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A Simple inexpensive detection method of Nickel in Water using Optical Sensor

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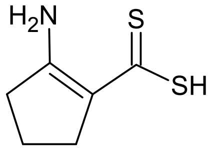
Abstract: A thio carboxylic acid derivative: 2-aminocyclopent-1-ene-1-carbodithioic acid (ligand) was synthesized and characterized. It was used as a colorimetric chemo sensor (chads) for Ni^{2+}. The absorption maximum of ligand and Ni^{2+} shows a shift from 390 nm to 420 nm in absence of buffer solutions. The change in color is very easily observed by the naked eye, while other metal cations, such as Fe^{3+}, Co^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Ag^{+}, Pb^{2+}, alkali metal and alkaline earth metal cations do not induce such a change with these chads. The response time upon exposure to Ni^{2+} is instantaneous. The significant problem of nickel poisoning requires new methods of detection that are sensitive and selective. Here we report a simple system that takes advantage of the unique optical properties generated by ACDA-Nickel complexes.

Keywords: chads; instantaneous; nickel poisoning; sensitive and selective.

Introduction:

The importance of the determination of heavy metal ions, such as nickel, in environment samples can hardly be overemphasized because they have undoubtedly a serious potential hazard to the human organism. US EPA has classified nickel as one of 13 priority metal pollutants for its widespread use. [1] Several techniques such as atomic absorption, [2] atomic fluorescence, [3] X-ray fluorescence, [4] voltammetric,[5, 6] electro thermal atomic absorption or inductively coupled plasma mass spectrometry [7,8] have been used for the determination of this ion in different samples. Spectrophotometric methods based on the UV-visible spectra are widely used due to their simplicity, rapidity, low costs and wide application. The main reagents available for spectrophotometric determination of nickel are dimethyl glyoxime,[9] 5,17-bis(quinolyl-8-azo)-25,26,27,28-tetrahydroxy calyx(4)arene,[10] 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline,[11]benzothiaxolyl diazao aminoazo -benzene,[12] 2-[2-(5-methylbenzothiazolyl) azo]-5-dimethylamino benzoic acid,[13] p-acetyl -arsenazo,[14] 1-(2-pyridylazo)-2-naphthol-6-sulfonic acid,[15] 2-(2-imidazolylazo) phenol-4-sulfonicacid,[16] 3-(4-methoxyphenyl)-2-mercapto propenoic acid,[17] 5-(6-methoxy-2-benzo thiazoleazo)-8-aminoquinoline,[18] 2- (2benzothiazolylazo)-5-dimethylaminobenzoic acid, [19]7-(4,5-dimethyl-2 thiazolylazo)-8-hydroxy - quinoline.[20] However, most of these methods lack sensitivity or selectivity, the procedures are sometimes rather complicated because of the need for extraction to separate interfering ions or expensive surfactants. The spectro photometric determination of nickel with dimethyl glyoxime (DMG) is widely used, and the reaction is carried out in aqueous alkaline medium.[21–23] The procedure involves oxidation of Ni2+ by bromine, iodine or persulfate. Other procedures for nickel determination with DMG without addition of an oxidizing agent require one additional step for extraction of the Ni–DMG complex with organic solvent, thus increasing the operator handling and the susceptibility to contamination.[24] Other ions such as Cu2+, Co2+ and Fe2+ also react with DMG in alkaline media yielding stable complexes that absorb in the visible region, thus leading to interferences in the nickel determination. Also the determination of nickel could be carried out directly by X-ray fluorescence in electroplating solution,[25] flame atomic adsorption spectrometry (FAAS) in water samples [26] and gasoline,[27] graphite furnace atomic absorption spectrometry (GFAAS) in fingernails and forearm skin, [28] gasoline[29] and residual fuel oil,[30] electro thermal atomic absorption spectrometry (ETAAS) in aluminium-base alloys[31] and marine sediments,[32] inductively-coupled plasma atomic emission spectrometry (ICP-AES) in plant samples,[33] square-wavead sorptive stripping voltammetry (SWASV) in duraluminium, iron ore and a reference river water sample[34] and flow-injection solid-phase spectrophotometry (FI-SPS) in copper-based alloys.[35] Each of these proposed methods often offer their own set of advantages and disadvantages.

Hence the development of sensitive chromogenic probes has been receiving much attention in recent years because of the potential application in clinical biochemistry and environment. There are already many chromogenic chemosensors developed for selective recognition of different species.[36–38] However, chromogenic chemosensors for selective detection of transition metal ions, although Ni2+ plays a very important role in Nickel biogeochemical cycling and environmental toxicology .Thus, it is highly desirable to design and synthesize novel Ni2+ colorimetric sensors in which a signal could be easily read by the naked eye without resort to any spectroscopic instrumentation and time consuming methods.



2-aminocyclopent-1-ene-1-carbodithioic acid (ligand)

These colorimetric optical chads generally make use of a reagent that binds selectively with the analyte to give a distinctive color change, directly or via a chromoionophore.The reagent must be immobilized onto a suitable matrix. Several methods have been used to immobilize reagents in optical sensors used for heavy metal ions, such as covalent binding, [39, 40] electrostatic attraction to a resin,[41, 42] incorporation into PVC membranes [43–46] and entrapment inside Nafion films.

In continuation of our investigations on development of new sensors, herein we report a new and environmental friendly (without PVC binding) Ni2+-sensitive chromogenic sensor, in which the chromogenic moiety itself acts as a ligand for metal cations. In this intrinsic chromogenic ligand, metal cation binding may affect the spectroscopic properties dramatically so that a very obvious color change can be observed by the naked eye.

In early literatures,[47-49] Ali A.Ensafi et al described that this chromogenic moiety act as sevier interference by the Fe(II), Fe(III), Mn(II),Pb(II),Co(II) and Cu(II) ions, but in our research these are not visually reporting by our chads in water analysis. By referring figure-3, it can be clearly understood.

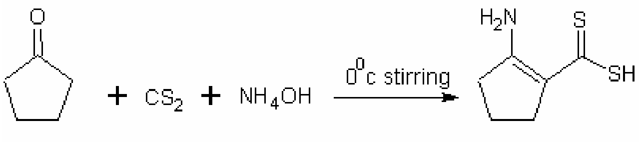
Experimental:

Instruments and materials:

The 1H NMR spectra were recorded at 90MHz on a Zeol-FTNMR-90. All absorption spectra in this work were recorded in Hitachi U-3010 UV–Vis spectrometer and concentrations were measured by AA-6300 Atomic Absorption spectrometer. Ligand was synthesized and characterized by the method showed below. The metal ions are perchloride salts of Ag+,Cu2+, Zn2+, Cd2+, Pb2+, Hg2+, Fe2+,Fe3+, Co2+, Ca2+, Na+, and Mg2+, which were purchased from Aldrich and used as received. All of other chemicals used here were analytical reagents.

Synthesis of Ligand:

Cyclopentanone (25.02g) was mixed with 27.5 ml carbon disulfide in 100 ml concentrated ammonium hydroxide (28% solution) in a 250-ml flask. The mixture was stirred at 00C in an ice bath for 6 h (scheme-1). A yellow precipitate gradually falls out of the solution. The crude product was recrystalized from ethanol. That was ammonium salt from the dithio acid and was fairly unstable. Thus, the salt was collected by suction filtration and was immediately dissolved in about 200 ml of water. Then, with vigorous stirring, 2 M HCl was added until the pH reached 4-5.A yellow precipitate would be formed. That was the free dithio acid. The free acid was collected by suction filtration and was washed several times with water and was dried. This procedure was done according to the earlier recommended report.[50] The crystals were recrystalized from ethanol. The IR spectra showed (KBr disk method) 3450,1618,1605,1470,1450, 1425.The NMR spectra showed (in DMSO) δ 10.7(m, NH), 9.0(s, SH), 3.40(t, C-1 H), 2.95(t, C-5 H2), 2.72 (t, C-3 H2), 1.85(m, C-4 H2).



ACDA (ligand)

Reagents and Chemicals:

Nickel (II) solutions:

Solutions with nickel (II) concentrations of 0.5, 3.0, 5.0 and 10.0 ppm were prepared in Nalgene bottles by mixing the appropriate mass of a nickel atomic absorption standard (1000 ppm) with deionized water and bringing the solution to a final mass of 30.0 g.

Sample preparation for spectroscopic measurement:

The per chloride salts of Ag+, Cu2+, Zn2+, Cd2+, Pb2+, Hg2+, Fe2+, Fe3+, Co2+, Ca2+, Na+, and Mg2+ were dissolved into deionized water to prepare the stock solution 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.

Selectivity:

The optical selectivity of the optode was investigated for several ions and the selectivity coefficients were carried out by separated sample solution method (SSM). The selectivity of the optode membrane with respect to several metal ions is induced mainly by the relative stabilities of the ion–ionophore complexes. Ni2+ as a “soft” metal ion displays a great affinity for soft sulfur coordination centers and therefore, high selectivity over “hard” metal ions is achieved. As seen from Fig.3, the ligand showed excellent selectivity for Ni2+ over the hard alkali, alkaline earth, Mn(II), Fe(II), Fe(III), Ni(II), Co(II), Zn(II), Cd(II), Pb(II) and Cu(II) ions. Even these metal ions are also “soft” with great affinity for soft sulfur co-ordination centers, at tenfold excess the visual colour change was not observed by these chads. The results showed that their selectivity coefficients are less. Based on the high selectivity of the optode membrane, it seems that the structural features of ACDA and its coordination sites fit the coordination tendencies of Ni2+ (Fig.1) better than any of the remainder cations tested, and explains its high selectivity towards Nickel(II) ion.

Analytical application:

To investigate the potential use of the new sensor in complex matrices, an attempt was made to determine Ni^{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 h 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-I).

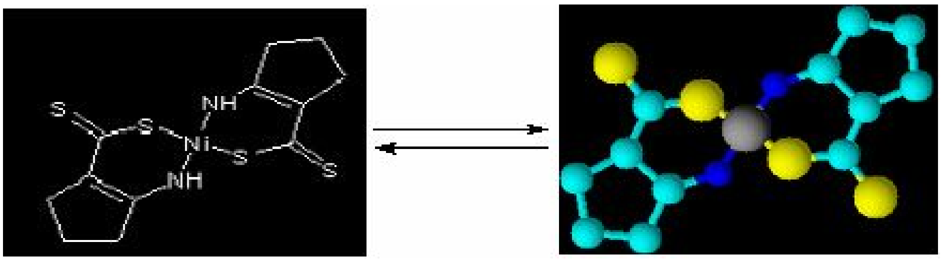


Figure 1

Table: I

Element	Industrial-Water		River-Water		Tap water/potable water	
	PM	AAS	PM	AAS	PM	AAS
Ni(II)	DRC	2.21	LRC	0.885	LRC	0.546

PM-Present method, AAS-Atomic Absorption spectrometer, DRC-Dark red colour,
LRC-Light red colour

ACDA chads (Optical Chemical Chads):

A solution of ACDA was prepared by dissolving 0.250 g of ACDA in 100 ml of ethanol. Whatman no. 1 qualitative filter paper was cut into 25mm chads. Each chad was then treated with the ACDA 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 II.

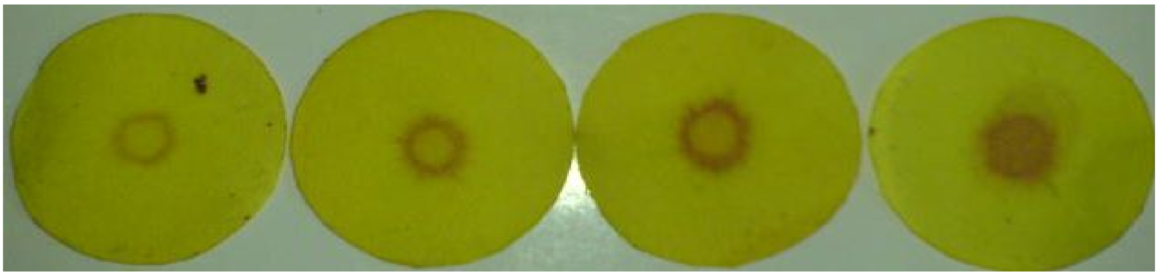


Figure 2. Demonstration of optode coated “dip-sticks” for four different concentrations of Ni^{2+} (1, 3, 5 and 10 ppm Res.,).

Table II. Response characteristics of sensor

Parameter	**Characteristics**
Detection limit	1ppm
Response time	<20 s
pH range	3.2–7.9
Shelf life	6 months

Results and Discussions:

Determination of Ligand with metal ions using spectroscopy:

The recognition between ligand and different metal cations were investigated by UV–Vis spectroscopy in the solution EtOH: H2O (v/v = 50:50). The stock solution of ligand with concentration of 1.0×10−5 mol/L, and the concentration of the metal ions stock solution with 1.0×10−3 mol/L were prepared and kept ready. From the absorption spectrum of ligand in a solvent EtOH:H2O (v/v = 50:50), it was found that an intensive absorption band appeared in visible region peaked at 410 nm, which could be assigned to 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 Fe2+, Co2+, Hg2+, Zn2+, Cd2+, Cu2+, Fe2+, Ag+, Pb2+, alkali metal and alkaline earth metal cations, is recorded and shown in Fig. 3.

However, it was found that the maximum absorption of ligand shifts from 390 to 420 nm upon addition of Ni2+ .The studies show an obvious color change from yellow to red was observed by the naked eyes after the addition of ligand , as shown in Fig.4. These results indicate that ligand has high-binding affinity toward Ni2+ ions.

The chads prepared has a fast response time of <20 s (measured with stop-watch) 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 nickel ions without any pH addition over a large number of mono-, bi- and trivalent cations.

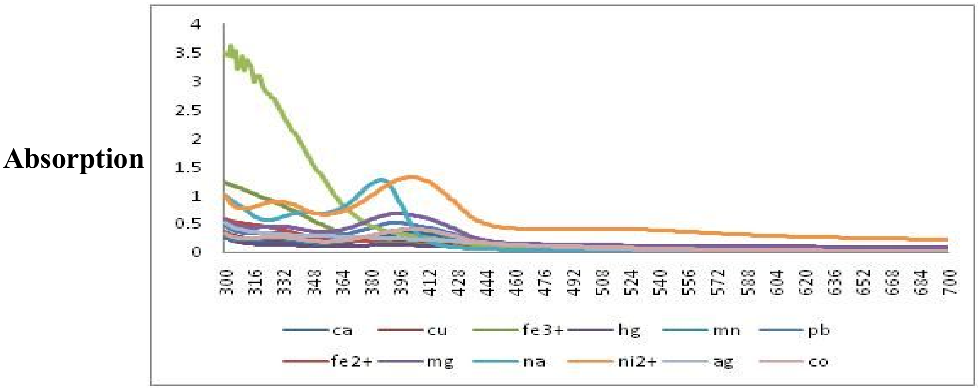


Figure-3

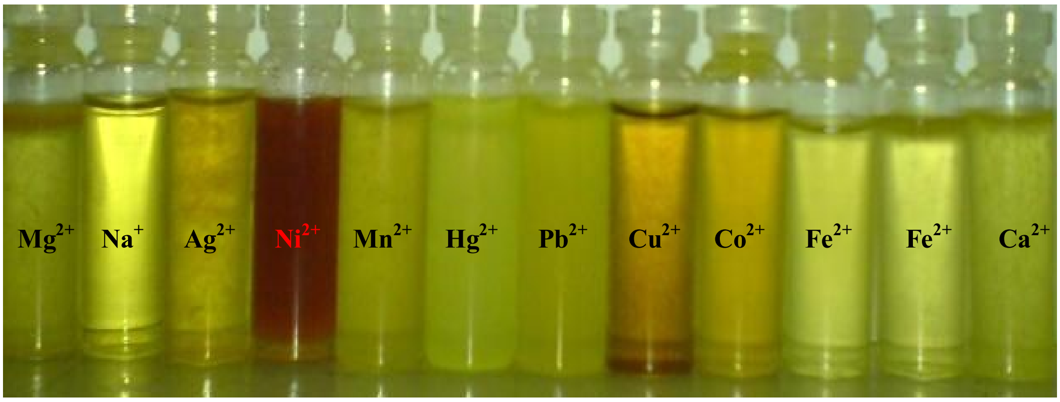


Figure-4: The specific color change to red of Ligand is only observed upon addition of Ni(II). This color change is also observed in the presence of competitive metal ions, even at tenfold excess. No red color is observed for other environmentally relevant bivalent metal ions.

Figure 5a: 0.5, 3, 5 and 10 ppm of Ni^{2+}

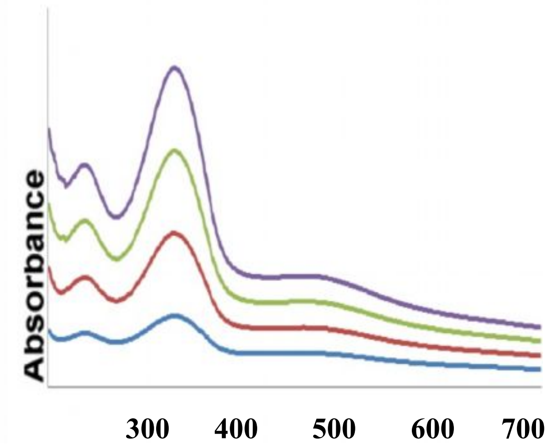


Figure 5b: Wavelength (nm)

To determine the detection limit, the amount of Ni2+ added to solutions of ligand was gradually increased as shown in Figure 3a (From left to right). By "naked-eye" detection, a lower limit of 0.5 ppm Ni2+ could be seen in these solutions (Figure 5a). To further quantify the detection limit, a conventional UV/Visible spectrometer was employed to record the changes in the absorption spectra as shown in Figure 5b. Color change from left to right (as indicated by the arrow) due to increasing Ni concentration. The initial volume of Ni2+ was 0.5 ppm and the final volume was 10 ppm. Absorption spectra of ligand in EtOH/water with increasing Ni2+. Right: A plot of absorption versus wavelength of Ni2+ concentrations for 0.5ppm, 3ppm, 5ppm and 10ppm.

Conclusion:

A new chromogenic chemosensor (chads) based on thio carboxylic acid derivative was developed for Ni2+ in water samples. It shows a good selectivity for Ni2+ over other metal cations. An obvious color change from yellow to 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. In simple words, a common human can easily detect the nickel in water with these chads.

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