SENSITIVE SEPARATION, PRECONCENTRATION MOLYBDENUM (VI)  
VIA CLOUD POINT EXTRACTION METHODOLOGY  
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ABSTRACT

This paper is focusing more on the Cloud Point Extraction Methodology. In the lab, we extracted molybdenum (VI) as molybdate MoO$_4^{2-}$ from aqueous solution, according to cloud point extraction methodology by using complexing agent 2-[Benzene thiozoly] azo -4- Benzene naphthol (BTABN) from Acidic Media 0.1 M HCl in presence 0.8 ml for 1% Triton X-100 and 1×10$^{-5}$ M BTABN, the cloud point layer formation at 85 Cº and 25 minutes the ion pair complex extracted was[H-BTABN]$^+;\text{HMoO}_4$ or [2H-BTABN]$^{2+};\text{MoO}_4^{2-}$ as well as for determination the Mo(VI) in different samples spectrophotometrically, by prepared calibration curve at optimum conditions, with D. L= 2.62104×10$^{-6}$ and the ion pair complex extracted has $\lambda_{\text{max}}=473$ and $E=411227.6$ L mole$^{-1}$ cm$^{-1}$ R. S.d= 0.0168, Sandell’s sensitivity= 0.000233301 µg cm$^{-2}$.

KEYWORDS: Pair, Media, Calibration, Optimum

INTRODUCTION

Cloud point extraction methodology described as ideal procedure used for extraction preconcentration large group of metals as cations and anions, is one of the applications for the method to extract Zn$^{2+}$ from aqueous solution. As chloro anion complex by using new synthesized azo derivative, 3-[2-pyridylazo]-1-nitroso -2- naphthol (PANN) from acidic media of 1M HCl in presence 0.6 ml of Non ionic surfactant Tritonx-100, the ion pair complex extracted has maximum absorbance of $\lambda_{\text{max}}=414$ nm, as well as the method appear detection limit equal to 0.0292 ppm and $E=70583$ L/mol cm and sandell's sensitivity equal to 63 ×10$^{-9}$ µg/cm$^{2}$ [1]. CPE Methodology as sensitive procedure used for separation nickel (II) from acidic aqueous media as chloro anion complex by one crown ether DBISC6 and Non ionic surfactant Triton X-100, the ion pair complex extracted has maximum absorbance at the $\lambda_{\text{max}}=295$ nm of optimum Condition, 0.5 M HCl, 0.25 M NaCl, 1×10$^{-4}$M DB18C and 0.6 ml of 1% TritonX-100 [2]. Cloud point Extraction coupled with electro thermal atomic absorption spectrophotometer method. As new approach used for determination. Bismuth (III) From acidic aqueous solution at PH=3.0-3.5. by use Triton x–114 as surfactant and complexing agent 2-amino-cyclopentene-1- dithio carboxylic acid, the phase separation happens at 50 Cº the surfactant rich phase was diluted by tetra hydro furan (THF). This method giving detection limit 0.04 ngmL$^{-1}$ [3]. By cloud point methodology, we extracted trace amount of Bismuth (III), by used bromo pyrogaccol red (BPR) and non ionic surfactant Triton X-114 in this study limited the optimum condition for extraction as well as the detection limit of this method was 2.0 ngm L$^{-1}$ [4]. Spectrophotometric determination of selenium in King Kony after sensitive separation by cloud point method after complexation with Dithizone from 0.4M for HCl and 0.4% Tritony-100, with detection limit of 6.634 ppb and R. S. D less than 5% the method was successful to determination. Trace amount of Selenium with recovery 92.833 %[5]. Combination. Between
CPE method and flame atomic absorption spectrometry, was developed for extraction. And determination of trace amount of iron in environmental samples. By use complexing agent N, N-(2,2-(ethan-1,2- di bis(oxy)bis(ethane-2,1-diyl)bis (2-Chloro acetamide) (IDBOGA) at PH=5 for total iron in presence another ions and Triton X-114, this method appear detection limit 1.22 µgL⁻¹ and RSD was 4.2%[6]. Coupling CPE methodology with spectrophotometric method for separation and determination. Of Norfloxacin and Iron(III) in biological and pharmaceutical samples, where the drug Norfloxacin Combined with Fe(III) to form Complex (Fe(III)-NOR) with maximum absorbance, at λmax= 432 nm with detection limit 0.692 µg/L for NOR and 3.42 µg/L for Fe (III) [7]. The yellow complex prepared by reaction between Nickel (II) and complexing agent 3-hydroxy-5- hydroxymethyl-2-methyl pyridine 4-carbaldehyde thio semicarbazone or pyridoxal-3- thiosemicarbazon (PPT) extracted into isobutanol from sodium acetate and acetic acid buffer at PH=6 with maximum absorbance, at λmax=430 nm and molar absorptivity found to be 1.6×10⁴ Lmol⁻¹cm⁻¹. And sandell's sensitive 3.6×10⁻³ µg cm⁻². As well as developed this complexation method for determination nickel (II) in different samples [8]. 

A new approach based on simultaneous mixed–micelle mediated (MMME) and ion association complex for determination of trace amount of cadmium(II) by using spectrophotometric method. used zwitterions surfactant 3-[(3-cholamidopropyl)-dimethyl-ammonium]-1-propanesulphonate, chaps, there is interaction between cd(II), chaps, amaranth, Triton X-114 and Tri octyl amine (TOA) this method developed for determination cd(II) in water samples with detection limit 4.05 µg/cm [9]. cloud point methodology used for preconcentration. chromium(VI) by using laboratory made azo 2-[benzenthazolylace]-4-benzene-naphthal (BTABN), the ion association complex extracted was [HBTABN]+ [HCr₂O₇]⁻ by use Triton X-100 and Cr(VI) detected spectrophotometrically. At λmax=465nm E=4.47×10⁴ L/mol cm [10]. by cloud point methodology. Coupled with spectrophotometer method for separation and determination trace amount of Nickel(II) by use Nonionic surfactant Triton X-100 with detection limit 0.534 µg/L and RSD=0.22% [11]. Separation and pre concentration. For Nickel by cloud point method coupled with GFAAs for determination trace amount of nickel(II) by use Di-2-pyridyl salcycoylhydrazone as complexing agent and Triton X-114 as surfactant [12].

EXPERIMENT

Instrument

For spectrophotometric studies, we used double beam spectrophotometer Bio chrome model (80-7000-11) Libra s60 Cambridge CB40FJ Spectrophotometric with 1cm quartz cell is used for recording the absorbance spectra and absorbance measurement (England) and Electrostatic water bath (WNB7-45)(England). For absorption measurements used single beam spectrophotometer optima. Model sp-300, serial No. 322951 (Japan) FTIR- spectrophotometer 8400s. Shimadzu (Japan) electrosation water bath No. A21274501282Lp (Japan).

Material and Solution

All chemical used as received from commercial company without farther more purification, primary stock solution. Of Mo(VI) 1mg/ml prepared by dissolved 0.1839 gm of ammonium molybdate (NH₄)₂MoO₄ (incoming Fluka 99%) in 100 ml distilled water by use volumetric flask, other working solution prepared by dilution with distilled water, ammonium ferrous sulphate solution (BDH 98%) in 0.255 M concentration prepared by dissolved 10 gm in 100ml of 0.01N H₂SO₄ In volumetric flask and from (equipping Merk 99% KSCN) prepared solution 10% by dissolved)10 gm in 100ml (distilled water by use volumetric flask as well as instantaneously prepared 0.447M SnCl₂2H₂O (incoming Merck 99%) by dissolved 10 gm in 100 ml 0.1N HCl by used volumetric flask.
Sensitive Separation, Preconcentration Molybdenum (VI) Via Cloud Point Extraction Methodology

**Principal Method**

10 ml aqueous solution contain 100µg Mo(VI), optimum concentration of HCl, 1×10^{-4}M 2-[Benzene thiozolylazo]-4-benzene naphthol (BTABN) and suitable volume of 1% Triton X-100 heating this solution for favorable temperature and leave until produce cloud point layer with higher density and smaller volume afterward separated CPL. From aqueous and dissolved CPL in 5 ml ethanol and determine its absorbance at λ of maximum absorbance for complex against ligand prepared at the same manner without metal ion, as well as aqueous solution treated according to spectrophotometer method (SnCl_2.2H_2O method and after return to calibration curve Fig(1) determine remainder quintals of Mo (VI) in aqueous solution after extraction and by subtraction this quantity from origin quantity of Mo (VI) in aqueous solution to determine transfer quantity to CPL as complex after that calculate Distribution ratio values (D). In standard experiment shaking ethanolic solution of CPL with to portion of middle concentration ammonium solution and stripping metal ion to aqueous solution and treated according to (SnCl_2.2H_2O) spectrophotometer method to determine transfer quantity of metal ion. The results show transfer quantity of metal ion determined by striping is equal to the same quantity determined by subtraction remainder quantity from origin quantity then we depend on subtraction to determine transfer quantity of Mo (VI) to CPL in all experiment because easier and faster

**RESULT AND DISCUSSIONS**

Spectrophotometric study about the ion pair complex extracted to CPL show maximum absorbance at wave length 473nm as in figure (2).

**Figure 1: Calibration Curve For SnCl_2.2H_2O Spectrophotometric Method**

**Figure 2: UV-Vis Absorption Spectrum of Ion Pair Complex of Molybdenum (VI) As Molybdate MoO_4^{2-}**
Effect of HCl Concentration

Extracted 50µg Mo(VI) as molybdate MoO$_4^{2-}$ from 10ml aqueous solution contain 1×10$^{-4}$M (BTABN) and deferent concentrations of HCL and 0.5 ml of 1% Tritonx – 100 heating these solution at 80°C for 15 minutes and then determined Absorbance and D values after separated CPL from aqueous solution according to procedure detailed in principal method. The results were as in Figures (3,4).

![Figure 3: Effect of HCl Concentration on Ion Pair Complex Formation and Extraction](image)

![Figure 4: D=F[HCl]](image)

The results show optimum concentration giving higher extraction efficiency was 0.3 M HCL. At this concentration reached favourable Thermodynamic equilibrium to from liquid ion exchanger more stable with BTABN to form by liquid ion exchange ion pair association more stable extracted into CPL

$$\text{BTABN} + \text{HCl} \leftrightarrow (\text{H.BTABN})^+;\text{Cl}^-$$

$$\text{BTABN} +2\text{HCl} \leftrightarrow (2\text{H-BTARN})^{2+};2\text{Cl}^-$$

Or $$(\text{H-BTABN})^+;\text{Cl}+\text{HMoO}_4^- \leftrightarrow (\text{H-BTABN})^+;\text{HMoO}_4^-;2\text{Cl}^-$$

$$(2\text{H-BTABN})^{2+};2\text{Cl}^-+\text{MoO}_4^{2-};2\text{Cl}^-$$

HCl concentration less than optimum value not favourable and not allow to reach equilibrium state. This effect to decline extraction efficiency. As well as any concentration of HCl more than optimum value effect to decrease extraction efficiency too. By reason of increase backward direction of thermodynamic equilibrium of formation ion exchange that is mean decrease in ion pair association complex formation
Effect of Mo (VI) Concentration

Extracted Mo (VI) as molybdate $\text{MoO}_4^{2-}$ from 10ml aqueous solution contain different quantity of molybdenum in presence 0.5ml of 1% Triton X-100, $1 \times 10^{-4}$ BTABN and 0.3 M HCl heating these solution to 80˚C for 15 min and then determine absorbance and D-values according to procedure detailed in principal method. the results demonstrated in figures(5,6).

![Figure 5: Effect of Mo Concentration on Ion Pair Complex Formation and Extraction](image)

The results appear 50µg was the optimum metal ion concentration giving higher absorbance and D-value by help to reach favorable thermodynamic equilibrium for extraction, less quantity of Mo(VI) not suitable to reach equilibrium as well as any concentration more than optimum value effect to deviate the extraction from equilibrium and decrease absorbance and D-value according to man achon law and le chtelier principle.

Effect of Surfactant Concentration

Extracted 50µg Mo(VI) as molybdate from 10ml aqueous solution in presence 0.3M HCl, $1 \times 10^{-4}$ BTABN and different volume of 1% Triton X-100, heated these solutions at 80˚C for 15 minutes and after separated CPL from aqueous solutions determine absorbance and D-values as in procedure detailed in principal method. The results were as in figures (7,8)

![Figure 7: Effect of Triton X-100 Concentration on Extraction Activity](image)
Figure 8: Effect of Triton X-100 Concentration on Ion Pair Complex Formation and Extraction

The result show 0.8ml of 1% Triton X-100 was the optimum concentration giving higher extraction efficiency, but any concentration less than optimum not enough to extracted higher concentration of ion pair complex as well concentration more than optimum effect to decrease extraction efficiency by effect of increase diffusion of micelles.

Effect of Temperature

Extracted 50µg (VI) as molybdate MoO$_4^{2-}$ from 10mL aqueous solution by 1×10$^{-4}$M BTABN in presence 0.3M HCl and 0.8ml of 1% Triton X-100 heating these solution at different temperature for 15min, afterward determined absorbance and D-values after separated cloud point layer from aqueous solution according to procedure detailed in principle method.

The result were as in fig.9,10

Figure 9: Effect of Temperature on Extraction Activity

Figure 10: D=F (Tc°)

The results show extraction efficiency change as a function to temperature and the optimum temperature was 85°C. at this temperature obtained higher absorbance and D-value because at this temperature reach to favorable thermodynamic equilibrium for extraction and separation ion pair complex but any temperature less than optimum not suitable for thermodynamic equilibrium and effect to decline extraction efficiency as well as any temperature more than optimum effect to decrease extraction efficiency also by effect of increase diffusion of micelles for determine thermodynamic data calculated extraction constant $k_{ex}$ by application relation below.
The result was demonstrated in figure (11)

\[
k_{ex} = \frac{D}{[Mo(VI)][BTABN]}
\]

Figure 11: Relation between Extraction Constant and Temperature

\[
\text{slope} = \frac{-\Delta H_{ex}}{2.303R} ; \Delta G_{ex} = -RT \ln k_{ex}
\]

\[
\Delta G_{ex} = \Delta H_{ex} - T \Delta S_{ex}
\]

\[
\Delta H_{ex} = 0.1423 \text{ kJ mol}^{-1}
\]

\[
\Delta G_{ex} = -57.20 \text{ kJ mol}^{-1}
\]

\[
\Delta S_{ex} = 160.17 \text{ J mol}^{-1} \text{ K}^{-1}
\]

The low value of enthalpy demonstrate the large to approach one another the ion pair complex and increase electrostatic binding in between and increase stability. As well as the large value of enthalpy reflect the extraction method was intropic in region.

Effect of Heating Time

Extracted 50\( \mu \)g Mo(VI) an molybdate MoO\(_4^{2-}\) from 10ml aqueous solution 1×10\(^{-4}\)M BTABN in presence 0.3M HCl and 0.5ml of non-ionic surfactant 1% Triton x-100, heating these solution at 85\(^\circ\)C for different time. Afterward determine absorbance and D-values according to procedure detrilled principle method after separation CPL for aqueous solution. The results demonstrated in figures (12,13)
The results show the optimum time of heating 25 minutes, at this time reaching the best thermodynamic equilibrium and giving higher absorbance and distribution ratio because at this time complete aggregation of micelles and complete dehydration to giving cloud point layer with smallest volume and higher density and good extraction, time less than optimum giving less extraction because not suitable for complete dehydration and aggregation of micelles as well as time more than optimum also giving decrease in extraction efficiency because increase the quantity of heating in the solution which is effect to increase diffusion of micelles.

**Stoichiometry**

For predicting the structure of ion pair complex extracted using two spectrophotometer method, refer to these two method demonstrated in figures (14,15a and b)
The results demonstrate the more probable structure of ion pair complex extracted was 1:1

(H-BTABN)+; HMoO$_4$ or (2H-BTABN)+2MoO$_4^{2-}$

**Interferers Effect**

Extracted 50mg Mo(VI) as MoO$_4^{2-}$ from 10ml aqueous solution by $1 \times 10^{-4}$BTABN in presence 0.3M HCl, 0.5ml of 1% Triton x-100 and 0.1M of different anions, after heating these solution at 85˚c for 25 minutes and separated CPL from aqueous solution and determined absorbance and D-values according to procedure detailed in principal method the results demonstrated in table(1)

<table>
<thead>
<tr>
<th>Interferences</th>
<th>CPL Absorbance</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$^{-}$</td>
<td>0.168</td>
<td>27.696</td>
</tr>
<tr>
<td>CH$_3$COO$^{-}$</td>
<td>0.154</td>
<td>17.00</td>
</tr>
<tr>
<td>M2O$_4^{2-}$</td>
<td>0.109</td>
<td>3.545</td>
</tr>
<tr>
<td>NO$_3^{-}$</td>
<td>0.122</td>
<td>10.765</td>
</tr>
<tr>
<td>C$_2$O$_4^{2-}$</td>
<td>0.152</td>
<td>14.263</td>
</tr>
<tr>
<td>Cr$_2$O$_7^{2-}$</td>
<td>0.172</td>
<td>36.692</td>
</tr>
</tbody>
</table>

The results show all the anions giving interference with molybdate MoO$_4^{2-}$ but in different degree according to the behavior of these ions in aqueous solutions and its ability to form ion pairs complex and this complexes must be more stable than ion pair complex of molybdate extracted having stability may be effect on.
Effect of Electrolytes

Extracted 50mg Mo(VI) as molybdate $\text{MoO}_4^{-2}$ from 10ml aqueous solution by $1\times10^{-4}$M BTABN in presence 0.3M HCl, 0.5ml of non ionic surfactant 1% Triton x-100 and 0.1M of different electrolyte sallies, heating these solution to 85˚c for 25 minutes and then determine absorbance and d-value according to procedure. Detailed in principal method after separate CPL from aqueous solution, the results demonstrate in table(2)

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>CPL Absorbance</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>0.366</td>
<td>325</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.324</td>
<td>288</td>
</tr>
<tr>
<td>KCl</td>
<td>0.309</td>
<td>265</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>0.298</td>
<td>228</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>0.322</td>
<td>278</td>
</tr>
<tr>
<td>AlCl$_3$</td>
<td>0.331</td>
<td>294</td>
</tr>
<tr>
<td>CdCl$_2$</td>
<td>0.140</td>
<td>87.15</td>
</tr>
</tbody>
</table>

The result in presence electrolyte salts effect to enhancement extraction efficiency except (CdCl$_2$) which is participate Mo(VI) to form ion pair association after change to chloro anion complex CdCl$_4^{-2}$ with HCl, but another electrolytes giving arise in extraction efficiency because increase the dehydration and increase micelles agrigation and destroyed the hydration shell of $\text{MoO}_4^{-2}$ and increase the change of binding to form ion pair complex extracted to CPL, these behavior related with the iones diameter of metal ion in electrolyte and depending on this rule Licl giving higher absorbance and D-value because it has smallest ionic diameter and higher charge density

Spectrophotometric Determination of Mo(VI)

For determined Mo (VI) spectrophotometrically in different sample depending on prepare calibrate curve according to principal method under optimum condition. The result in figure (16)

![Figure 16: Calibration Carve for Spectrophotometric Determination of Mo (VI)](image)

This research appear $\varepsilon= 411227.6$ L mol$^{-1}$ cm$^{-1}$, R. S. D= 0.0168, Sandell’s sensitivits= 0.000233301 µg cm$^{-2}$.

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