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 costal 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 on 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 (Bedioui *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 CCl_4 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 105ºC).

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,
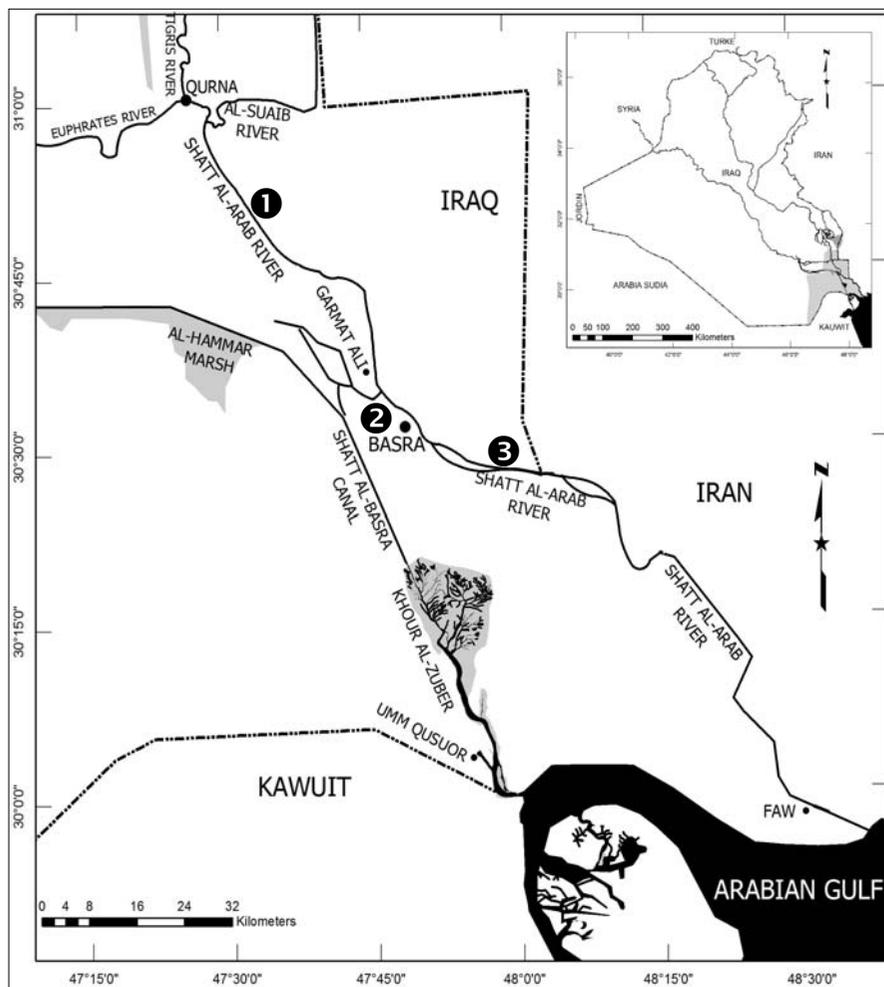
Figure 1. Location map of Shatt Al-Arab River showing the sampling stations.

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).
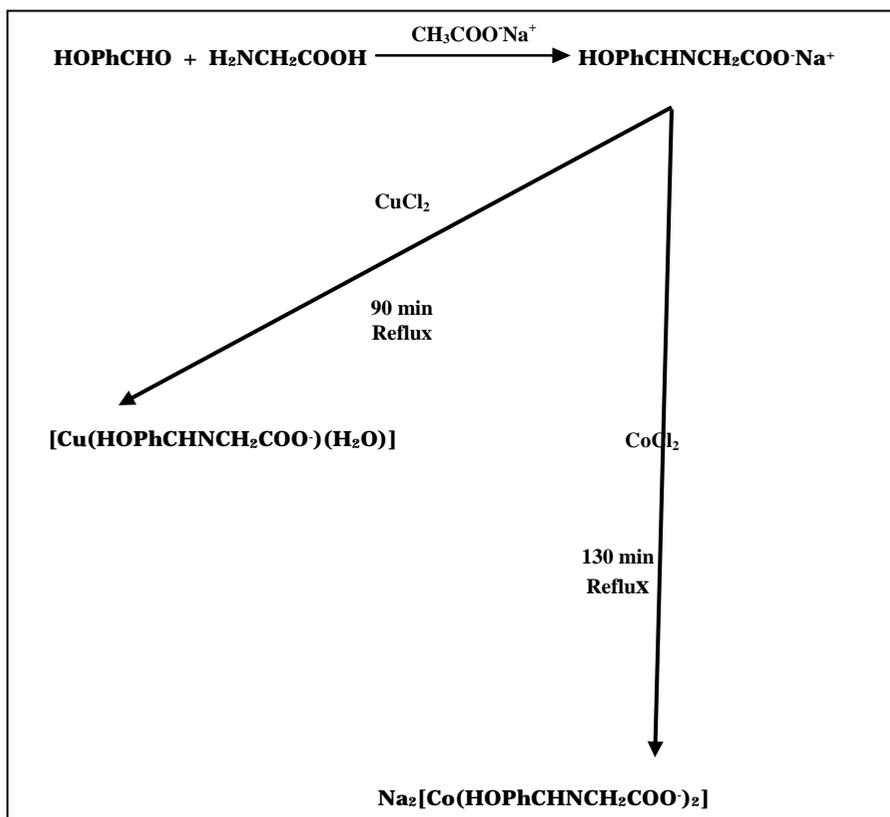
Table 1. Moles for ligand and schiff base in the reaction.

Complex	Moles of Ligand HOPhCHNCH$_2$COO$^-$Na$^+$	Moles of chloride		Reaction Time (min)
		CoCl$_2$	CuCl$_2$	
Na$_2$[Co(HOPhCHNCH$_2$COO$^-$)$_2$]	0.02	0.01	-	130
[Cu(HOPhCHNCH$_2$COO$^-$)(H$_2$O)]	0.01	-	0.01	90

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

Symbol	C% T/(F)	H% T/(F)	N% T/(F)	Co% T/(F)	Cu% T/(F)	M.P °C
HOPhCHNCH$_2$COO$^-$Na$^+$	53.73 (53.94)	3.98 (3.80)	6.96 (6.73)	-	-	130-132
Na$_2$[Co(HOPhCHNCH$_2$COO$^-$)$_2$]	47.05 (46.91)	3.05 (3.26)	6.10 (6.34)	12.85 (12.70)	-	340-342
[Cu(HOPhCHNCH$_2$COO$^-$)(H$_2$O)]	41.78 (41.60)	3.48 (3.33)	5.41 (5.67)	–	24.56 (25.01)	232-234

All the above reactions can be shown in scheme (1):

$$\text{HOPhCHO} + \text{H}_2\text{NCH}_2\text{COOH} \xrightarrow{\text{CH}_3\text{COO}^-\text{Na}^+} \text{HOPhCHNCH}_2\text{COO}^-\text{Na}^+$$

CuCl$_2$

90 min
Reflux

[Cu(HOPhCHNCH$_2$COO$^-$)(H$_2$O)]

CoCl$_2$

130 min
RefluX

Na$_2$[Co(HOPhCHNCH$_2$COO$^-$)$_2$]

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 compenent 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 cupper, 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 (HOPhCHNCH$_2$COO$^-$Na$^+$) and Schiff Base (Na$_2$[Co(HOPhCHNCH$_2$COO$^-$)$_2$]) in benzene as solvent because of good salvation of the complex in this solvent.

The calibration curve of the (Na$_2$[Co(HOPhCHNCH$_2$COO$^-$)$_2$]) complex is shown in Fig.(4) which helps in estimation of Co^{2+} 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 (Na$_2$[Co(HOPhCHNCH$_2$COO)$_2$]) 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 (HOPhCHNCH$_2$COO$^-$Na$^+$) and Schiff Base [Cu(HOPhCHNCH$_2$COO$^-$)(H$_2$O)] in benzene as solvent because of good salvation of the complex in this solvent.

The calibration curve of the [Cu(HOPhCHNCH$_2$COO$^-$)(H$_2$O)] complex is shown in Fig. (6) which helps in estimation of Cu^{2+} 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 (HOPhCHNCH$_2$COO$^-$) (H$_2$O)] 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
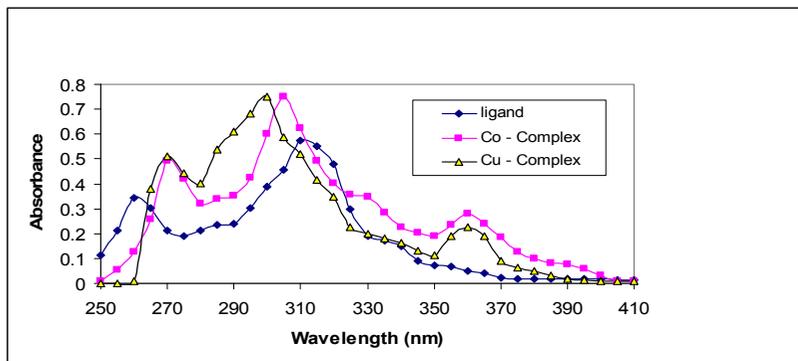
Figure 2. Visible spectra of Ligand (HOPhCHNCH$_2$COONa$^+$ and Na$_2$[Co(HOPhCHNCH$_2$COO$^-$)$_2$] and [Cu(HOPhCHNCH$_2$COO)(H$_2$O)] in Benzene.
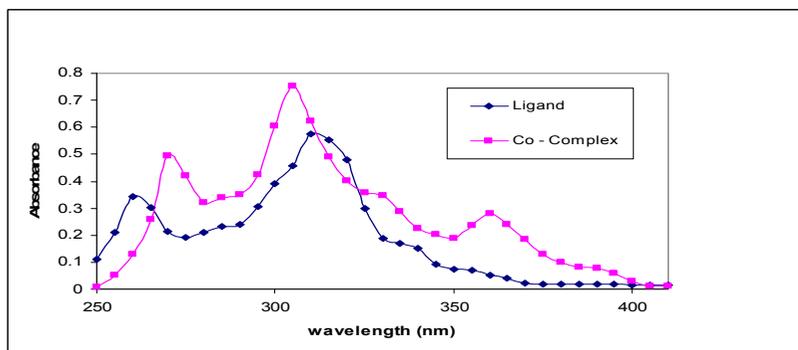
Figure 3. Visible Spectra of HOPhCHNCH$_2$COO$^-$Na$^+$ and Na$_2$[Co(HOPhCHNCH$_2$COO$^-$)$_2$] in Benzene.
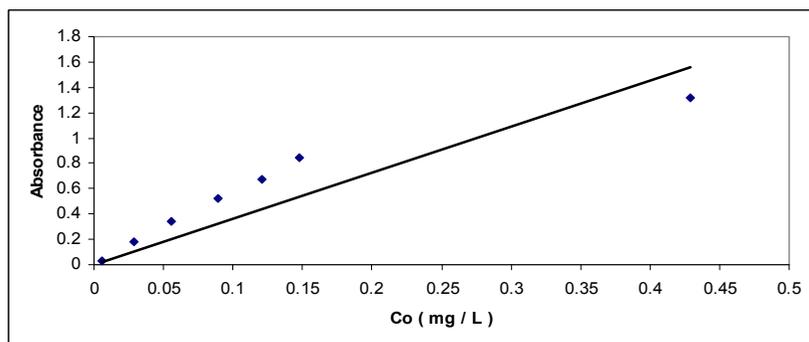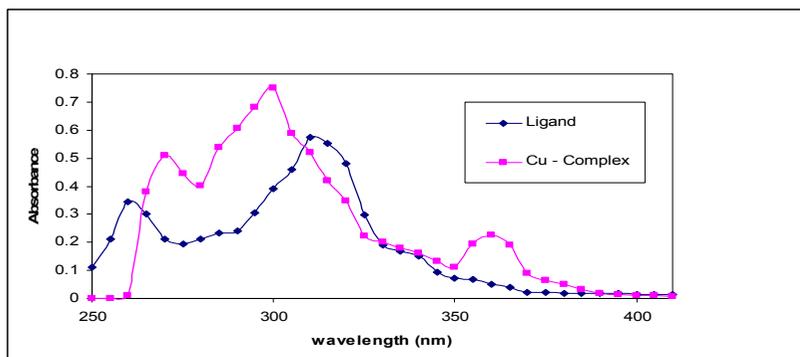
Figure 4. Calibration Curve for Co ion (mg/l) Complex to Na$_2$[Co(HOPhCHNCH$_2$COO$^-$)$_2$].

Table 3. The Concentration of Co^{2+} (mg.l^{-1}) in water from selected stations.

Location	Absorbance At $\lambda = 270$ nm	Calibration Curve		AAS	
		Concentration	Standard Deviation S.D	Concentration	Regulation Coefficient R^2
5 Km south of the Basra paper factory	0.551	0.152		0.153	
Qarmatt Ali Bridge	0.631	0.174	0.00184	0.214	0.986
Shatt Al-Arab (Siba)	0.598	0.165		0.168	

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

Complex	No. of samples	Sensitivity gm.cm.l^{-1}	Accuracy	Stander Deviation S.D	Detection Limit D.L
$Na_2[Co(HOPhCHNCH_2COO^-)_2]$	10	0.0235	3.05×10^{-6}	0.00184	0.52×10^{-7}

Figure 5. Visible spectra of $HOPhCHNCH_2COO^-Na^+$ and $[Cu(HOPhCHNCH_2COO)(H_2O)]$ in Benzene.
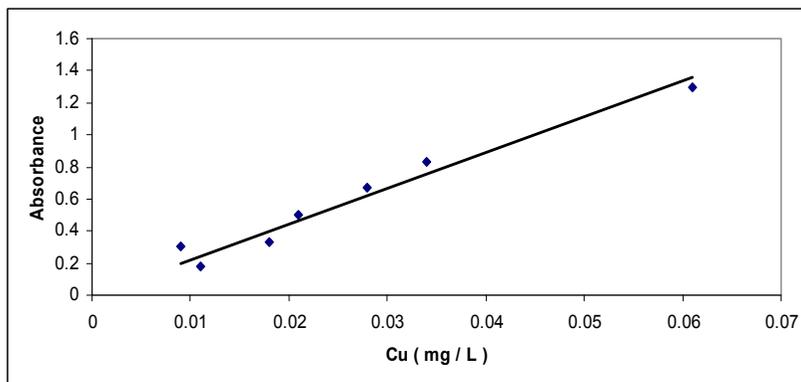
Figure 6. Calibration curve for Cu ion (mg/l) complex to $[Cu(HOPhCHNCH_2COO^-)(H_2O)]$

Table 5. The Concentration of Cu^{2+} (mg.l^{-1}) in water from selected stations.

Location	Absorbance at $\lambda = 295$ nm	Calibration Curve		AAS	
		Concentration	Standard Deviation S.D	Concentration	Regulation Coefficient R^2
5 Km south of the Basra paper factory	0.311	0.014		0.013	
Qarmatt Ali bridge	0.467	0.021	0.00215	0.009	0.988
Shatt Al-Arab (Siba)	0.511	0.023		0.021	

Table 6. Some Analytical Parameters for Cu – Complex

Complex	No. of samples	Sensitivity gm.cm.L^{-1}	Accuracy	Standard Deviation S.D	Detection Limit D.L
$[Cu(HOPhCHNCH_2COO^-)(H_2O)]$	10	0.0135	3.31×10^{-7}	0.00215	0.6×10^{-8}

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

References

Aksu, S.K., Cetinoglu, A. and Gucer, S. 2004. Determination of trace elements in cow milk by ICP-MS, Adnan Menderes University. 4th AACD Congress, 29Sejkpt-3Oct. 2004, Kusadasi-Aydin, Turkey.

Al-Imarah, F.J.M., Ghadban, R.A. and Al-Shaway, S.F. 2000. Levels of trace metals in water from southern part of Iraq. Marina Mesopotamica, 15(2): 365-372.

Al-Saad, H.T., Mustafa, Y.Z. and Al-Imarah, F.J. 1997. Distribution of trace metals on the tissues of fish from Shatt Al-Arab estuary, IRAQ. Marina Mesopotamica, 15(1): 145-156.

Atria, A.M., Moreno, Y., Spodine, E., Garland, T and Baggio, R. 2002. A Discrete Dinuclear Cu(II)-Gd(II) Complex Derived from a Schiff Base Ligand,[CuGd(ems)(NO3)3H2O]Cu(ems)(ems:N,N' − ethylene-bis-5-methoxy salicyalldiimine). Inorganic Chimica Acta., 335: 1-6.

Bedioui, G., Gutierrez, G. and Charreton, C.B. 1999. Metalloporphyrin, Metallophtalocyanine and related Macrocycle Complex-Base Film Modified Electrodes: Review of Selected Significant Designs and Applications to the Electrochemical Detection of Pollutants, Resent Res Devel. Electrochemical, Reviews Paris., 2:91-108.

Begerow, J., Turfeld, M. and Dunemann, L. 2000. New horizons in human biomonitoring of environmentally and occupationally relevant metal-sector-field ICP-MS versus electrothermal AAS. J. Anal. At.Spectrom., 15: 347-352.

Campos, A., Anacona, J.R. and Campos, M.M. 1999. Synthesis and IR Study of Zn(II) Comlex Containing a Tetradentate Macrocyclic Schiff Base Ligand Antifungal Properties, Main Group Met. Chem., 22: 283-288.

Chen, C.W., Kao, C.M. and Dong, C.D. 2007. Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. Chemosphere, 66: 1431-1440.

Cucdeva, K., Stafilov, T., Zendelovska, D. and Pavlovska, G. 2002. Application of co-precipitate flotation as a method for selective

separation of traces of Co, Cu, Ni and Pb in Dolomite and Gypsum and their determination by ETAAS. Bull. Chem. Technol. Macedonia, 21(1): 43-52.

Dalman, O., Demirak, A. and Balci, A. 2006. Determination of heavy metals (Cd, Pb) and trace elements (Cu, Zn) in sediments and fish of the Southeastern Aegean Sea (Turkey) by atomic absorption. Food Chem., 95: 157-162.

EQS (Environmental quality standards for water pollution). 2001. Ministry of Environment of Japan, 7 pp.

Fenton, D.E. and Najera, B. 2001. A new Expanded Schiff Base Cryptand, J. Coordination Chemistry, 54: 239-246.

Ip, C.C.M., Li, X.D., Zhang, H.W. and Li, Y.S. 2007. Trace metal distribution in sediment of the Pearl River Estuary and the surrounding coastal area, Suoth China. Environ. Poll., 147: 311-323.

Laitinen, H.A. and Harris, W.E. 1975. Chemical analysis, 2nd Ed., Mc Graw-Hill, Inc., 540 pp.

Loska, K. and Wiechula, D. 2003. Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediment from the Rybik Reservoir.Chemosphere, 51: 723-733.

MacFarlane, G.R and Burchett, M.D. 2000.Cellular distribution of copper, lead and zinc in the grey mangrove, Avicennia m arine (Forsk.) Vierh. Aquat. Bot., 68: 45-59.

Mi, J., Li, Y., Zhou, X., Zheng, B. and Zhou, Y. 2006. Simultaneous determination of iron, copper and cobalt in food samples by CCD-diode Array detection-flow injection analysis with partial least squares calibration model, J. Phy. Conf. ser. 28:66-69.

Mohammed, M.H., Al-Rassol, K.S. and Al-Jorany, Y.S. 2009. Synthesis and Spectroscopic Study of some Complexes of Cobalt and Copper Derived From Schiff Base of Salicyaldehyde and Amino Acids. J. Basrah Res. Sci., 35(6): 129-139.

Mohammed, M.H., Zaidan, A.M. and Al-Imarah, F.J.M. 2008. Modified Method for the Determination of Mercury II by Adopting Porphyrin Complex. J. Basrah Res. Sci., 34(3): 15-20.

Morton, B. and Blackmore, G. 2001. South China Sea. Mar. Poll. Bull., 42: 1236-1263.

Sunatsuki, Y., Motoda, Y. and Matsumoto, N. 2002. Copper (II) Complexes with Multidentate Schiff Base Ligands Containing Imidazole Groups: ligand-Complex or Self-Complementary Molecule, Coordination Chemical Reviews, 226(1-2): 199-209.

Teo, K.C. and Chen, J. 2001. Determination of cobalt and nickel in water samples by flame atomic absorption spectrometry after cloud point extraction. Anal. Chim. Acta., 434(2): 325-330.

Tokalioglu, S., Kartal, S. and Elci, L. 2002. Determination of trace metals in waters by FAAS after enrichment as metal-HMDTC complexes using solid phase extraction, Bull. Koraen Chem. Soc., 23(5): 693-698.

US-EPA, Environmental Protection Agency. 2004. Contaminated sediment in Water Report to Congress. p 3.

WHO/EU. 1993. Drink water standards comparative table. WHO Regional Office for South-East Asia, p 3.

طريقة معدلة لتقدير أيوني الكوبلت الثنائي والنحاس الثنائي اعتماداً على تكوين معقدات مع قواعد شف في مياه شط العرب

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المستخلص ـ استخدمت طريقة جديدة بتكوين معقد بين ايوني الكوبلت أو النحاس مع قواعد شف (المشتقة من قاعدة شف للساليسالدهيد والاحماض الأمينية) لتقدير الكوبلت والنحاس في عينات مياه من ثلاث محطات على طول نهر شط العرب وعلى النحو التالي: 1) عند نقطة التصريف لمخلفات معمل الورق والعجينة في شط العرب، 2) قناة كرمة علي و 3) السيبة في الاتجاه الجنوبي لشط العرب. تم تقدير الكوبلت والنحاس بعد تكوين معقد مع قواعد شف والذي تمت دراسته طيفيا" عند الطول الموجي 270 و 295 نانومتر على التوالي.ووجد ان تركيز الكوبلت بحدود (0.152 ، 0.174 ، 0.165) ملغم/لتر وتركيز النحاس هو (0.014 ، 0.021 ، 0.023) ملغم/لتر في المحطات 1 ، 2 و 3 على التوالي. يمكن الاعتماد على هذه الطريقة لكونها تتميز بحساسية ودقة وانحراف معياري وحدود قياس هي: (0.0135 غم.سم/لتر ، 3.05×10^{-6} ، 0.00184 ، 0.52×10^{-7}) لمعقد الكوبلت و (0.0135 غم.سم/لتر ، 3.31×10^{-6} ، 0.00215 ، 0.6×10^{-8}) لمعقد النحاس على التوالي.