

## *CHAPTER V*

**EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF  
MOLYBDENUM(VI) WITH 2,6-DIACETYL-PYRIDINE BIS-4-PHENYL-3-  
THIOSEMICARBAZONE(2,6-DAPBPTSC)**

### 5.1. Introduction

Molybdenum is one of the utmost important elements for many organisms and has a wide distribution throughout nature<sup>1</sup>. Molybdenum is a transition element, which can exist in several oxidation states ranging from 0 to VI, where VI is the most common form found in agriculture soils<sup>2</sup>. Molybdenum is a bio-essential element and its occurrence in water samples is of interest from both environmental and chemical points of view<sup>3</sup>. Molybdenum is commercially important in metallurgical and agricultural laboratories. Besides its widespread industrial uses, molybdenum is an essential trace element required by both plants and animals<sup>4</sup>. In plant tissues, the lack of molybdenum may result in reduced growth, yield loss and even death due to accumulating nitrate, reducing amino acid concentration and falling level of vitamin metabolism. Superfluous molybdenum is very harmful to the plant, controlling the correct molybdenum content is required. For this reason, some fertilizer and feed stuff containing molybdenum was widely used<sup>5</sup>. Molybdenum deficiencies are primarily associated with poor nitrogen health particularly when nitrate is the predominant nitrogen form available for plant growth. Inability to synthesize molybdenum co-factor will reduce the activity of the critical nitrogen reducing and assimilatory enzymes including NR and XDH<sup>2</sup>. Molybdenum poisoning causes severe gastrointestinal irritation with diarrhea, coma ruminants and death from cardiac failure<sup>3</sup>. All these facts make it a prime necessity for an accurate determination of molybdenum at trace levels.

### 5.2. Review of known methods

As per review of literature some standard, sensitive and/or selective reagents for the spectrophotometric and extractive spectrophotometric determination of molybdenum(VI) are discussed here.

A number of spectrophotometric and extractive spectrophotometric methods are available in literature<sup>6</sup>.

Alizarin Red S<sup>7</sup> is used for the spectrophotometric determination of molybdenum(VI). The complex has maximum absorbance at 500 nm in the pH range of 3.4-4.0. The molar

absorptivity of the complex is found to be  $2.1 \times 10^4$  lit mol<sup>-1</sup> cm<sup>-1</sup>. The method has been successfully applied for the determination of molybdenum(VI) in geological samples.

Zaijun et al<sup>8</sup> have reported p-carboxyphenylfluorone for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 531 nm in acidic medium. The molar absorptivity of the complex is found to be  $1.03 \times 10^5$  lit mol<sup>-1</sup> cm<sup>-1</sup> and the Beer's law is obeyed upto 2.0 ppm of molybdenum(VI). The method has been successfully used for the determination of molybdenum(VI) in food samples.

Anik et al<sup>9</sup> have reported 6-chloro-3-hydroxy-2-(5-methylfuryl)4H-chromene-4-one for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 438 nm in acidic medium. The molar absorptivity of complex is found to be  $5.36 \times 10^4$  lit mol<sup>-1</sup> cm<sup>-1</sup> and the Beer's law is obeyed upto 1.9 ppm of molybdenum(VI).

5,7-dibromo-8-hydroxyquinoline<sup>10</sup> is used for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 401 nm in acidic medium. The molar absorptivity of the complex is found to be  $4.13 \times 10^3$  lit mol<sup>-1</sup> cm<sup>-1</sup> and the Beer's law is obeyed in the 0.1-50.0 ppm of molybdenum(VI). The method has been successfully applied for the determination of molybdenum(VI) in industrial, environmental, biological and soil samples.

9-(2,4-dihydroxyphenyl)-2,3,7-trihydroxy-6-fluorone<sup>11</sup> is used for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 523 nm. The molar absorptivity of the complex is found to be  $1.4 \times 10^5$  lit mol<sup>-1</sup> cm<sup>-1</sup> and the Beer's law is obeyed upto 6.0 ppm of molybdenum(VI).

Babel et al<sup>12</sup> have reported 3-hydroxy-3-p-tolyl-1-m-tolyltriazene for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 410 nm in the pH range of 2.3-3.3. The molar absorptivity of the complex is found to be  $0.80 \times 10^4$  lit mol<sup>-1</sup> cm<sup>-1</sup> and the Beer's law is obeyed range 1.0-6.0 ppm of molybdenum(VI).

3-Hydroxy-2-(2-trienyl)-4h-chromen-4-one<sup>13</sup> is used for the extractive spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 420 nm in the acidic medium and the complex is extracted into chloroform. The molar absorptivity of the complex is found to be  $2.28 \times 10^4$  lit mol<sup>-1</sup> cm<sup>-1</sup> and the Beer's law is obeyed upto 2.85 ppm of molybdenum(VI).

Keshavan and Nagaraja et al<sup>14</sup> have reported perazinedimalonate and thiocyanate for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 460 nm. The molar absorptivity of the complex is found to be  $1.06 \times 10^4$  lit mol<sup>-1</sup> cm<sup>-1</sup> and the Beer's law is obeyed in the range 0.1-14.0 ppm of molybdenum(VI). The method has been successfully applied for the determination of molybdenum(VI) in synthetic mixtures.

*o*-Nitrophenylfluorone and cetyltrimethylammonium bromide<sup>15</sup> is used for the spectrophotometric determination of molybdenum(VI). The complex has maximum absorbance at 530 nm in acidic medium. The molar absorptivity of the complex is found to be  $1.55 \times 10^5$  lit mol<sup>-1</sup> cm<sup>-1</sup> and the Beer's law is obeyed upto 10.0 ppm of molybdenum(VI).

Some other standard and/or sensitive reagents that are reported for the spectrophotometric and extractive spectrophotometric determination of molybdenum(VI) are 2-aminobenzene thiol<sup>16</sup>, 1-amino-2-naphthol-4-sulfonic acid<sup>17</sup>, brazilin-ascorbic acid<sup>18</sup>, bromopyrogallol red-zephiramine<sup>29</sup>, *p*-chloro-mandelic acid and malachite green<sup>20</sup>, 7,8-dihydroxy-4-methylcoumarin<sup>21</sup>, 3,4-dithiol and tributyl phosphate<sup>22</sup>, dithioamide<sup>23</sup>, *N*-*P*-methoxyphenyl,2-furylacrylohydroxamic acid<sup>24</sup>, phenylfluorone<sup>25</sup> polyoxometalates<sup>26</sup>, 3,3',5,5'-tetramethylbenzidine<sup>27</sup>, thiocyanate<sup>28</sup>, thionine<sup>29</sup>, 2,3,7-trihydrox-9-[3,5-dibromo-4-(2,4-dihydroxy)phenylazo] phenylfluorone<sup>30</sup>.

Carbonyl derivatives like oximes, hydrazones, thio- and phenylthiosemicarbazones are also used for the spectrophotometric as well as extractive spectrophotometric determination Mo(VI). Some of the sensitive and/or selective methods are discussed below.

Salinas and March<sup>31</sup> have reported benzohydroxamic acid-adogen 464 for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 300 nm in the pH range of 0.7-1.0. The molar absorptivity of the complex is found to be  $1.23 \times 10^3 \text{ lit mol}^{-1} \text{ cm}^{-1}$  and the Beer's law is obeyed in the range of 0.7-7.0 ppm of molybdenum(VI).

3,5-Dichloro-2-hydroxy acetophenoneoxime<sup>32</sup> is used for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 400 nm in the pH range of 2.5-3.5. The molar absorptivity of the complex is found to be  $5.1 \times 10^2 \text{ lit mol}^{-1} \text{ cm}^{-1}$  and the Beer's law is obeyed in the range 2.0-18.0 ppm of molybdenum(VI).

Abdul et al<sup>33</sup> have reported 2,4-dihydroxyacetophenoneoxime for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 400 nm in the pH range of 2.0-4.0.

2-hydroxy-4-ethoxyvalerophenoneoxime<sup>34</sup> is used for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 420 nm in the pH 3.0. The molar absorptivity of the complex is found to be  $1.51 \times 10^2 \text{ lit mol}^{-1} \text{ cm}^{-1}$  and the Beer's law is obeyed upto 121 ppm of molybdenum(VI).

2-Hydroxy-1-naphthaldoxime<sup>35</sup> is used for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 400 nm in the pH range of 2.5-3.5. The molar absorptivity of the complex is found to be  $1.75 \times 10^3 \text{ lit mol}^{-1} \text{ cm}^{-1}$  and the Beer's law is obeyed upto 5.3 ppm of molybdenum(VI).

Thiophene-2-hydroxamic acid<sup>36</sup> is used for the extractive spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 370 nm and the complex is easily extractable into toluene. The molar absorptivity of the complex is found to be  $2.34 \times 10^4 \text{ lit mol}^{-1} \text{ cm}^{-1}$  and the Beer's law is obeyed in the range 0.2-3.8 ppm of molybdenum(VI). The method has been successfully applied for the spectrophotometric determination of molybdenum(VI) in steel samples.

Other oximes used for the spectrophotometric and extractive spectrophotometric determination of molybdenum(VI) are  $\alpha$ -benzoinoxime<sup>37</sup>, nicotinohydroxamic acid<sup>38</sup>, salicylhydroxamic acid<sup>39</sup>.

P-Hydroxybenzoylhydrazone(PHBH)<sup>40</sup> is used for the simultaneous spectrophotometric determination of molybdenum(VI) and titanium(IV). The Mo(VI)-PHBH complex shows a maximum absorbance at 405 nm in the pH 3.0. The molar absorptivity of the complex is found to be  $4.2 \times 10^4$  lit mol<sup>-1</sup>cm<sup>-1</sup> and the Beer's law is obeyed in the range 0.18-1.90 ppm of molybdenum(VI). The method has been successfully applied for the spectrophotometric determination of molybdenum(VI) in steel alloy, mineral and soil samples.

Podchainova<sup>41</sup> have reported 2-hydroxy-1-naphthalhydrazide-isonicotinylhydrazone for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 370 nm in acidic medium. The molar absorptivity of the complex is found to be  $0.80 \times 10^4$  lit mol<sup>-1</sup>cm<sup>-1</sup>.

Resacetophenone isonicotinylhydrazone<sup>42</sup> is used for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 440 nm in the pH range of 3.0-6.0. The molar absorptivity of the complex is found to be  $0.9 \times 10^4$  lit mol<sup>-1</sup>cm<sup>-1</sup> and the Beer's law is obeyed in the range 0.5-8.0 ppm of Mo(VI).

Kavlentis<sup>43</sup> have reported salicylaldehyde isonicotinylhydrazone for the extractive spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 520 nm in acidic medium and the complex easily extractable into isomylalcohol. The molar absorptivity of the complex is found to be  $6.5 \times 10^3$  lit mol<sup>-1</sup>cm<sup>-1</sup> and the Beer's law is obeyed in the range 0.4-12.0 ppm of Mo(VI).

Other hydrazones used for the spectrophotometric and extractive spectrophotometric determination of molybdenum(VI) are N-cyanoacetylacetaldehydehydrazone<sup>44</sup>, 2,4-dihydroxyacetophenonebenzoylhydrazone<sup>45</sup>, 2,4-dihydroxyacetophenoneisonicotinoyl hydrazone<sup>46</sup>, 3,4-dihydroxybenzaldehydeguanylhydrazone<sup>47</sup>, 2,4-dihydroxybenzaldehyde isonicotinoylhydrazone<sup>48</sup> and 2-hydroxyacetophenonebenzoylhydrazone<sup>49</sup>,

Thio- and phenylthiosemicarbazones have emerged as very important analytical reagents for the spectrophotometric and extractive spectrophotometric determination of molybdenum(VI).

Acetonethiosemicarbazone<sup>50</sup> is used for the extractive spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 472 nm in acidic medium and the complex is easily extractable into chloroform. The molar absorptivity of the complex is found to be  $1.90 \times 10^4$  lit mol<sup>-1</sup>cm<sup>-1</sup> and the Beer's law is obeyed in the range 0.1-9.5 ppm of molybdenum(VI).

Fernandez et al<sup>51</sup> have reported 2,2'-dihydroxybenzophenone thiosemicarbazones for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 500 nm in the pH range of 0.7-1.8. The molar absorptivity of the complex is found to be  $3.3 \times 10^3$  lit mol<sup>-1</sup>cm<sup>-1</sup> and the Beer's law is obeyed upto 20.0 ppm of molybdenum(VI).

3,6-dihydroxyphthalimide bis thiosemicarbazones<sup>52</sup> is used for the extractive spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 425 nm in the pH 2.6 and the complex is extracted into isopentyl alcohol.

1,4-dihydroxyphthalimidethiosemicarbazone<sup>53</sup> is used for the spectrophotometric determination of molybdenum(VI). The complex shows maximum absorbance at 425 nm in the pH range of 2.5-3.5. The molar absorptivity of the complex is found to be  $0.90 \times 10^4$  lit mol<sup>-1</sup>cm<sup>-1</sup> and the Beer's law is obeyed in the range 1.6-9.0 ppm of molybdenum(VI).

Kumar et al<sup>54</sup> have reported 2-hydroxy-3-methoxybenzaldehyde thiosemicarbazone for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 375 nm in the pH range of 1.0-2.0. The molar absorptivity of the complex is found to be  $2.3 \times 10^4$  lit mol<sup>-1</sup>cm<sup>-1</sup> and the Beer's law is obeyed in the range 0.24-4.32 ppm of molybdenum(VI).

2-hydroxy-4-methoxy-5-sulfobenzophenone thiosemicarbazone<sup>55</sup> is used for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 505 nm in the pH 1.3. The molar absorptivity of the complex is found to be

$0.5 \times 10^4$  lit mol<sup>-1</sup>cm<sup>-1</sup> and the Beer's law is obeyed in the range 2.0-18.0 ppm of molybdenum(VI).

Bendito et al<sup>56</sup> have reported salicylaldehydethiosemicarbazone for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 520 nm in the pH 1.5. The molar absorptivity of the complex is found to be  $4.80 \times 10^3$  lit mol<sup>-1</sup>cm<sup>-1</sup> and the Beer's law is obeyed in the range 1.0-18.0 ppm of molybdenum(VI).

Thiophene-3-aldehyde-4-phenyl-3-thiosemicarbazone<sup>57</sup> is used for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 470 nm in acidic medium. The molar absorptivity of the complex is found to be  $0.79 \times 10^4$  lit mol<sup>-1</sup>cm<sup>-1</sup> and the Beer's law is obeyed in the range 0.1-4.6 ppm of molybdenum(VI).

Thimmaiah<sup>58</sup> have reported vanillinthiosemicarbazone for the spectrophotometric determination of molybdenum(VI). The complex shows a maximum absorbance at 470 nm in acidic medium and the complex is easily extractable into chloroform. The molar absorptivity of complex is found to be  $1.98 \times 10^4$  lit mol<sup>-1</sup>cm<sup>-1</sup> and the Beer's law is obeyed in the range 0.1-4.6 ppm of molybdenum(VI).

A thorough literary survey have revealed that a number of thiosemicarbazones are available for the spectrophotometric and extractive spectrophotometric determination of molybdenum(VI). But many of the thiosemicarbazones are either less sensitive or non-selective. Hence, a new reagent namely 2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone(2,6-DAPBPTSC) is synthesized to develop a simple, selective and sensitive extractive spectrophotometric method for the determination of molybdenum(VI). In the present investigation, the researcher has studied the reactivity of 2,6-DAPBPTSC with molybdenum(VI) and the results are reported in terms of its maximum absorbance, pH, molar absorptivity and stoichiometry, which provides the basis for judging the potential utility of 2,6-DAPBPTSC as an analytical reagent for molybdenum(VI). Finally, the developed method is successfully applied for the determination of molybdenum(VI) in food and water samples.



### 5.3. Results and Discussion

2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone(2,6-DAPBPTSC) forms a 1:1(M:L) yellowish orange coloured complex with molybdenum(VI), which is extracted into n-butanol, from sodium acetate-acetic acid buffer (pH 3.5). The yellowish orange Mo(VI)-2,6-DAPBPTSC complex has a maximum absorbance at 500 nm and is stable for 42 hours. The conditions for effective extraction are established after studying the effects of various factors such as pH, reagent concentration, metal ion concentration and influence of diverse ions, in order to develop a sensitive and selective spectrophotometric method for the determination of molybdenum(VI) at trace levels.

#### 5.3.1. Absorption spectra of reagent and Mo(VI)- 2,6-DAPBPTSC complex

The absorption spectrum of Mo(VI)-2,6-DAPBPTSC complex was recorded against the reagent blank. Similarly the absorption spectrum of the 2,6-DAPBPTSC reagent was recorded against the solvent blank. The absorption spectra of both the complex and reagent are shown in Fig. 5.1. From the absorption spectra it is clear that the complex and reagent have shown maximum absorptions at 500 nm and 360 nm, respectively. The reagent has minimum absorbance at the maximum absorbance of the complex and the reagent does not interfere with the determination of molybdenum(VI). Hence, further absorbance measurements of the complex were recorded at 500 nm.

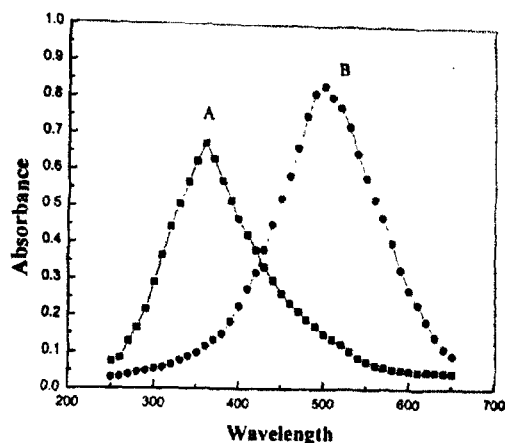


Fig. 5.1 (A) Absorption spectrum of 2,6-DAPBPTSC; (B) Absorption spectrum of Mo(VI)-2,6-DAPBPTSC complex: Mo(VI)= 1.0 mL of  $1.0 \times 10^{-4}$  M; 2,6-DAPBPTSC= 1.0 mL of  $1.0 \times 10^{-3}$  M and pH= 2.0 mL of pH 3.5.

### 5.3.2. Effect of pH

To arrive at the optimum pH required for maximum colour development, the effect of pH on the color intensity was studied. In each case, a mixture containing 1.0 mL of  $1.0 \times 10^{-4}$  M molybdenum(VI), 2.0 mL of suitable buffer, 1.0 mL of  $1.0 \times 10^{-3}$  M 2,6-DAPBPTSC solution was taken and the aqueous phase was adjusted to 10.0 mL with double distilled water. It was shaken with 10.0 mL of portion of n-butanol for one minute. The organic phase was collected into a 25 mL of standard flask and made upto the mark with n-butanol. The same procedure was applied for buffers of different pH values, ranging from 1.0-6.5. The absorbances of organic phases were measured at 500 nm, using their corresponding reagent blanks and the values are noted in Table 5.1. A plot was executed between the pH and the absorbance, and the same is represented in Fig. 5.2. The plot shows that there is maximum absorbance and constancy in the pH range 3.0-4.0. Hence, pH 3.5 is chosen for further studies, considering this as an optimum pH.

**Table 5.1 Effect of pH on Mo(VI)- 2,6-DAPBPTSC complex**

S.No.	pH	Absorbance
1	1.0	0.235
2	1.5	0.370
3	2.0	0.520
4	2.5	0.704
5	3.0	0.832
6	3.5	0.840
7	4.0	0.835
8	4.5	0.746
9	5.0	0.638
10	5.5	0.530
11	6.0	0.425
12	6.5	0.294

Mo(VI) = 1.0 mL of  $1.0 \times 10^{-4}$  M; 2,6-DAPBPTSC = 1.0 mL of  $1.0 \times 10^{-3}$  M and  $\lambda_{\text{max}} = 500$  nm.

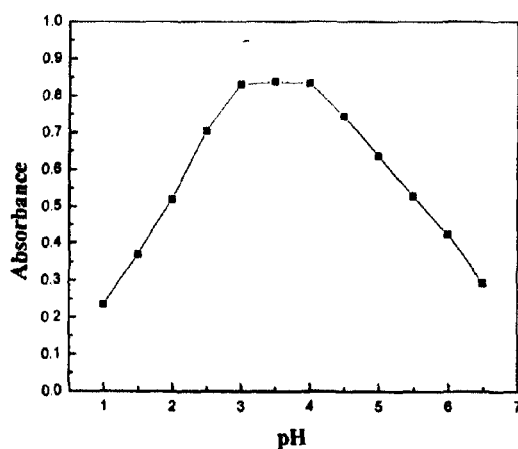


Fig.5.2. Effect of pH on Mo(VI)-2,6-DAPBPTSC complex: Mo(VI)=1.0 mL of  $1.0 \times 10^{-4}$  M; 2,6-DAPBPTSC = 1.0 mL of  $1.0 \times 10^{-3}$  M and  $\lambda_{\text{max}} = 500$  nm

### 5.3.3. Effect of solvents

The effect of various solvents such as isoamylalcohol, cyclohexanol, chloroform, toluene, benzene, n-butanol, carbontetrachloride, ethylacetate, butylacetate, xylene, tributyl phosphate, n-propylalcohol and methylisobutylketone on the extraction of

molybdenum(VI) with 2,6-DAPBPTSC is at pH 3.5 for registering the effect of solvent. Among the various solvents studied, n-butanol is selected as the suitable solvent, because the Mo(VI)-2,6-DAPBPTSC complex in it has shown maximum absorbance and has greater extraction ability. The results are reported in Table 5.2.

**Table 5.2 Effect of solvent on the extraction of Mo(VI)- 2,6-DAPBPTSC complex**

Solvent	Absorbance
cyclohexanol	0.523
isoamylalcohol	0.625
methylisobutyl ketone	0.432
n-butanol	0.836
chloroform	0.729
benzene	0.426
carbontetrachloride	0.587
xylene	0.256
hexane	0.432
butyl acetate	0.525
ethyl acetate	0.546
toulene	0.562

Mo(VI)=1.0 mL of  $1.0 \times 10^{-4}$  M; 2,6-DAPBPTSC =1.0 mL of  $1.0 \times 10^{-3}$  M; pH=3.5 and  $\lambda_{\text{max}} = 500\text{nm}$

#### 5.3.4. Effect of reagent concentration

The effect of reagent concentration was studied, using different aliquots containing constant volumes of  $1.0 \times 10^{-4}$  M molybdenum(VI) solution, 2.0 mL of pH 3.5 buffer solution and 1.0 mL of 2,6-DAPBPTSC solution containing different concentration ranging from  $1.0 \times 10^{-4}$  to  $20.0 \times 10^{-4}$  M, in order to obtain the maximum colour formation. The total volumes of aqueous phases were brought to 10.0 mL with double distilled water. The aqueous phases were shaken with 10.0 mL n-butanol in each case and the organic phases were collected into 25 mL standard flasks. The organic phases were made up to the mark with n-butanol. The absorbances of the organic phases were measured at 500 nm, against their corresponding reagent blanks and the values are noted in Table 5.3. It is clearly observed from the absorbance values, that a maximum fifteen- fold molar

excess of the reagent is sufficient to get maximum colour formation of the complex. The plot is shown in Fig. 5.3.

**Table 5.3 Effect of reagent concentration on Mo(VI)- 2,6-DAPBPTSC complex**

Concentration of reagent, $\times 10^{-4}$ M	No. of folds of reagent concentration with respect to metal	Absorbance
1.0	1	0.112
2.0	2	0.196
3.0	3	0.274
4.0	4	0.355
5.0	5	0.432
6.0	6	0.510
7.0	7	0.586
8.0	8	0.672
9.0	9	0.75
10.0	10	0.838
11.0	11	0.905
12.0	12	0.984
13.0	13	1.060
14.0	14	1.103
15.0	15	1.120
16.0	16	1.132
17.0	17	1.139
18.0	18	1.142
19.0	19	1.143
20.0	20	1.144

Mo(VI) = 1.0 mL of  $1.0 \times 10^{-4}$  M; 2,6-DAPBPTSC = 1.0 mL of  $1.0 \times 10^{-4}$  to  $20.0 \times 10^{-4}$  M; pH = 3.5 and  $\lambda_{\text{max}} = 500$  nm.

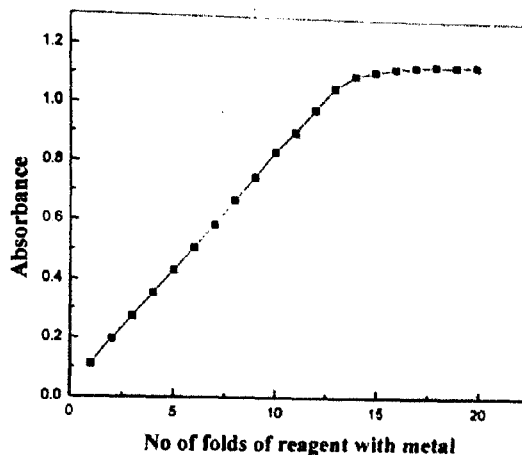


Fig. 5.3 Effect of reagent on Mo(VI)-2,6-DAPBPTSC complex: Mo(VI)= 1.0 mL of  $1.0 \times 10^{-4}$  M; 2,6-DAPBPTSC = 1.0 mL of  $1.0 \times 10^{-4}$  to  $20.0 \times 10^{-4}$  M; pH=3.5 and  $\lambda_{\text{max}} = 500$  nm.

### 5.3.5. Applicability of Beer's law

Various aliquots containing different concentrations of molybdenum(VI) ranging from  $1.0 \times 10^{-5}$  to  $17.0 \times 10^{-5}$  M (0.9-15.3 ppm), 2.0 mL of pH 3.5 buffer and 1.0 mL of 2,6-DAPBPTSC reagent ( $15.0 \times 10^{-4}$  M) solution were taken and their volumes adjusted to 10.0 mL with double distilled water. The aqueous phases were shaken with *n*-butanol in each case and the organic phases were collected into 25 mL standard flasks. The organic phases were made up to the mark with *n*-butanol. The absorbances of all the solutions were recorded at 500 nm, against their corresponding reagent blanks. The obtained results are noted in Table 5.4. A graph plotted between the amount of molybdenum(VI) and its absorbance is shown in Fig.5.4. It is observed from the graph that a linear plot passing through the origin obeys Beer's law in the concentration range  $0.9-9.0 \mu\text{g mL}^{-1}$  (ppm) of molybdenum(VI). The molar absorptivity of the complex is calculated and noted as  $1.212 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and the Sandell's sensitivity of the complex is  $0.0079 \mu\text{g cm}^{-2}$ . The correlation coefficient value of the Mo(VI)-2,6-DAPBPTSC complex, with an independent variable as concentration in  $\mu\text{g mL}^{-1}$  and a dependent variable as absorbance, is found to be 0.954. This indicates a satisfactory linearity between the two variables.

**Table 5.4 Applicability of Beer's law to Mo(VI)- 2,6-DAPBPTSC complex**

Concentration of metal, $\times 10^{-5} \text{M}$	Amount of metal, ppm	Absorbance
1	0.9	0.122
2	1.8	0.235
3	2.7	0.342
4	3.6	0.450
5	4.5	0.562
6	5.4	0.675
7	6.3	0.792
8	7.2	0.905
9	8.1	1.012
10	9.0	1.123
11	9.9	1.165
12	10.8	1.192
13	11.7	1.210
14	12.6	1.221
15	13.5	1.230
16	14.4	1.235
17	15.3	1.239

Mo(VI)=1.0 mL of  $1.0 \times 10^{-3}$  to  $17.0 \times 10^{-3}$  M; 2,6-DAPBPTSC=1.0 mL of  $15.0 \times 10^{-4}$  M; pH=3.5 and  $\lambda_{\text{max}}=500$  nm.

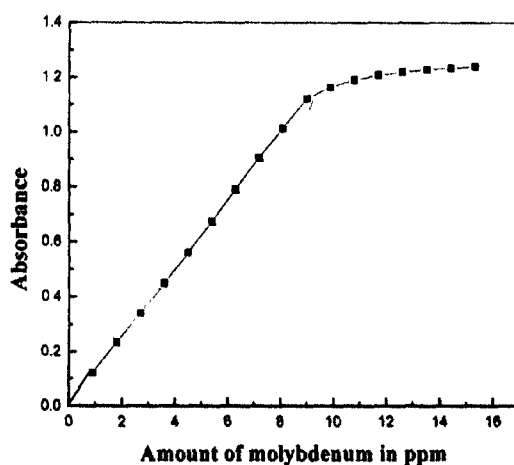


Fig. 5.4 Applicability of Beer's law to Mo(VI)-2,6-DAPBPTSC complex: Mo(VI)=1.0 mL of  $1.0 \times 10^{-3}$  to  $15.0 \times 10^{-3}$  M; 2,6-DAPBPTSC=1.0 mL of  $15.0 \times 10^{-4}$  M; pH = 3.5 and  $\lambda_{\text{max}}= 500$  nm

### 5.3.6. Ringbom plot for Mo(VI)- 2,6-DAPBPTSC complex

Ringbom plot is the standard adopted to know the optimum range of the concentration for a system, which emaciates Beer's law. The values are noted in Table 5.5. The plot is drawn between  $\log C$  of Mo(VI) and  $(1-T)$  [where  $T$  is the transmittance]. The plot has a sigmoid shape with a linear segment at intermediate concentration values ranging from 3.43-3.94  $\mu\text{g L}^{-1}$ . The slope of the plot from Fig.5.5 is 0.80. Based on this value at 1% photometric error, the ratio between the relative error in concentration and the photometric error is 2.878. Hence, the relative error in concentration is 0.0287.

**Table 5.5 Ringbom plot for Mo(VI)- 2,6-DAPBPTSC complex**

Amount of molybdenum(VI), $\mu\text{g L}^{-1}$ , C	Log C	Absorbance	Transmittance (T)	(1-T)
900	2.95	0.122	0.885	0.115
1800	3.24	0.235	0.790	0.210
2700	3.43	0.342	0.710	0.290
3600	3.55	0.450	0.637	0.363
4500	3.65	0.562	0.570	0.430
5400	3.73	0.675	0.509	0.491
6300	3.79	0.792	0.452	0.548
7200	3.85	0.905	0.404	0.596
8100	3.9	1.012	0.363	0.637
9000	3.95	1.123	0.325	0.675
9900	3.99	1.165	0.311	0.689
10800	4.03	1.192	0.303	0.697
11700	4.06	1.210	0.298	0.702
12600	4.10	1.221	0.294	0.706
13500	4.13	1.230	0.292	0.708

Mo(VI)= 900-13500  $\mu\text{g L}^{-1}$ ; 2,6-DAPBPTSC=1.0mL of  $15 \times 10^{-4}$  M; pH=3.5 and  $\lambda_{\text{max}} = 500 \text{ nm}$ .



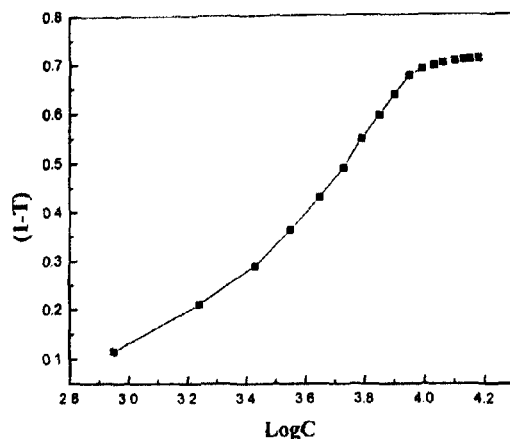


Fig. 5.5 Ringbom plot for Mo(VI)- 2,6-DAPBPTSC complex: Mo(VI)= 900-13500  $\mu\text{g L}^{-1}$ ; 2,6-DAPBPTSC= 1.0 mL of  $15.0 \times 10^{-4}$  M; pH = 3.5 and  $\lambda_{\text{max}} = 500$  nm

### 5.3.7. Precision, accuracy and detection limit of the method

To assess the precision and accuracy of the method, determinations were carried out for a set of five measurements, with different concentrations of Mo(VI), under optimum conditions. Calculations reveal that the standard deviation of method was not more than 0.001 and the relative standard deviation was less than 0.894%. It is evident from these results, that the method is precise, besides being accurate. The detection limit,  $C_{\text{min}}$  is determined as the amount of Mo(VI) corresponding to three times the standard deviation of the blank values and a value of  $0.0056 \mu\text{g L}^{-1}$  is obtained.

### 5.3.8. Determination of the composition of Mo(VI)- 2,6-DAPBPTSC complex

Job's method of continuous variation, molar ratio method and Asmus' method were employed to elucidate the composition of the complex.

#### 5.3.8.1. Job's method of continuous variation

Equimolar solutions of molybdenum(VI) and 2,6-DAPBPTSC ( $1.0 \times 10^{-3}$  M) were used to determine the metal to ligand ratio by job's method of continuous variation. The absorbance values were recorded at 500 nm against their corresponding reagent blanks.

The values are reported in Table 5.6 and the corresponding graph drawn between absorbance and  $V_M / V_L + V_M$  (where  $V_L$  and  $V_M$  are the volumes of the reagent and the metal, respectively) is shown in Fig.5.6. From the graph, it is observed that one mole of molybdenum(VI) reacts with one mole of ligand shows the composition of metal to ligand complex is 1:1.

Table 5.6 Job's method of continuous variation

Volume of Mo(VI), $V_M$ , mL	Volume of 2,6-DAPBPTSC, $V_L$ , mL	$V_M / V_M + V_L$	Absorbance
0.2	1.8	0.1	0.348
0.4	1.6	0.2	0.565
0.6	1.4	0.3	0.742
0.8	1.2	0.4	0.902
1.0	1.0	0.5	1.015
1.2	0.8	0.6	0.903
1.4	0.6	0.7	0.752
1.6	0.4	0.8	0.543
1.8	0.2	0.9	0.318

$[Mo(VI)] = [2,6-DAPBPTSC] = 1.0 \times 10^{-3} M$ ;  $pH = 3.5$  and  $\lambda_{max} = 500 \text{ nm}$ .

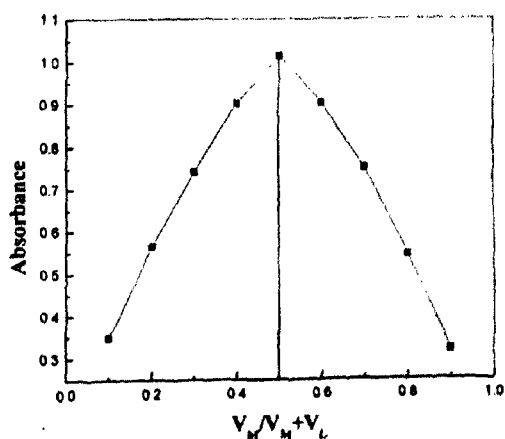


Fig. 5.6 Job's method of continuous variation:  $[Mo(V)] = [2,6-DAPBPTSC] = 1.0 \times 10^{-3} M$ ;  $pH = 3.5$  and  $\lambda_{max} = 500 \text{ nm}$

**5.3.8.2. Molar ratio method**

In molar ratio method, different aliquots containing 1.0 mL of  $1.0 \times 10^{-3}$  M molybdenum(VI), 2.0 mL of sodium acetate- acetic acid buffer (pH 3.5) and varying concentrations have ( $0.25 \times 10^{-3}$ - $2.0 \times 10^{-3}$ M) of 2,6-DAPBPTSC were used to determine the metal ligand ratio. The absorbances of the solutions were recorded at 500 nm against their respective reagent blanks. The values are noted in Table 5.7. A plot (Fig.5.7.) is drawn between the absorbance and the concentration of the reagent. From the obtained curve, it is confirmed that one mole of molybdenum(VI) complexes with one mole of 2,6-DAPBPTSC.

**Table 5.7 Molar ratio method**

No. of moles of 2,6-DAPBPTSC per one mole of Mo(VI)	Absorbance
0.25	0.350
0.50	0.580
0.75	0.820
1.00	1.075
1.25	1.120
1.50	1.160
1.75	1.220
2.00	1.260

Mo(VI)= 1.0 mL of  $1.0 \times 10^{-3}$  M; 2,6-DAPBPTSC=1.0 mL of  $0.25 \times 10^{-3}$  to  $2.0 \times 10^{-3}$  M; pH=3.5 and  $\lambda_{\text{max}} = 500$  nm.

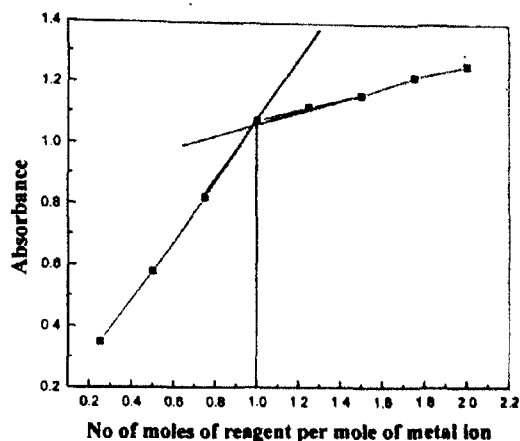


Fig.5.7 Molar ratio method: Mo(VI)= 1.0 mL of  $1.0 \times 10^{-3}$  M; 2,6-DAPBPTSC=1.0 mL of  $0.25 \times 10^{-3}$  to  $2.0 \times 10^{-3}$  M; pH=3.5 and  $\lambda_{\max} = 500$  nm.

### 5.3.8.3. Asmus' method

For Asmus' method the data obtained from molar ratio method was used.  $1/m$  values (where 'm' is extinction modulus) were calculated by dividing the optical density with the cell width, along with  $1/V$ ,  $1/V^2$  and  $1/V^3$  and are given Table 5.8. The plots between  $1/m$  and  $1/V$ ,  $1/V^2$  and  $1/V^3$  are indicated in Fig.5.8. Among the plots between  $1/m$  and  $1/V$ ,  $1/V^2$  and  $1/V^3$ , only the plot between  $1/m$  and  $1/V$  is linear indicating that the composition of the complex is 1:1 (M: L).

Table 5.8 Asmus' method

Volume of 2,6-DAPBPTSC, (V)	Absorbance (m)	1/m	1/V	1/V <sup>2</sup>	1/V <sup>3</sup>
0.25	0.350	3.06	4.00	16.00	64.00
0.50	0.580	1.85	2.00	4.00	8.00
0.75	0.820	1.33	1.33	1.77	2.37
1.00	1.075	1.05	1.00	1.00	1.00
1.25	1.120	0.97	0.80	0.64	0.51
1.50	1.160	0.90	0.66	0.44	0.29
1.75	1.220	0.85	0.57	0.32	0.18
2.00	1.260	0.80	0.50	0.25	0.12

Mo(VI)= 1.0 mL of  $1.0 \times 10^{-3}$  M; 2,6-DAPBPTSC= 1.0 mL of  $0.25 \times 10^{-3}$  to  $2.0 \times 10^{-3}$  M; pH=3.5 and  $\lambda_{\max}$  = 500 nm.

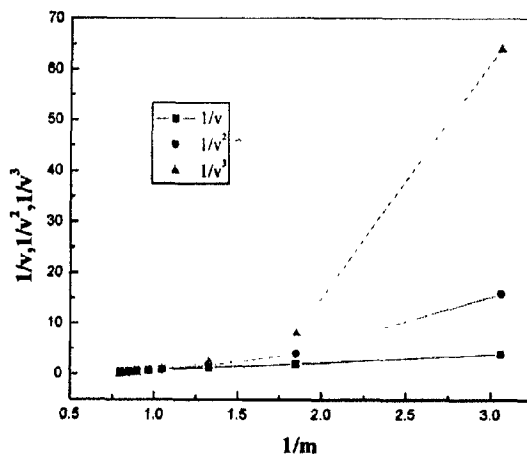


Fig.5.8 Asmus' method: Mo(VI)= 1.0 mL of  $1.0 \times 10^{-3}$  M; 2,6-DAPBPTSC= 1.0 mL of  $0.25 \times 10^{-3}$  to  $2.0 \times 10^{-3}$  M; pH=3.5 and  $\lambda_{\max}$  = 500 nm.

### 5.3.9. Calculation of instability constant of Mo(VI)-2,6-DAPBPTSC complex

The instability constant of Mo(VI)-2,6-DAPBPTSC complex was calculated by using Asmus' method. The absorbance values were obtained at 500 nm for the solutions containing fixed volumes of molybdenum(VI) (1.0 mL of  $1.0 \times 10^{-3}$  M) and 2.0 mL of pH 3.5 buffer with different known volumes of 0.25-2.0 mL of  $1.0 \times 10^{-3}$  M of 2,6-DAPBPTSC.

The instability constant of Mo(VI)-2,6-DAPBPTSC complex is calculated to be  $6.476 \times 10^{-5}$  at room temperature.

#### 5.3.10. Effect of foreign ions on the extraction of Mo(VI)- 2,6-DAPBPTSC complex

Interference of a number of cations and anions is studied in the colour absorbance of the Mo(VI)-2,6-DAPBPTSC complex. A change in absorbance of  $\pm 0.0025$  was taken as the tolerance limit for interference. In respect of some interfering ions, an increased tolerance limit is achieved by the addition of masking agents such as thiosulphate, citrate, acetate and tartate. Increasing the amount of masking agents proportionately could mask higher amount of interfering ions. In this study, cations like As(III), As(V), Mg(II), Mn(II), Zr(IV), Sb(III), Ca(II), Sr(II), Ba(II), and Tl(III) do not interfere, when present upto  $5500 \mu\text{g mL}^{-1}$  and cations like Bi(III), Hg(II), Be(II), Th(VI), U(VI), Al(III), and V(V) are tolerated upto  $3000 \mu\text{g mL}^{-1}$ , but Co(II), Cu(II), Ni(II), Zn(II), Fe(II), Fe(III), Cd(II) and Pd(II) do interfere with the determination of molybdenum(VI), when present in more than  $2000 \mu\text{g mL}^{-1}$ . The interference of Cu(II) can be eliminated by using 1.0 mL 0.2 % thiosulphate as a masking agent. Fe(II) and Fe(III) are masked with 1.0 mL of 3% of sodium fluoride. The interference of Zn(II), Cd(II) and Pd(II) can be eliminated by using 1.0 mL of 0.5% of citrate solution. The interference of Co(II) and Ni(II) can be eliminated by using 1.0 mL 0.2 % thiocyanate as a masking agent. Anions like, bromide, chloride, fluoride, thiosulfate and thiourea do not interfere when present upto  $3000 \mu\text{g mL}^{-1}$ , with the determination of molybdenum(VI) in the method. Oxalate and phosphate interfere, even present in trace amounts. These results are given in Table 5.9.

**Table 5.9 Effect of foreign ions on the extraction of Mo(VI)-2,6-DAPBPTSC complex**

Foreign Ion	Tolerance Limit, $\mu\text{g mL}^{-1}$	Foreign Ion	Tolerance Limit, $\mu\text{g mL}^{-1}$
As(III),	5500	V(V)	3000
As(V)	5500	Zn(II)	2000
Mn(II)	5500	Fe(III)	2000
Mg(II)	5500	Ni(II)	2000
Ca(II)	5500	Cu(II)	2000
Sb(III)	5500	Co(II)	2000
Sr(II)	5500	Thiosulfate	3000
Ba(II)	5500	Thiourea	3000
Zr(IV)	5500	Fluoride	3000
Tl(III)	5500	Citrate	1500
Hg(II)	3000	Borate	1500
Bi(III)	3000		
Be(II)	3000		
Th(VI)	3000		
U(VI)	3000		
Al(III)	3000		

#### 5.4. Applications

The developed extractive spectrophotometric method for molybdenum(VI) is applied for its determination in foods and water samples.

##### 5.4.1. Determination of Mo(VI) in food samples

The foods like Rampala (*Kalanchoe lanceolate*), kakara, jama, gundu malle, pappu kura, kummupotlaku, payalaku samples were analyzed for molybdenum(VI) using the proposed method. The contents of the molybdenum(VI) present in the developed solutions were determined by using a calibrated plot and results obtained were conformed by direct atomic absorption spectrophotometer. The data obtained in the analyses of medicinal leaves and leafy vegetables samples are given in Table 5.10.

**Table 5.10 Determination of Mo(VI) in foods samples**

Samples	Amount of molybdenum(VI) found <sup>a</sup>					
	AAS method <sup>b</sup>	Present method <sup>b</sup>	Present method			
			SD	RSD (%)	F-Test	T-Test
Kakara (Momordica charantia)	2.99	2.98	0.025	0.838	1.562	0.790
Rampala (Kalanchoe lanceolate)	4.09	4.07	0.025	0.636	1.801	1.638
Jama (Psidium guajava)	2.60	2.56	0.193	0.753	1.493	4.002
Gundu malle (Jasminum angustifolium)	3.17	3.14	0.158	0.503	1.490	3.002
Pappu kura (Portulaca oleracea)	2.18	2.16	0.193	0.893	1.493	2.001
Kummupotlaku (Tiliacora acuminata)	3.49	3.46	0.223	0.644	1.336	2.457
Payalaku	6.04	5.99	0.158	0.263	1.666	5.003

<sup>a</sup> Average of five determinations, <sup>b</sup> Concentration in µg/g.

#### 5.4.2. Determination of Mo(VI) in Water samples

The present method is also applied for the determination of molybdenum(VI) in water samples. The concentration of molybdenum(VI) was determined by adopting the procedure described in general procedure. The data obtained in the analyses of water samples are given in Table 5.11.

**Table 5.11 Determination of Mo(VI) in water samples**

Name of the area	Amount of molybdenum(VI) found <sup>a</sup>					
	AAS method <sup>b</sup>	Present method <sup>b</sup>	Present method			
			SD	RSD (%)	F-Test	T-Test
River water (Penna)	2.51	2.48	0.015	0.637	1.803	3.002
Lake water (Kollate)	2.99	2.96	0.013	0.445	2.580	3.593
Polluted water	3.52	3.50	0.019	0.551	1.493	2.001
Pump water	4.02	4.00	0.015	0.395	1.682	2.591

<sup>a</sup> Average of five determinations, <sup>b</sup> Concentration in µg/mL.



### **5.5. Conclusions**

The present investigations proved that 2,6-DAPBPTSC is a promising complexing agent for Mo(VI) and its subsequent determination by spectrophotometry was rapid and precise. The method has good sensitivity when compared to other existing extractive spectrophotometric methods. The selectivity of this method is improved by using masking agents for Co(II), Ni(II), Fe(II), Fe(III), Cu(II), Zn(II), Pd(II) and Cd(II). It has been successfully applied for the extractive determination of molybdenum(VI) in foods and water samples.

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