1.25	60(0.62)
Ni(II)	Dimethylglyoxime	Chloroform	pH 7.0	8.5(100)
<i>Soil sample</i>				
Mo(VI)	DB18C6	Ethylene chloride	3M HCl	98.5(100)
Fe(III)	Diethylether	Ether	8M HCl	55(53)
Cr(VI)	Symm. diphenyl carbazide	Chloroform	2M H ₂ SO ₄	71(72)
Ni(II)	Dimethylglyoxime	Chloroform	pH 7.0	81(86)

Applications to analysis of real samples — The proposed method was extended for the analysis of molybdenum from sample of standard steel (BCS-No 466) and soil sample.

About 0.5 g of steel sample (BCS-NO 466) was dissolved in a mixture of hydrochloric, nitric and hydrofluoric acid in the ratio of 4 : 2 : 1 in teflon container. It was almost evaporated to dryness and the residue was dissolved in 2 mL of concentrated hydrochloric acid. The solution was made to 100 mL. From this an aliquot of diluted solution containing molybdenum(VI) was extracted as per the general procedure, when iron, chromium, manganese and nickel remained behind in aqueous phase as unextracted species. The separation of these elements from each other was carried out by selective extraction as shown in Table 6 (ref. 12).

Similarly about 3 g of finely powdered soil sample was digested and brought into solution by standard procedure¹³. From the known aliquot of solution, molybdenum(VI) was extracted as usual with DB18C6. The elements remaining behind in the aqueous phase like iron, chromium and nickel were subsequently extracted¹⁴ as per procedure outlined in Table 6.

The proposed method is simple, rapid and selective. It permits separation and determination of molybdenum in just 30 min. The method is reproducible and the relative standard deviation is $\pm 1.2\%$. As small as 4 μg of molybdenum can be separated and determined. The method is applic-

able for separation of molybdenum(VI) from real samples.

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