Spectrophotometric Determination of Copper(II) in Natural Waters and High Purity Thermal Boiler Water

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A facile, highly sensitive and selective spectrophotometric procedure was developed for the determination of copper(II) in thermal boiler water using a newly synthesized reagent, N,N'-*bis*(salicylidene)ethylenediamine (Salen). It is based on the reaction at pH 4-9 between the synthesized Salen and Cu(II) forming a deep green complex, Cu(II) Salen (1:1), that floats quantitatively with oleic acid surfactant. It exhibits a constant and maximum absorbance at 550 nm in both aqueous and surfactant layers. Beer's law is obeyed over the concentration range 0.25-6.35 mg L^{-1} with a detection limit of 0.005 mg L^{-1} for a standard aqueous solution of Cu(II) with a concentration of 3.82 mg L^{-1}, molar absorptivities of 5.5×10^3 and 1.3×10^4 mol L^{-1} cm^{-1} in aqueous and surfactant layers, respectively. Sandell's sensitivity was calculated to be 0.244 µg cm^{-2} and the relative standard deviation (n = 9) was 0.19 %. The different analytical parameters affecting the flotation and determination processes were examined. The proposed procedure has been successfully applied to the analysis of Cu(II) in natural waters and high purity thermal water samples. The results obtained agree well with those samples analyzed by atomic absorption spectrometry.

Key Words: Copper, Spectrophotometry, Natural waters, High purity thermal water, Salen.

INTRODUCTION

Many industrial wastewater streams contain heavy metals, which are of great environmental concern and must be removed prior to water discharge or water recycling[1,2]. Copper is utilized in electrical industries and in industrially useful alloys. Biologically copper is essential in small amounts for the synthesis of haemoglobin. A deficiency of copper causes diseases such as anemia, while an excess of it causes Jaundice and Wilson disease. As a pollutant, copper is of particular concern because of its high degree of toxicity to aquatic organisms. Several analytical techniques have been monitored for the determination of copper(II), which include atomic absorption spectrometry[3-5], voltammetry[6-8], spectrophotometry[9-11], inductive coupled plasma-atomic emission spectrometry[12-14] and inductive coupled plasma-mass spectrometry[15]. A few reagents[16] are available for the spectrophotometric determination of copper(II). These reported reagent suffer from several disadvantages, such as poor sensitivity, selectivity and a few require special conditions for the formation of the complexes with the reagents and a few are commercial.

The reported list of toxic Cu species[17] often includes $Cu(OH)^+$, $Cu_2(OH)_2^{2+}$ and $CuCO_3$. However, Cu^{2+} ions present in various aqueous solutions (their presence is a function of pH) are considered to be the most toxic of dissolved copper species. Excess copper in water is not only harmful to human beings, but also interferes with the self-purification of bulk water[18] and exerts an adverse effect on the micro-biological treatment of wastewater[19]. Therefore, from the viewpoints of pollution, environmental chemistry, geochemistry, marine biology and analytical control in industrial, food, agricultural, pharmaceutical and clinical areas, it is necessary to establish a rapid, simple, sensitive and accurate procedure for the selective concentration of Cu^{2+} prior to its determination. Numerous techniques for the separation and concentration of metal ions including evaporation of solvents, electro deposition, liquid-liquid extraction, surface adsorption, precipitation, ion exchange, ion exchange impregnated materials, immobilized reagents, electro-osmosis and flotation have been reported[20]. Although some of these techniques may be tedious, having limited concentration factors, lengthy and rigid conditions for the separation of solid adsorbents[21], the flotation technique has many advantages that overcome these draw-backs. It has recently received considerable interest owing to its simplicity, rapidity, economy, good separation yields (R > 95 %) for small impurity agent concentrations (10^{-6}-10^{-2} M), a good prospect for application for species having different nature and structure, flexibility and friability of equipment and processing for recovery purpose[22]. It is believed that this process will soon be incorporated as a clean technology to treat water and wastewater[23]. Moreover, flotation is suggested as a method for elimination of interferences[24].

Spectrophotometry still represents an attractive technique for the determination of metal ions in aqueous media because of its simplicity, being inexpensive and is readily available[25]. Therefore, spectrophotometry after selective flotation was chosen for this investigation.

Copper has been removed and analyzed in simulated waste solutions, human hair and natural waters by flotation[26]. Although a vast number of reagents are available for the spectrophotometric determination of copper[27], less work has been done using N,N'-*bis*(salicylidene)ethylenediamine (Salen) and perhaps no trial has been made to float and analyze the analyte with this reagent. Therefore, this work aims to develop a simple and rapid procedure for the selective separation and determination of Cu(II) in natural waters, oleic acid as a surfactant and Salen as a chelating agent. The procedure involves the spectrophotometric determination of copper in the surfactant layer directly after separation by flotation and thus overcoming the problems of elution.

EXPERIMENTAL

All chemicals used were of analytical-reagent grade. Doubly distilled water was used for preparing aqueous solutions by dissolving the requisite amount of $CuCl_2.2H_2O$ in doubly distilled water.

Synthesis of salen ligand: The ligand salen was prepared by the condensation reaction of equimolar amounts of salicylaldehyde and ethylenediamine in ethanol media. The resulting yellow coloured solution was refluxed for 1 h. Slow evaporation of the filtrate lead to the formation of yellow crystals. The precipitated crystals were filtered and dried in air.

The purity was checked by TLC. The product is crystalline (m.p. 192 °C), sparingly soluble in ethanol but easily soluble in acetone, DMF and DMSO. hence its stock solution (1.0×10^{-3} M) was prepared in acetone. Oleic acid stock solution (6.36×10^{-2} M) was prepared by dispersing 20 mL of oleic acid in 1 mL of kerosene. Copper stock solution was prepared by dissolving the requisite amount of $CuCl_2.2H_2O$ in doubly distilled water.
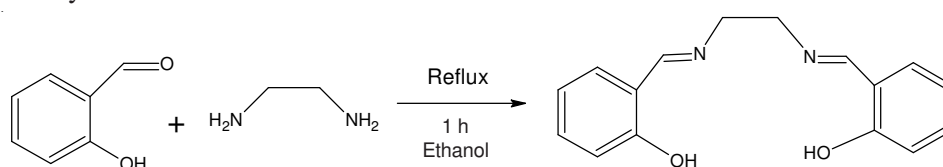
Synthesis of complex from thermal plant boiler water: For the preparation of monomeric Cu(II) complex, to a hot methanolic solution (25 mL) of the ligand to a hot solution of (100 mL) thermal plant boiler water was added drop-wise. The mixture was stirred, refluxed for 0.5 h and then cooled to give a green precipitate which was collected by suction filtration and washed with cold methanol and finally dried in air.
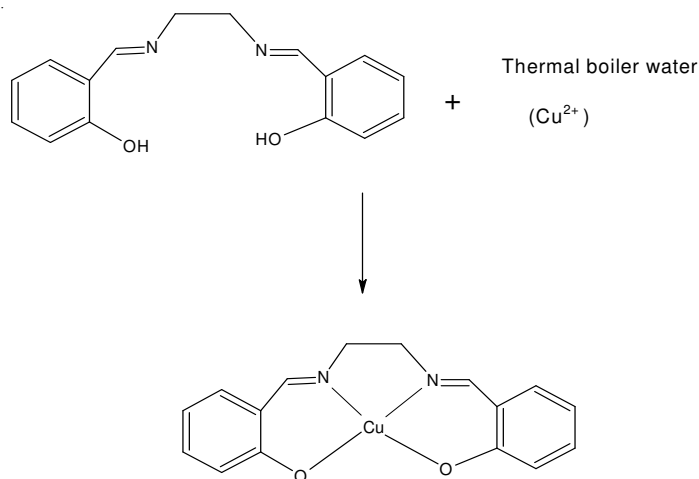
Sample collection and pretreatment: 1 L of tap, Cauvery river, sea water samples and thermal plant boiler water were filtered, the pH adjusted to 1 with concentrated HCl to prevent losses by sorption or co-precipitation and preserved in high quality clean plastic containers.

The flotation cell (a cylindrical tube with a 15 mm inner diameter and 290 mm length, a stop cock at the bottom and a stopper at the top) was the same type as previously described[28].

Procedure

Separation: All samples used in this investigation were in the form of aqueous solutions after suitable treatment. Therefore, the following procedure was applied to all samples.

A suitable aliquot containing a known amount of Cu(II), specified for each investigation, was mixed with a suitable amount of Salen followed by the addition of 3 mL of double distilled water. After adjusting with HCl and/or NaOH to the required pH, the solution was transferred to the flotation cell and the total volume was made up to 10 mL with an acetone-water mixture to ensure a final acetone volume fraction of 30 %. The cell was shaken well for a few seconds to ensure complexation. To this, 3 mL of oleic acid (of known concentration) was added. The cell was then inverted upside down 20 times by hand. Bubbles were created inside the cell. Meanwhile, the stopper of the cell was removed to permit air movement. After allowing it to stand for 5 min for complete flotation of the coloured complex, the concentration of Cu(II) in the surfactant layer was determined spectrophoto-metrically.

Determination: The concentration of Cu(II) in the floated layer was determined spectrophotometrically by transferring a suitable volume to the quartz cell and measuring the absorbance at 550 nm against the reagent blank Salen. The analyte concentration was calculated from a calibration curve constructed by taking different concentrations of Cu(II). The flotation efficiency (% F) was calculated from the relation % F = Cs/Ci × 100.

RESULTS AND DISCUSSION

In order to obtain the optimum conditions for the maximum flotation efficiency of Cu(II) with the oleic acid surfactant, the different factors affecting this process have been studied. It should be noted that the maximum absorbance of the complex Cu-salen corresponds to its maximum flotation efficiency. So, the maximum absorbance can be expressed by the maximum floatability of the analyte and the inverse is true, as well[29].

Absorption spectra: The absorption spectra of Cu(II), salen reagent and of Cu-salen complex formed in aqueous acetone solution (30 % v/v) and that floated into the oleic acid layer are given in Fig. 1. It is noticed that the absorption spectra of the complex and the ligand (curves a and b) have no absorption bands in the region that corresponds to that of the complexes Cu and salen, curves (c) and (d), having their maximum absorbance at 550 nm. Moreover, it is interesting to note that the floated complex has a higher maximum absorbance value in comparison with that formed in the aqueous solution resulting in an enhancement in the sensitivity of the spectrophotometric determination of Cu(II) after flotation. Hence, subsequent analysis of the coloured complex was carried out at 550 nm after flotation.
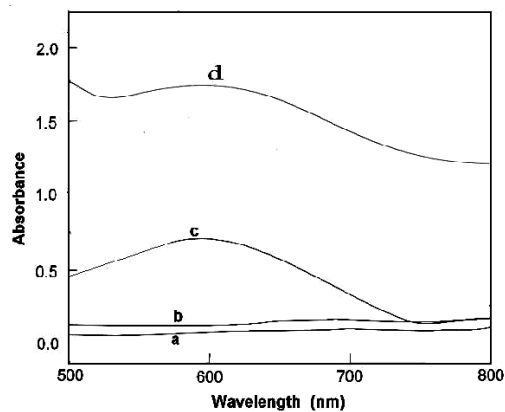
Fig. 1. Absorption spectra of (a) 4×10^{-4} M Cu(II), (b) 8×10^{-4} M Salen, (c) Cu-Salen- H_2O complex and (d) Cu-Salen-oleic acid complex. Where Ci and Cs denote the initial Cu(II) concentration and its concentration in the surfactant layer, respectively. All the experiments were carried out at room temperature, *ca.* 25 ºC

Composition of the complex: The composition of the copper complex was studied by the continuous variation method. A typical graph obtained (Fig. 2) by the former method showed that 1:2 and 1:1 (Cu-salen) complexes are formed in the surfactant and aqueous solutions, respectively (curves a and b). However, the difference in molar ratio between the floated complex and that formed in the aqueous solution may be attributed to the floatability of a small quantity of free reagent in addition to the complex[30]. Moreover, it must be noted from the data in Fig. 2 that the oleic acid surfactant intensifies the colour of the complex (higher absorbance than in the aqueous solution) which confirms the determination of Cu(II) after floatation of its complex[31].
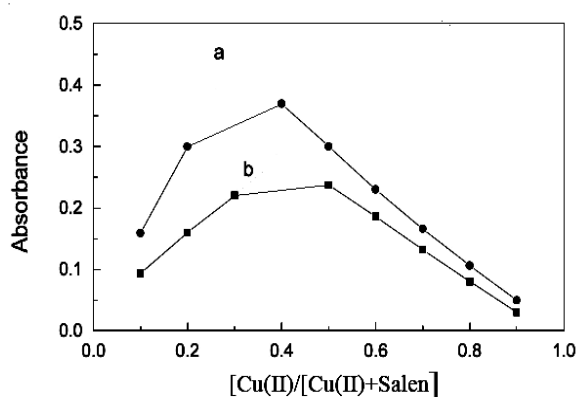

Fig. 2. Composition of Cu(II) complex by the continuous variation methods. (a) Cu(II) complex floated by oleic acid surfactant. (b) Cu(II) complex in aqueous solution. The measurements were carried out at 550 nm and pH~7, using 1×10^{-4} M Salen as a blank

Effect of pH: Since the pH of the medium is a highly significant factor in flotation processes, pH was the first variable to be optimized. A series of experiments was carried out to study the effect of pH on the flotation efficiency of 1.0×10^{-4} M Cu(II) with 1.0×10^{-3} M oleic acid in the presence of 2.0×10^{-4} M Salen. The results presented in Fig. 3 show range that the floatability of the Cu-salen complex increases with increasing pH, reaching its maximum value (maximum and nearly constant absorbance) in the pH range 5-9. The pH~7 was attained by direct addition of reagents and unless otherwise stated, adjustment of the solution pH was not required. Therefore, pH~7 was used as the optimal pH for other experiments.
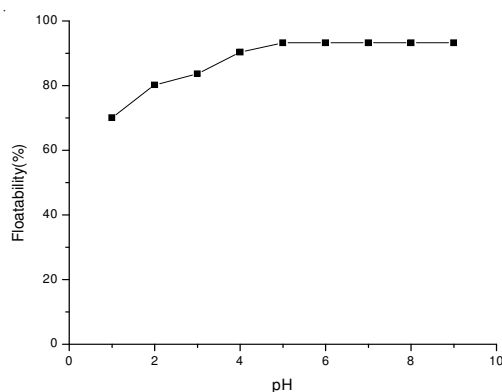

Fig. 3.   Floatability of 1.0×10^{-4} M Cu(II) *vs.* pH using 2.0×10^{-4} M Salen
and 1.0×10^{-3} M oleic acid

Effect of ligand concentration: Initial experiments were performed to float Cu(II) with oleic acid surfactant alone. However, the flotation efficiency did not exceed 40 %. Therefore, a trial was made to improve this process using different reagents. The floatability of a series of solutions containing 1.0×10^{-4} M Cu^{2+}, 1.0×10^{-3} M oleic acid and various amounts of Salen at pH~7 was investigated. The results are shown in Fig. 4. As can be seen, the flotation efficiency (equivalent to the maximum absorbance) increases with increasing concentration of the ligands, reaching its maximum value (*ca.* 100 %) at a 1:2 (Cu:Salen) ratio. These results agree well with those obtained in Fig. 2. Moreover, the excess of ligand has no adverse effect on the flotation process and so the procedure be applied to real samples containing Cu(II). Accordingly, a concentration of Salen equal to twice that of Cu(II) was used in the recommended procedure.

Effect of copper concentration: To confirm the data obtained in Fig. 4, another series of experiments were carried out to float various amounts of Cu^{2+} ions in the presence of 2.0×10^{-4} M Salen using 1.0×10^{-3} M oleic acid at pH~7. As can be seen, the floatability reaches 100 % at a Cu(II) concentration of 1.0×10^{-4} M, corresponding to 1:2 molar ratio (Cu:Salen), which agrees well with the data obtained in Fig. 4. At higher concentrations of the analyte, the flotation efficiency decreases.

This may be attributed to the fact that the amount of Salen is insufficient to bind all Cu^{2+} ions that exist in the solution. Consequently, in the analysis of copper in its natural unknown samples, excess ligand can be safely used.
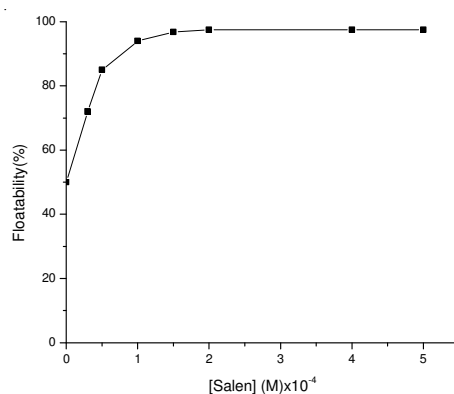

Fig. 4. Floatability of 1.0×10^{-4} M Cu(II) vs salen concentration at pH~7 using 1.0×10^{-3} M oleic acid

Effect of ionic strength: Table-1 summarizes the effect of varying the ionic strength of different salts on the flotation efficiency of 1.0×10^{-4} M Cu(II) ions with 1.0×10^{-3} M oleic acid in the presence of 2.0×10^{-4} M Salen at pH~7. The salts used in adjusting the ionic strength generally resemble those present in natural water samples. As can be seen, the ionic strength of the medium has not markedly affected the flotation process nor the determination of Cu(II).

TABLE-1
EFFECT OF IONIC STRENGTH ON THE FLOATABILITY OF Cu(II)*

Salt	Concentration (M)	F (%)
NaCl	0.02	100.0
	0.10	99.7
	0.50	99.0
KCl	0.02	100.0
	0.10	99.8
	0.50	98.8
CaCl$_2$	0.02	100.0
	0.10	99.0
	0.50	98.3
MgSO$_4$	0.02	100.0
	0.10	98.5
	0.50	95.0

*1.0×10^{-4} M Cu(II), 2.0×10^{-4} M Salen, 1.0×10^{-3} M Oleic acid, pH~7.

Applications: To investigate the applicability of the recommended procedure to natural water samples (taken from different locations), the recoveries of known amounts of Cu(II) added to these samples were examined (Table-2). To 10 mL

TABLE-2
DETERMINATION OF Cu(II) SPIKED IN NATURAL WATER AND
THERMAL BOILER WATER SAMPLES

Type of water procedure (location)	Cu(II) added (mg L^{-1})	Spectrophotometric procedure		AAS Procedure	
		Found (mg L^{-1})	Recovery (%)	Found (mg L^{-1})	Recovery (%)
Distilled water	-	ND	-	ND	-
	0.5	0.495	99.0	0.494	98.8
	1.5	1.498	99.8	1.498	99.9
	2.5	2.495	99.8	2.496	99.8
Tap water (Our laboratory)	-	ND	-	ND	-
	0.5	0.497	99.8	0.496	99.2
	1.5	1.492	99.4	1.491	99.4
	2.5	2.497	99.9	2.498	99.9
Cauvery water (Mettur dam)	-	ND	-	ND	-
	0.5	0.494	99.3	0.493	98.6
	1.5	1.496	99.7	1.495	99.6
	2.5	2.496	99.8	2.496	99.7
Sea water (Chennai)	-	ND	-	ND	-
	0.5	0.497	99.5	0.498	99.6
	1.5	1.497	99.8	1.497	99.8
	2.5	2.495	99.8	2.495	99.8
Lake water (Salem Yercaud)	-	ND	-	ND	-
	0.5	0.496	99.2	0.496	99.2
	1.5	1.494	99.6	1.494	99.6
	2.5	2.493	99.7	2.494	99.8
Thermal plant boiler water	-	ND	-	ND	-
	0.5	0.496	99.2	0.493	98.6
	1.5	1.494	99.6	1.495	99.6
	2.5	2.493	99.7	2.496	99.7

aliquots of clear uncontaminated, filtered water samples, 0.5 or 1.5 mg L^{-1} of Cu(II) were added and the pH was adjusted to *ca.* 7. After flotation, the concentration of Cu(II) was determined either spectrophotometrically in the surfactant layer at 600 nm or by atomic absorption spectrometry (Table-2) in the mother liquor at 324 nm. Spectrophotometric determination of Cu(II) after flotation gives satisfactory results compared to those obtained by AAS. Thus the spectrophotometric determination of Cu(II) after flotation makes the procedure highly selective and sensitive.

Conclusion

The proposed spectrophotometric method is simple, highly sensitive and selective for the determination of Cu(II) in water samples and high purity boiler water. The limit of detection of the proposed method is superior when compared to reported methods[32-36]. The method has additional advantages over the reported methods due to easy preparation of complexation agent (salen), high sensitivity of the stable complex, low consumption of the reagent and minimal interferences.

REFERENCES

1. Y. Goksungur, S. Uren and U. Guvenç, *Bioresour. Technol.*, **96**, 103 (2005).
2. J.S. Kim, S. Akeprathumchia and S. Wickramasinghe, *J. Membr. Sci.*, **182**, 161 (2001).
3. Seung-Hynuntee and Hu-Sennchoi, *Bull. Korean Chem. Soc.*, **21**, 1705 (2003).
4. M. Soyak, *Frensen's Environ. Bull.*, **7**, 383 (1998).
5. N. Pourreza and K. Ghanemi, *Spectrosc. Lett.*, **39**, 127 (2006).
6. M.P. Kumar, P.C. Mouli and S.J. Reddy, *Anal. Lett.*, **38**, 463 (2005).
7. C.L. Giancarlotorsi, *Coll. Czech. Chem. Commun.*, **68**, 437 (2003).
8. G. Gillain, G. Duyckarets and A. Disteche, *Anal. Chim. Acta*, **106**, 23 (1979).
9. A. Asan, M. Andal and I. Isolidak, *Anal. Sci.*, **17**, 1125 (2001).
10. J. Wei, N. Teshima, S. Ohno and T. Sakia, *Anal. Sci.*, **19**, 731 (2003).
11. V.A. Jadhav and A.G. Vandre, *J. Indian Chem. Soc.*, **68**, 186 (1992).
12. Y. Gub, B. Din, Y. Liu, X. Chang and S. Meng, *Talanta*, **62**, 209 (2004).
13. Y. Liu, P. Liang and L. Guo, *Talanta*, **68**, 25 (2005).
14. A. Ramesh, K. Ramamohan, K. Seshaiah and N.D. Jaya Kumar, *Anal. Lett.*, **34**, 219 (2001).
15. J.W. McLaren, K.E. Jarnis, A.L. Gray and R.S. Houk, Handbook of Inductively Coupled Plasma-Mass Spectrometry, Blackie & Son Ltd., Glasgow, p. 226 (1992).
16. M.J. Ahmed, I. Jahan and S. Banoo, *Anal. Sci.*, **18**, 805 (2002).
17. E.M.B. Sorensen, Metal Poisoning in Fish, CRC Press, Boston, MA, USA (1991).
18. T. Yubin, C. Fangyan and Z. Honglin, *Adsorp. Sci. Technol.*, **16**, 595 (1998).
19. S.E. Ghazy, S.E. Samra and S.M. El-Morsy, *Adsorp. Sci. Technol.*, **19**, 175 (2001).
20 . S.E. Ghazy, S.E. Samra, A.-F.M. Mahdy and S.M. El-Morsy, *Anal. Sci.*, **19**, 1401 (2003).
21. D.E. Leyden and W. Wegscheider, *Anal. Chem.*, **53**, 1059A (1981).
22. L. Stoica, M. Dinculescu and C.G. Plapcianu, *Water Res.*, **32**, 3021 (1998).
23. J. Rubio, M.L. Souza and R.W. Smith, *Min. Eng.*, **15**, 139 (2002).
24. D. Zendelovska, G. Pavlovska, K. Cundeva and T. Stafilov, *Talanta*, **54**, 139 (2001).
25. S.E. Ghazy and G.A.E. Mostafa, *Egypt J. Chem.*, **45**, 855 (2002).
26. T. Nagahiro, K. Uesugi, M. Sataki and B.K. Puri, *Bull. Chem. Soc. (Japan)*, **58**, 1115 (1985).
27. Z. Marczenko, Separation and Spectrophotometric Determination of Elements, John Wiley & Sons, New York (1986).
28. S.E. Ghazy and M.A. Kabil, *Bull. Chem. Soc. (Japan)*, **67**, 474 (1994).
29. S.E. Ghazy, *Anal. Sci.*, **11**, 33 (1995).
30. R.S. Lokhande, S. Nirupa and A.B. Chaudhary, *Asian J. Chem.*, **14**, 149 (2002).
31. G.A.E. Mostafa and S.E. Ghazy, *Anal. Sci.*, **17**, 1189 (2001).
32. M.E. Khalifa, M.A. Akl and S.E. Ghazy, *Chem. Pharm. Bull.*, **49**, 664 (2001).
33. M.S.H. Kumar, P. Nagaraja and H.S. Yathirajan, *Anal. Bioanal. Chem.*, **375**, 315 (2003).
34. S.E. Ghazy, R.M. El-Shazly and M.S. El-Shahawi, *J. Iranian Chem. Soc.*, **3**, 140 (2006).
35. H. Lin, Z. Liya, Z. Huang, Q. Hu, G. Zhang and G. Yang, *Asian J. Chem.*, **19**, 836 (2007).
36. J.V. Rao and K.V. Prakash, *Asian J. Chem.*, **20**, 6051 (2008).