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Development of rapid, accurate optode for low level detection of cobalt in potable water

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ABSTRACT

The present investigations describe a novel absorption-based optode for cobalt(II) detection. *m*-(mercapto acetamido)phenol (L') is used as a specific ligand for Co²⁺ in water, which undergo a color change from colourless to purple red by the formation of the corresponding monochelated complex [CoL]. The characterization of an optical sensor membrane is described for the determination of Co²⁺ ions based on the immobilization of *m*-(mercapto acetamido) phenol (L') on a triacetylcellulose membrane. The response time of the optode was about 0.5-3 min, depending on the concentration of cobalt(II) ions. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Optode;
Co(II) ions;
m-(mercapto
acetamido)phenol (L');
Triacetylcellulose.

INTRODUCTION

Cobalt is an important element, not only for industry but for biological systems. It is an essential micronutrient for all living systems. It is present in vitamin B12, which is involved in the production of red blood cells (RBC) and the prevention of pernicious anemia. However, in larger amounts at higher concentrations, it is toxic and causes pulmonary disorders, dertitis, nausea and vomiting^[2]. Dissolved cobalt occurs in the environment at concentrations ranging 0.5-12 µg L⁻¹ in sea water and upto 100 µg L⁻¹ in wastewater^[3]. Due to the importance of cobalt, its detection from associated elements by spot detection is highly desirable. Metal ions were generally determined with atomic absorption spectrophotometry (AAS) or inductively coupled plasma

atomic emission spectrophotometry (ICPAES). But, separation and simultaneous determination of mixtures of metal ions as their metal-chelates with an organic chelating reagent by reversed-phase high- performance liquid chromatography (RPHPLC) had been accepted in inorganic analysis in recent years^[4-7].

The design and synthesis of new chemosensors for metal ions is an important task in the field of supramolecular chemistry due to their fundamental role in biological, environmental and chemical processes. Environmental contamination of toxic heavy metals can result in death or severe damage to brain. Over recent decades, considerable progress has been made in analytical methodology for detection, including voltametry, mass spectrometry, atomic absorption or emission spectrometry and chromatography. Although the methods

MATERIALS AND METHODS

are sensitive and accurate, most require tedious sample pre-treatment, sophisticated performance and/or expensive equipment. Optochemical sensors can offer advantages in terms of size, cost, not requiring a reference element and the fact that analytical signal is free of the influence of an electromagnetic field^[8]. Calculation of the inorganic complexation of cobalt using an ion-pairing model and stability constants^[9] shows that it is weakly complexed by inorganic ligand.

On the other hand, there is evidence that cobalt is strongly complexed by organic ligand especially in burdened waters and solids^[10]. From the literature reports, α -nitroso β -naphthol, rubeanic acid, sodium-1-nitroso-2-hydroxy naphthalene 3:6 disulphate, sodium thiosulphate and ammonium thiocyanate are used as reagents for the detection of cobalt in micro amounts. The spot test reagents are subsequently developed for the detection of cobalt are 2-nitroso-1-naphthol-4-sulphonic acid, chromotropic acid dioxime, p-nitrophenyl hydrazone of di acetyl monoxime and p-nitrophenyl hydrazone of 3-hydroxy amino pentan-2-one. There are so many reports^[11-22] on the extractive spectroscopic determination of cobalt. *m*- (mercapto acetamido) phenol is one such reagent attracted us towards the detection of cobalt selectively. In continuation of our investigations^[23] to develop optical sensors for the detection of metal ions selectively here we report, an ecofriendly sensor (with out PVC binding) for the detection of cobalt in water samples. The optical sensor was tested in presence of different metal ions and it gave response for cobalt ions only in the basic medium. The selectivity of the reagent is upto 1 ppm levels. Color change was observed from colorless to purple red.

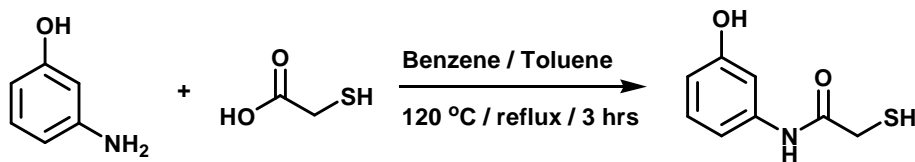
The IR spectra were recorded on Shimadzu FTIR Affinity. All absorption spectra were recorded in Shimadzu U-3010 UV-Vis spectrometer and concentrations were measured by Shimadzu AA-6300 Flame Atomic Absorption spectrometer. Ligand was synthesized and characterized by the method showed below. The metal ions are chloride salts of Ag(I), Cu(II), Zn(II), Cd(II), Pb(II), Hg(II), Fe(II), Fe(III), Ni(II), Ca(II), Na(I) and Mg(II) which were purchased from Aldrich, Merk and used as received. All of other chemicals used here were analytical reagents. Samples were prepared using 3D-water throughout the work.

Cobalt(II) solutions

Cobalt(II) Solutions of 1, 10, 50 and 100 ppm concentrations were prepared in Nalgene bottles by mixing the appropriate mass of a cobalt atomic absorption standard (1000 ppm) with deionised water.

Synthesis of *m*-(mercapto acetamido) phenol^[24]

The synthesis of ligand was presented in scheme 1. Equimolar amounts of mercapto acetic acid (0.01 moles) and *m*-amino phenol (0.01 moles) were condensed at about 110°C for 3 hours under a peripheral layer of 1:1 benzene and toluene using a moderately long air condenser. After 3 hrs, the reaction mixture was left for cooling to room temperature, a white colour solid separated slowly. The solid was filtered and the solid was scrubbed with 1% aq. HCl for three times to remove the unreacted reactants. The crude solid was recrystallized from ethanol to obtain colourless crystals. The pure compound thus obtained was characterized by spectroscopic methods.



Scheme 1 : Synthesis of *m*-(mercapto acetamido) phenol

Sample preparation for spectroscopic measurement

The chloride salts of Ag(I), Cu(II), Zn(II), Cd(II), Pb(II), Hg(II), Fe(II), Fe(III), Ni(II), Ca(II), Na(I) and Mg(II) were dissolved into deionised water to prepare

the stock solutions with the concentration of 1.0×10^{-3} M, synthetic ligand was dissolved in the mixed solution of EtOH:H₂O (v/v = 50:50) to give the stock solution (1.0×10^{-5} to 2.0×10^{-5} M). The prepared stock solution of the metal ions and ligand were directly used in the spectroscopic measurement.

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Methodology

The reagent, *m*-(mercapto acetamido) phenol was dissolved in 5 ml of ethanol and made to a slurry form. Then cellulose paper (4x2 cm size) was dipped into it and air dried. The reagent coated cellulose paper was used as an optode for the detection of cobalt ion. Before commencement to the test, optode was dipped into a solution of NH_4OH for maintaining basic atmosphere. Now place a drop of test solution on the optode. If the colour of the optode changes from colorless to purple red, it indicates the presence of cobalt (II) ion in the test solution.

Opto chemical chads

A solution of ligand (L') was prepared by dissolving 0.250g of *m*-(mercapto acetamido) phenol in 100 ml of ethanol. Whatman no. 1 qualitative filter paper was cut into 25mm chads. Each chad was then treated with the ligand solution and allowed to air dry. These optical sensors were coated by a dipping method. This technique involved dipping the chad, clamped at one end, into a solution containing ligand. The film was allowed to dry in air and a homogeneous film remained on the chad. The response characteristics of the sensor were discussed in the TABLE 1

Preparation of the complex

An ethanolic solution of Co(II) chloride hexahydrate (0.469g, 2m.mol) was added drop wise to the ligand (1m.mole) solution in ethanol while stirring followed by the addition of 2-3 drops of triethylamine. The reaction mixture was refluxed for 3-4 hrs after cooling, refrigerated overnight. The crystals thus obtained were filtered and washed successively with ethanol and ether and dried *in vacuo*.

RESULTS AND DISCUSSIONS

Determination of ligand with metal ions using spectroscopy

UV-Vis spectra

The recognition between ligand and different metal cations were investigated by UV-Vis spectroscopy in EtOH: H_2O (v/v = 50:50) solution. The stock solutions of ligand and metal ions were prepared in 1.0×10^{-5} mol/L and 1.0×10^{-3} mol/L concentrations respectively. From

the absorption spectrum of ligand in EtOH: H_2O (v/v = 50:50) solution, it was found that an intensive absorption band appeared in visible region at 480 nm, which could be assigned as the charge transfer (CT) absorbance [as observed in other compounds with intra molecular charge transfer (ICT)] character. Variation of absorption spectra of ligand upon addition of different metal cations including Fe^{2+} , Ni^{2+} , Hg^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} , Fe^{2+} , Ag^+ , Pb^{2+} , alkali metal and alkaline earth metal cations is recorded and shown in Figure 1. However,

TABLE 1 : Response characteristics of sensor

Parameter	Characteristics
Detection limit	1ppm
Response time	<40 s
pH range	6.5-10
Shelf life	6 months

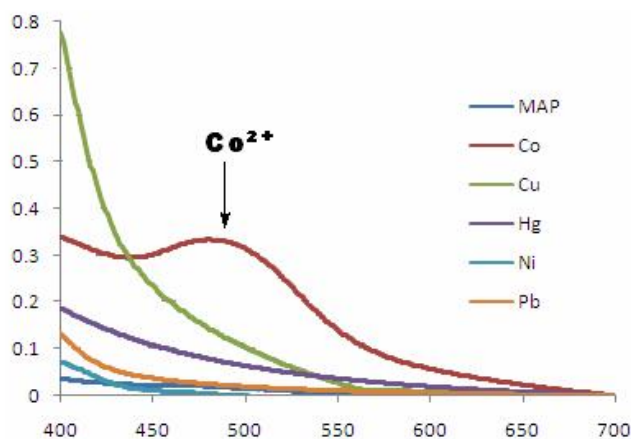


Figure 1 : UV-Vis spectral data of the different metal ions with the ligand (L).

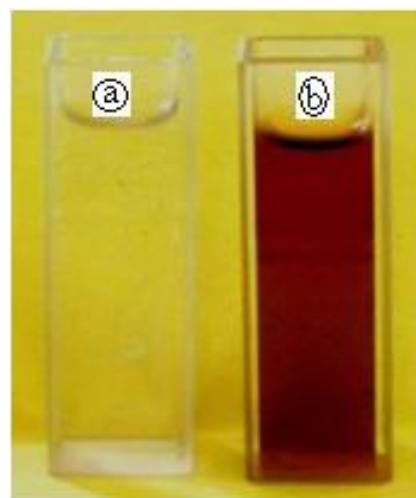


Figure 2 : (a) Blank solution of ligand in ethanol; (b) colour change of the ligand solution with the addition of cobalt (II) ions (1.0×10^{-3} M)

it was found that the maximum absorption of ligand shifts from 410 to 480 nm upon addition of Co^{2+} . The studies showed an obvious colour change from colourless to purple red which was observed by naked eye, as shown in Figure 2. These results indicate that the ligand had high binding affinity towards Co^{2+} ions.

Effect of pH

C. Appadoo et al.^[16] reported that the absorption band remains constant at pH 9.0 and showed a single peak at 480 nm. Hence we carried out the whole reactions at pH 9.0.

IR spectra

The IR spectra of ligand and complex were studied to know the chelating group. The IR spectra were recorded on KBr pellet method. The IR spectra of ligand showed a strong stretching vibrations at 3321 cm^{-1} corresponds to $-\text{NH}$ group of amide, 3448 cm^{-1} corresponds to phenolic $-\text{OH}$ group, 1639 cm^{-1} for the carbonyl stretching of the amide carbonyl and a strong band at 2549 cm^{-1} corresponds to S-H stretching of thiol group, as shown in Figure 3. The IR spectra of the complex is represented in Figure 4. From the figure we observed the absence of thiol stretching and a shift in the carbonyl stretching values. Hence, these above observations support us to consider that the coordination occurred through the carbonyl oxygen and the thio group of the ligand. Further in the IR spectra of the complex, there are two absorption bands in the far infrared region 420-440 cm^{-1} and 480-520 cm^{-1} which are assigned to M-O and M-S vibrations respectively.

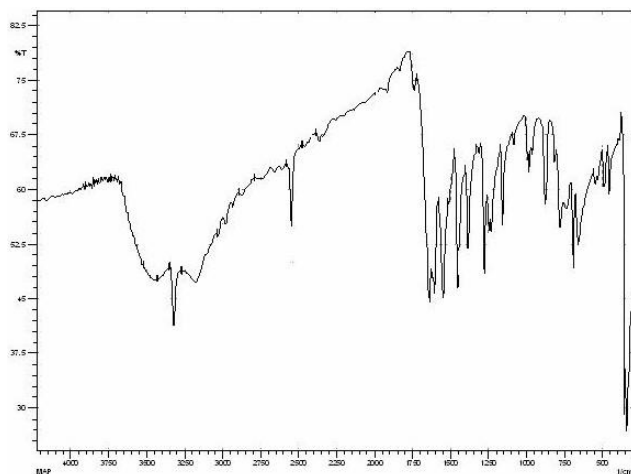


Figure 3 : IR spectra of ligand (L)

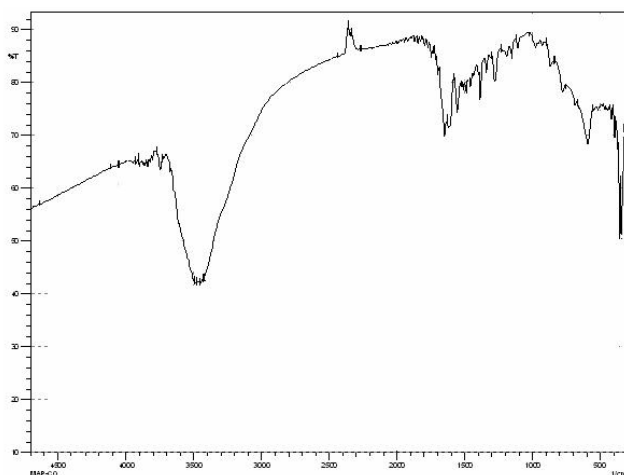


Figure 4 : IR spectra of complex CoL'

The chads prepared has a fast response time of <40 s (measured with stopwatch) and can be used for a period of six months with good ability. The sensor is highly suitable for use in aqueous solutions. The sensor showed high selectivity to cobalt ions without any pH addition over a large number of mono-, bi- and trivalent cations. By "naked-eye" detection, a lower limit of 1 ppm Co^{2+} could be seen in these solutions (Figure 6). To further quantify the detection limit, a conventional UV-Visible spectrometer was employed to record the changes in the absorption spectra. The initial volume of Co^{2+} was 1 ppm and the final volume was 100 ppm.

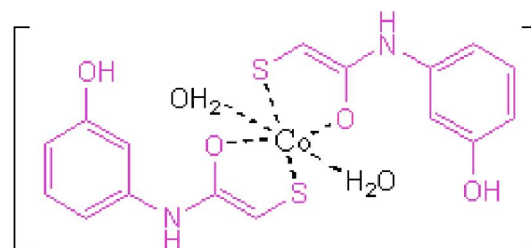
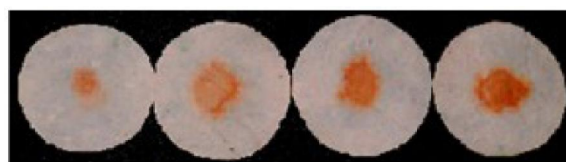


Figure 5 : Tentative structure of the cobalt complex with ligand (L)



1ppm 10ppm 50ppm 100 ppm

Figure 6 : Opto chemical chads for detection of cobalt at 1, 10, 50, 100 ppm levels

Effect of diverse ions

For study the diverse ions effect in the spot test, a drop of cobalt solution (1.0×10^{-3} M) was mixed with a

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drop of solution containing foreign ion (1.0×10^{-3} M) and proceeded as described above. The colour change was compared with blank prepared under similar conditions containing no foreign ion. Calcium(II), Mercury(II), Lead(II), Barium(II), Magnesium(II), Manganese(II), Nickel(II), Iron(II), Iron(III), Zinc(II) and silver(II) did not interfere even when they are present in large excess by this optical chemical chads method. From the above observations it is evident that the reagent is specific for the spot detection of cobalt in environmental and drinking water samples instantaneously. None of the other reagents earlier reported were as sensitive or selective than *m*-(mercaptop acetamido)-phenol.

ANALYTICAL APPLICATION

To investigate the potential use of the new sensor in complex matrices, an attempt was made to determine Co^{2+} ions in nearby industrial waste-water, river water, and in tap water samples. The samples were collected by a routine technique, preserved and stored in polyethylene bottles and analyzed within 12 hrs of the collection. Each sample was analyzed in triplicate, using the chads by standard addition method which showed good results and also using flame atomic absorption spectrometry (FAAS) as a standard method (TABLE 2).

TABLE 2 : Analysis of water samples by AAS & optical chads

Sr. No	Water sample*	Co(II) detection by Sensor	Co(II) concentration by FAAS
1	Tap water	----	----
2	Ground water	----	0.2 ppm
3	Industrial water	Light red colour	2 ppm
4	Sea water	Light red colour	0.8 ppm

CONCLUSION

The present study demonstrates a rapid, simple, highly selective procedure for the development of a cellulose based optical sensor for Co(II) determination at trace levels (ppm). It shows a good selectivity for Co^{2+} over other metal cations. An obvious colour change from colourless to purple red was observed by

the naked eyes, in other words, a signal could be easily read by the naked eye without resort to any spectroscopic instrumentation. Our method is mainly focused for household and industrial purpose. The capability of the sensor for cobalt determination was kept for at least 6 months without any change in the physical and chemical characteristics of the sensor. The sensor can be applied for the determination of cobalt in different real samples with good precision and accuracy.

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