Modified method for the determination of cobalt (II) and copper (II) ions by adopting schiff base complexes in water of Shatt Al-Arab river

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Abstract - A new method of complex formation between cobalt or copper ions and Schiff Base (derived from Schiff Base of salicyldehyde and amino acids) was adopted for the determination of cobalt and copper ions in water samples of Shatt Al-Arab River. For water sampling three stations along Shatt Al-Arab River were selected as follows: 1) discharging point in Shatt Al-Arab from Basrah paper and mill industries, 2) Karmatt Ali Bridge, and 3) Siba downstream to the southern region of Shatt Al-Arab river. After the formation of a complex with Schiff Base, Cobalt and Copper in the water of Shatt Al-Arab were determined spectrophotometricaly at wave length of 270 nm and 295 nm respectively. It is found that cobalt concentrations were (0.152, 0.174, 0.165) mg.l⁻¹ and copper concentrations were (0.014, 0.021, 0.023) mg.l⁻¹ in stations 1, 2 and 3, respectively. The method is reliable with sensitivity, accuracy, standard deviation and detection limit of (0.0235 gm.cm.l⁻¹, 3.05×10⁻⁶, 0.00184, 0.52×10⁻⁷) for cobalt complex and (0.0135 gm.cm.l⁻¹, 3.31×10⁻⁶, 0.00215, 0.6×10⁻⁸) for copper complex, respectively.

Key words: Spectrophotometry, AAS, Trace Metals, Schiff Base, Shatt Al-Arab.

Introduction
Cobalt, copper and iron are all trace essential elements for human bodies. Lack of these essential elements can induce some diseases while it is harmful and deleterious for overtaken (Mi et al., 2006). Co, Cu and Zn from the essential group of metals required some metabolic activities in organisms. Toxicological effects of large amounts of Co include vasodilatation, flushing and cardiomyopathy in human and animals (Teo and Chem, 2001).

During the last few years, interest in the role of trace elements in biological systems has increased. Pollution of natural environment by heavy metals is a worldwide problem because these metals are indestructible and most of them has toxic effects on living organisms where they exceed a certain concentration (MacFarlane and Burchett, 2000; Dalman et al., 2006; Chen et al., 2007; Begerow et al., 2000). Heavy metals are of high ecological significance since they are removed from water as self purification, but accumulate in reservoirs and enter food chain (Loska and Wiechula, 2003). Trace metals contamination in marine costal environment is related to sources of pollution in the adjacent estuaries and rivers. Metals are mainly transported to the marine environment by rivers through
estuaries. In most circumstances, the major contribution of anthropogenic metals in a marine coastal area is of terrestrial origin, i.e., from mining, industrial and urban development and other human practices near rivers and estuaries (Morton and Blackmore, 2001; IP et al., 2007). In fact, during the last few decades, industrial and urban activities have contributed the increase of metals contamination into marine environment and have directly influenced the coastal ecosystems. When metals are present as minor trace components in substrates of food, they are probably associated with macromolecular compounds as proteins, lipids or carbohydrates (AKSU et al., 2004).

Atomic absorption spectrometry (AAS) is one of the most frequently used methods dealing with determination of trace elements in water samples (Cundera et al., 2002). Effort to determine trace metals directly and reliably by flame atomic absorption spectrometry (FAAS) is limited owing to the low concentration of analytics and matrix interferences. Therefore, separation and enrichment techniques are of great importance in trace metals analysis by modern instrumental methods. To enhance the sensitivity and precision of the method, preconcentration and separation techniques, such as co precipitation, liquid-liquid phase extraction, ion exchange and recently, solid-phase extraction are most frequently used (Tokalioglu et al., 2002).

There has been a considerable effort in recent years towards the preparation of new material containing polyfunctional units (ligands) able to bind metallic ions. The Schiff base macroligands are synthesized from the reaction of dialdehydes and amino compounds (Fenton and Najera, 2001; Atria et al., 2002; Sunatsuki et al., 2002). Given that these materials form stable complexes, they provide the opportunity to design new systems selective to specific metallic ions. These materials could be applied in different areas such as electrochemistry, bioinorganic, catalysis, metallic deactivators, separation processes and environmental chemistry among others (Bediou et al., 1999; Campos et al., 1999).

Aim of the Study:

The method presented here is the attempt to determine cobalt and copper in water samples using Schiff Base complexes as a chelating agent.

Sampling and Analysis

Three stations were chosen to collect water for the determination of cobalt and copper, (1) Discharging point of waste from Basrah Paper and Mill industries to Shatt Al-Arab river, (2) Garmatt Ali Bridge and (3) Siba which is down stream southern Shatt Al-Arab river, as shown in Fig.1. Dark glass bottles (5 L) were used for the collection of subsurface (30 cm) water sample during (Oct. 2010). In the laboratory, 30-40 ml of CCl4 were added to each water samples and followed by severe shaking for 30 minutes for extraction of petroleum hydrocarbons, where the organic content was separated for petroleum hydrocarbon’s while the aqueous layer was used for the determination of cobalt and copper, after drying on hot plate (at 105°C).

The remaining salts were allowed to react with Schiff Base according to the following procedure (Mohammed et al., 2009): Freshly distilled glycine (0.01 mole, 0.75 gm) was dissolved in (30 ml) distil water with (0.01 mole,
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1.22 gm) 2-hydroxy benzaldehyde (Salicyaldehyde) dissolved in (30 ml) ethanol in presence of sodium acetate (0.01 mole, 0.82 gm). After refluxing for (45 min) the solution was dried and kept at room temperature and finally dried under vacuum, to yield(85 %) of the ligand (Sodium Glycine Salicyaldehyde imin). Melting point was (130-132 °C). Then the Schiff Base complexes were prepared according to the method as following: in three-neck round bottom flask with condenser, an amount of Schiff Base ligands was dissolved in (20 ml) hot ethanol and moles of Co (II) or Cu (II) chloride dissolved in (20 ml) of same solvent were added and refluxing the mixture as in the Table (1).

The reaction vessel is removed from the hot plate and cooled and the resulting product crystalline is filtered by a Buckner funnel until the filtrate will be clear. The filtered material is washed with ethanol and then dried. The results of C H N, and melting point are shown in Table (2).
Table 1. Moles for ligand and schiff base in the reaction.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Moles of Ligand HOPhCHNCH₂COO⁻Na⁺</th>
<th>Moles of chloride CoCl₂</th>
<th>Reaction Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂[Co(HOPhCHNCH₂COO⁻)_2]</td>
<td>0.02</td>
<td>0.01</td>
<td>130</td>
</tr>
<tr>
<td>[Cu(HOPhCHNCH₂COO⁻)(H₂O)]</td>
<td>0.01</td>
<td>-</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 2. C H N analysis and M.P for the Ligand and Schiff Base Complexes.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>Co%</th>
<th>Cu%</th>
<th>M.P °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPhCHNCH₂COO⁻Na⁺</td>
<td>53.73</td>
<td>3.98</td>
<td>6.96</td>
<td>-</td>
<td>-</td>
<td>130-132</td>
</tr>
<tr>
<td>Na₂[Co(HOPhCHNCH₂COO⁻)_2]</td>
<td>47.05</td>
<td>3.05</td>
<td>6.10</td>
<td>12.85</td>
<td>-</td>
<td>340-342</td>
</tr>
<tr>
<td>[Cu(HOPhCHNCH₂COO⁻)(H₂O)]</td>
<td>41.78</td>
<td>3.48</td>
<td>5.41</td>
<td>24.56</td>
<td>232-234</td>
<td></td>
</tr>
</tbody>
</table>
All the above reactions can be shown in scheme (1):

\[
\text{HOPhCHO} + \text{H}_2\text{NCH}_2\text{COOH} \xrightarrow{\text{CH}_3\text{COO}^+\text{Na}^+} \text{HOPhCHNCH}_2\text{COO}^-\text{Na}^+ \\
\text{CuCl}_2 \xrightarrow{90 \text{ min Reflux}} [\text{Cu(HOPhCHNCH}_2\text{COO}^-)(\text{H}_2\text{O})] \\
\text{CoCl}_2 \xrightarrow{130 \text{ min Reflux}} \text{Na}_2[\text{Co(HOPhCHNCH}_2\text{COO}^-)_{\text{2}}] \\
\]

Scheme 1. The Preparation Reaction

After that, a stoke solutions from the synthesized complexes, resulting from the above reactions was prepared. Then the absorbance of this solutions was scanned at (270) and (295) nm and compared with the calibration curves of Co\(^{2+}\) or Cu\(^{2+}\) ions respectively. All spectral measurements were taken by UV/VIS spectrophotometer and supplied by Philips Company model PU 8670 Vis/NIR spectrophotometer by using benzene as a solvent. The visible spectra for the ligand and Schiff Base were scanned along the wavelength, 250-410 nm. The optimum conditions for best absorbance measurements with lower error was done at wavelength of 270 nm for Co\(^{2+}\) and of 295 nm for Cu\(^{2+}\) as shown in Fig.(2). Then sample solutions of complexes were prepared and the absorbance for each solution was measured at 270 or 295 nm, then the Calibration Curves for Co\(^{2+}\), Cu\(^{2+}\) ions was plotted as shown in Fig.(4) and Fig.(6) respectively.

The calibration curve was plotted for both Co (II) and Cu (II) in ppm units (mg.L\(^{-1}\)). And for comparison cobalt and copper were determined by atomic absorption spectrophotometer (AA320N) by Ankistrom Company using distil water.
Results and Discussion

To insure a complete reaction between the ligand and Schiff Base the component have been distilled before the beginning of reaction to produce the complexes with maximum yield. Then the reaction was preceded between the ligand and products from dried samples. To distinguish between complexes formed for copper, it takes a time of 90 min., while for cobalt it takes 130 min., as shown in scheme 1.

For Cobalt ion:

Fig. (3) show the visible spectra of ligand (HOPhCHNCH₂COO⁻Na⁺) and Schiff Base (Na₂[Co(HOPhCHNCH₂COO⁻)₂]) in benzene as solvent because of good salvation of the complex in this solvent.

The calibration curve of the (Na₂[Co(HOPhCHNCH₂COO⁻)₂]) complex is shown in Fig. (4) which helps in estimation of Co²⁺ ion in the studied water samples.

And the determined concentrations of cobalt are presented in Table (3).

Table (4) shows some analytical parameters for the (Na₂[Co(HOPhCHNCH₂COO⁻)₂]) complex which supported the correctness of this methodology (Mohammed et al., 2008) for the determination of cobalt ion in this study.

For Copper ion:

Fig. (5) show the visible spectra of ligand (HOPhCHNCH₂COO⁻Na⁺) and Schiff Base [Cu(HOPhCHNCH₂COO⁻)(H₂O)] in benzene as solvent because of good salvation of the complex in this solvent.

The calibration curve of the [Cu(HOPhCHNCH₂COO⁻)(H₂O)] complex is shown in Fig. (6) which helps in estimation of Cu²⁺ ion in the studied water samples.

And the determined concentrations of cobalt are presented in Table (5).

Table (6) shows some analytical parameters for the [Cu(HOPhCHNCH₂COO⁻)(H₂O)] complex which supported the correctness of this methodology (Mohammed et al., 2008) for the determination of cupper ion in this study.

As could be seen from Table (3) and Table (5), there are high concentrations for Co and Cu in the discharging point of the pulp and mill factory in Basrah, Garmatt Ali Bridge and Siba downstream to the southern region of Shatt Al-Arab river. The values are comparable to values recorded spectrofluorometrically earlier in Tigris and Shatt Al-Arab rivers which where (0.02-0.04) ppm for Co and (3.59-0.35) ppm for Cu respectively (Al-Imarah et al., 2000).

Table (3) and Table (5) represent the results obtained in this study to estimate Co and Cu concentrations according to the spectral method and compared with values obtained by AAS. The results were very encouraging for convergence is high between the values recorded both ways and proves Table (4) and Table (6) through functions calculated from the accuracy, sensitivity and detection limit health work and the success of method adopted to determined the Co and Cu respectively.

Shatt Al-Arab water affected by operation of load and transport and discharge of oil as well as waste that has thrown the transport of waters
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Figure 2. Visible spectra of Ligand (HOPhCHNCH₂COONa⁺ and Na₂[Co(HOPhCHNCH₂COO⁻)₂] and [Cu(HOPhCHNCH₂COO)(H₂O)] in Benzene.

Figure 3. Visible Spectra of HOPhCHNCH₂COO⁻Na⁺ and Na₂[Co(HOPhCHNCH₂COO⁻)₂] in Benzene.

Figure 4. Calibration Curve for Co ion (mg/l) Complex to Na₂[Co(HOPhCHNCH₂COO⁻)₂].
Table 3. The Concentration of Co²⁺ (mg.l⁻¹) in water from selected stations.

<table>
<thead>
<tr>
<th>Location</th>
<th>Absorbance At λ = 270 nm</th>
<th>Calibration Curve</th>
<th>AAS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Concentration</td>
<td>Standard Deviation S.D</td>
</tr>
<tr>
<td>5 Km south of the Basra paper factory</td>
<td>0.551</td>
<td>0.152</td>
<td>0.00184</td>
</tr>
<tr>
<td>Qarmatt Ali Bridge</td>
<td>0.631</td>
<td>0.174</td>
<td>0.00184</td>
</tr>
<tr>
<td>Shatt Al-Arab (Siba)</td>
<td>0.598</td>
<td>0.165</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Some Analytical Parameters for Co – Complex (Calculations done according to Laitinen and Harris, 1975).

<table>
<thead>
<tr>
<th>Complex</th>
<th>No. of samples</th>
<th>Sensitivity gm.cm.l⁻¹</th>
<th>Accuracy</th>
<th>Stand. Deviation S.D</th>
<th>Detection Limit D.L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂[Co(HOPhCHNCH₂COO⁻)₂]</td>
<td>10</td>
<td>0.0235</td>
<td>3.05 × 10⁻⁶</td>
<td>0.00184</td>
<td>0.52 × 10⁻⁷</td>
</tr>
</tbody>
</table>

Figure 5. Visible spectra of HOPhCHNCH₂COO⁻Na⁺ and [Cu(HOPhCHNCH₂COO)(H₂O)] in Benzene.
Figure 6. Calibration curve for Cu ion (mg/l) complex to 
[Cu(HOPhCHNCH₂COO⁻)(H₂O)]

Table 5. The Concentration of Cu²⁺ (mg.l⁻¹) in water from selected stations.

<table>
<thead>
<tr>
<th>Location</th>
<th>Absorbance at λ = 295 nm</th>
<th>Calibration Curve</th>
<th>AAS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Concentration</td>
<td>Standard</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Deviation</td>
</tr>
<tr>
<td>5 Km south of the Basra paper factory</td>
<td>0.311</td>
<td>0.014</td>
<td>0.00215</td>
</tr>
<tr>
<td>Qarmatt Ali bridge</td>
<td>0.467</td>
<td>0.021</td>
<td></td>
</tr>
<tr>
<td>Shatt Al-Arab (Siba)</td>
<td>0.511</td>
<td>0.023</td>
<td></td>
</tr>
</tbody>
</table>

Table 6. Some Analytical Parameters for Cu – Complex

<table>
<thead>
<tr>
<th>Complex</th>
<th>No. of samples</th>
<th>Sensitivity gm.cm.L⁻¹</th>
<th>Accuracy</th>
<th>Standard Deviation S.D</th>
<th>Detection Limit D.L</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(HOPhCHNCH₂COO⁻)(H₂O)]</td>
<td>10</td>
<td>0.0135</td>
<td>3.31 × 10⁻⁷</td>
<td>0.00215</td>
<td>6 × 10⁻⁸</td>
</tr>
</tbody>
</table>
which represent a source of contaminate of trace metals due to contain the oil to certain ratios of these metals and increasing levels of pollution of these materials in the case of non-application of safety requirements and protect the environment from the leaking of oil or using the wrong tactics in dealing with oil or any of its derivatives (Al-Saad _et al._, 1997).

In general, concentrations of studied metals as an average values recorded from selected stations are higher than those-reported by studies of standard values of WHO, EPA and EQS (WHO/ EU, 1993; US-EPA, 2004; EQS, 2001).

**Conclusion**

The present method offers a rapid and accurate analysis for cobalt and copper ions in water samples.

**Acknowledgement**

I would like to express my utmost gratitude to Prof. Faris J.M. Al-Imarah for his assistance with different aspects to this work.

**References**


طرقية معدلة لتقدير أيوني الكوبالت الثاني والنحاس الثاني
اعتمادًا على تكوين معقدات مع قواعد شف في مياه شط العرب

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المستخلص - استخدمت طريقة جديدة بتكوين معقد بين أيوني الكوبالت أو النحاس مع قواعد شف (المستندة على قاعدة شف للساليسالدهيد والاحضام الأمينية) لتقدير الكوبالت والنحاس في عينات مياه من ثلاث محطات على طول نهر شط العرب وعلى النحو التالي: (1) عند نقطة التصريف لمختلف معمل الورق والعجينة في شط العرب، (2) قناة كرم (و 3) السيبية في الاتجاه الجنوبي لشط العرب. تم تقدير الكوبالت والنحاس بعد تكوين معقد مع قواعد شف والذي تم دراسته طيفيًا. عند الطول الموجي 270 و 295 نانومتر على التوالي. ووجد أن تركيز الكوبالت بحدود (0.152 ، 0.174 ، 0.165) ملغ/لتر وتركيز النحاس هو (0.014 ، 0.021 ، 0.023) ملغ/لتر في المحطات 1 و 2 و 3 على التوالي. يمكن الاستمرار على هذه الطريقة لكونها تميزاً بحساسية ودقة وانحراف معياري وحدود قياس هـ: (350.0135 غم/س/لتر ، 0.00184 × 10^{-6} ، 0.00215 × 10^{-8}) لمعقد الكوبالت و (0.00135 غم/س/لتر ، 0.00184 × 10^{-6} ، 0.00215 × 10^{-8}) لمعقد النحاس على التوالي.