Extraction chromatographic separation of molybdenum(VI) with high molecular weight liquid anion exchanger

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New and innovative separation method was developed for extraction of molybdenum(VI) from aqueous chloride media with N-n-octylaniline (liquid anion exchanger) coated on silica gel. Molybdenum(VI) was quantitatively extracted from 1.25 M HCl, eluted with distilled water and determined by spectrophotometric method. Different parameters viz. effect of HCl concentration, N-n-octylaniline concentration and flow rate of mobile phase were studied. The method was applied for separation of molybdenum(VI) from binary mixtures and synthetic mixtures corresponding to alloys and fertilizer samples.

Keywords: Extraction chromatography, Molybdenum(VI) separation, N-n-Octylaniline, Liquid ion exchanger

Molybdenum metal itself and its compounds play important role in plant, animal health and as catalysis. Hence the separation of molybdenum at trace level is an analytical merit. Reversed phase extraction chromatography is an extremely versatile technique and has been applied successfully for the separation of various metals using high molecular mass amine (HMMA)\textsuperscript{1,5}, trioctylphosphine oxide\textsuperscript{6-10} and n-octylaniline\textsuperscript{11}. Silica gel is found to act as a successful support since it does not swell or strain, has good mechanical strength, porous with large surface area and physically and chemically more stable\textsuperscript{12}. Das and Chattopadhyay have used Aliquot 336\textsuperscript{13} for radioanalytical separation of molybdenum and tungsten by solvent extraction and reversed phase extraction chromatography from phosphoric acid media. Molybdenum(VI), tungsten(VI) and rhenium(VII) were leached from liquors using diisododecylamine\textsuperscript{14}. α-Benzoin oxime (ABO)\textsuperscript{15} was used for selective separation and pre concentration of ultra trace molybdenum. High molecular weight amines have been used for solvent extraction of molybdenum but the method suffers from salting out effect\textsuperscript{16,17}. Moreover, solvent extraction requires huge quantity of organic solvents which are expensive and harmful but same separations can be carried out using extraction chromatography with small quantity of solvents. N-n-octylaniline and n-octylaniline were used for extraction paper chromatographic separation of zinc(II), cadmium(II), mercury(II)\textsuperscript{18}, copper(II), silver(I), gold(III)\textsuperscript{19} and gallium(III), indium(III), thallium(III)\textsuperscript{20}. Recently, N-n-octylaniline has been used for extraction chromatographic separation of some platinum group metals (PGMs)\textsuperscript{21-23}. Present investigation reports a systematic study of the extraction chromatographic separation of molybdenum with this reagent.

Experimental Procedure

An Elico spectrophotometer model SL-159 with 10 mm path length quartz cell was used for absorbance measurements. Control dynamic pH meter was used for pH measurements. A stock solution of molybdenum(VI) was prepared by dissolving appropriate weight of molybdic acid in dilute ammonia and making the total volume of 500 mL with distilled water. It was standardized with gravimetric method\textsuperscript{24}. N-n-octylaniline was prepared by method reported by Gardlund et al.\textsuperscript{25}. The stock solution of N-n-octylaniline was prepared in chloroform. Other standard solutions of different metal ions were prepared by dissolving respective salt in distilled water and dilute hydrochloric acid. All other chemical used were of AR, Grade.

Silica gel was rendered hydrophobic as described earlier\textsuperscript{25,26} and coated with N-n-octylaniline. A 5.0 g portion of the coated gel was slurried with 25 mL distilled water. A slurry of coated silica gel in distilled water was prepared by centrifugation at 2000 rpm and coated silica gel was packed into chromatographic column. The column was made from borosilicate glass tube, having bore 8 mm, length 30 cm, fitted with glass-wool plug at the bottom. The bed was then covered with a glass wool plug.

General procedure for extraction and determination of molybdenum(VI)

An aliquot of solution containing 30 µg of molybdenum(VI) was taken in 25 mL standard flask.
The concentration of hydrochloric acid was adjusted to 1.25 M with required volume. Finally the volume was made to 25 mL with distilled water. The solution was passed through the column containing silica coated with 0.04 M \(N-n\)-octylaniline at the flow rate 1.0 mL min\(^{-1}\). The extracted molybdenum(VI) was eluted with 40 mL of distilled water and was determined by spectrophotometric method\(^2\). The aqueous phase was neutralized by addition of 2 mL of concentrated acid, followed by addition of 1 mL of 1% ferrous ammonium sulphate and 3 mL of 10% stannous chloride and solution was diluted to 25 mL with double distilled water. The red coloured molybdenum-thiocyanate complex was extracted for 30 s with 10 mL of iso-amyl alcohol. After separation of layers, the organic layer was dried with anhydrous sodium sulphate and absorbance of complex was measured at 465 nm against reagent blank.

Results and Discussion
The molybdenum(VI) was extracted from hydrochloric acid media by varying the acid concentration from 0.25 to 1.5 M. The extraction of molybdenum(VI) increased with the increasing acid concentration, became quantitative at 1.25 M and then decreased (Fig. 1). The effect of flow rate on percentage extraction of molybdenum(VI) was studied from 0.5 to 3.0 mL min\(^{-1}\). It was observed that percentage extraction decreases with increase in flow rate. Therefore normal flow rate is kept 1.0 mL min\(^{-1}\) for further extraction studies. The optimum elution of the molybdenum(VI) was observed at different concentration of various eluting agents as reported in Table 1. Water gives quantitative recovery.

Effect of diverse ions
Various amounts of foreign ions were added to a fixed amount of molybdenum(VI) (30 \(\mu\)g) to study the effect of interference according to recommended procedure. The tolerance limit was set at the amount required to cause \(\pm 1.5\%\) error in metal recovery (Table 2). It was observed that method was free from interference from a large number of cations and anions.

Effect of reagent concentration
The concentration of \(N-n\)-octylaniline in chloroform was varied from 0.02 to 0.11 M over hydrochloric acid range 0.25 to 1.5 M at 1 mL min\(^{-1}\) flow rate (Fig. 2). It was observed that a concentration of 0.04 M of \(N-n\)-octylaniline was optimum in hydrochloric acid media.

Table 1—Effect of eluting agents

<table>
<thead>
<tr>
<th>Eluting agent</th>
<th>Acid conc. (M)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>1.5</td>
<td>64.0</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>60.7</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>56.7</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>53.5</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>50.9</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>59.5</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>75.0</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>78.9</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>88.4</td>
</tr>
<tr>
<td>H(_2)SO(_4)</td>
<td>1.25</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>86.5</td>
</tr>
<tr>
<td></td>
<td>1.75</td>
<td>83.2</td>
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<td>80.5</td>
</tr>
<tr>
<td></td>
<td>2.25</td>
<td>80.3</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>69.4</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>74.5</td>
</tr>
<tr>
<td>HNO(_3)</td>
<td>0.5</td>
<td>83.9</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>91.3</td>
</tr>
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<td></td>
<td>0.4</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>8.9</td>
</tr>
<tr>
<td>HBr</td>
<td>0.8</td>
<td>8.6</td>
</tr>
<tr>
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<td>1.0</td>
<td>3.8</td>
</tr>
<tr>
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<td>2.8</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>22.0</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>18.0</td>
</tr>
<tr>
<td>HClO(_4)</td>
<td>0.6</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>11.3</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
<td>99.9</td>
</tr>
</tbody>
</table>

Applications

Analysis of molybdenum(VI) from steel and fertilizers

The validity of the method was verified by applying proposed method for extraction separation of molybdenum(VI) from synthetic mixtures corresponding to alloys and fertilizer viz. alloy steel...
Table 2—Effect of diverse ions

<table>
<thead>
<tr>
<th>Foreign ion</th>
<th>Added as</th>
<th>Tolerance limit (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(III)</td>
<td>AlCl₃</td>
<td>100</td>
</tr>
<tr>
<td>Au(III)</td>
<td>HAuCl₄·4H₂O</td>
<td>100</td>
</tr>
<tr>
<td>Bi(III)</td>
<td>Bi(NO₃)₃·5H₂O</td>
<td>100</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>3CdSO₄·8H₂O</td>
<td>100</td>
</tr>
<tr>
<td>Co(II)</td>
<td>CoCl₂·6H₂O</td>
<td>50</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>CuSO₄·5H₂O</td>
<td>50</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>K₂Cr₂O₇</td>
<td>50</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>FeSO₄·7H₂O</td>
<td>100</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>FeCl₃·6H₂O</td>
<td>50</td>
</tr>
<tr>
<td>Ga(III)</td>
<td>GaCl₃</td>
<td>100</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>HgCl₂</td>
<td>50</td>
</tr>
<tr>
<td>In(III)</td>
<td>InCl₃</td>
<td>100</td>
</tr>
<tr>
<td>Ir(III)</td>
<td>IrCl₃</td>
<td>100</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>MnCl₂·2H₂O</td>
<td>150</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>MgCl₂·6H₂O</td>
<td>100</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>NiCl₂·6H₂O</td>
<td>50</td>
</tr>
<tr>
<td>Os(VIII)</td>
<td>OsO₄</td>
<td>100</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>PdCl₂·xH₂O</td>
<td>100</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Pb(NO₃)₂</td>
<td>100</td>
</tr>
<tr>
<td>Ru(III)</td>
<td>RuCl₃</td>
<td>100</td>
</tr>
<tr>
<td>Rh(III)</td>
<td>RhCl₃</td>
<td>100</td>
</tr>
<tr>
<td>Sn(II)</td>
<td>SnCl₂·2H₂O</td>
<td>100</td>
</tr>
<tr>
<td>Ti(I)</td>
<td>TiO₂</td>
<td>100</td>
</tr>
<tr>
<td>Ti(IV)</td>
<td>K₂TiF₆·H₂O</td>
<td>50</td>
</tr>
<tr>
<td>U(VI)</td>
<td>UO₂·(NO₃)·6H₂O</td>
<td>100</td>
</tr>
<tr>
<td>V(V)</td>
<td>V₂O₅</td>
<td>100</td>
</tr>
<tr>
<td>W(VI)</td>
<td>Na₂WO₄·2H₂O</td>
<td>100</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>ZnSO₄·7H₂O</td>
<td>100</td>
</tr>
<tr>
<td>Acetate</td>
<td>CH₃COONa·3H₂O</td>
<td>500</td>
</tr>
<tr>
<td>Citrate</td>
<td>C₆H₅O₂·H₂O</td>
<td>500</td>
</tr>
<tr>
<td>EDTA</td>
<td>EDTA (Disodium salt)</td>
<td>500</td>
</tr>
<tr>
<td>Oxalate</td>
<td>(COOH)₂·2H₂O</td>
<td>500</td>
</tr>
<tr>
<td>Salicylate</td>
<td>HOC₆H₅COONa</td>
<td>500</td>
</tr>
<tr>
<td>Thiourea</td>
<td>S₂N₂H₂C</td>
<td>500</td>
</tr>
</tbody>
</table>

(No NBS-153, BCS-320, BCS-387) and fertilizer samples such as multiplex (zinc high), multiplex (molybdenum) and multiplex (garden mixture). The compositions were prepared in laboratory and analyzed by proposed method. The result of analysis was in good agreement with certified value

### Conclusion

It is simple, rapid and reproducible. The reliability of the method is verified by analyzing synthetic mixture corresponding to alloys and fertilizer. The method is free from interference from large number of cations and anions.

### Acknowledgement

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### References


