

# DETERMINATION OF COBALT(II) BY COMPLEXATION WITH 3-(2'-THIAZOLYLAZO)-2,6-DIAMINOPYRIDINE AND PREPARATION OF CHELATING RESIN TO SEPARATE COBALT(II)

## INTRODUCTION

### Cobalt

Cobalt is a grayish lustrous metal. It is brittle and hard. The properties of cobalt are shown in Table 1. Cobalt is not found as the free metal. The abundance of cobalt in the earth's crust is 30 ppm. More than 200 ores are known to contain cobalt but only a few are of commercial value. The more important are arsenides and sulfides such as smaltite,  $\text{CoAs}_2$  and linnacite,  $\text{Co}_3\text{S}_4$ .

**Table 1** Some properties of the elemental cobalt

| Property                                                                 | Cobalt                  |
|--------------------------------------------------------------------------|-------------------------|
| Atomic number                                                            | 27                      |
| Number of naturally occurring isotopes                                   | 1                       |
| Atomic weight                                                            | 58.933                  |
| Electronic configuration                                                 | $[\text{Ar}] 3d^7 4s^2$ |
| Electronegativity                                                        | 1.7                     |
| Melting point / $^{\circ}\text{C}$                                       | 1495                    |
| Boiling point / $^{\circ}\text{C}$                                       | 2927                    |
| Thermal conductivity / $\text{W m}^{-1} \text{K}^{-1}$                   | 100                     |
| Density (20 $^{\circ}\text{C}$ ) / $\text{g cm}^{-3}$                    | 8.9                     |
| Electrical resistivity (20 $^{\circ}\text{C}$ ) / $\mu\Omega \text{ cm}$ | 6                       |

Source: Greenwood (1997)

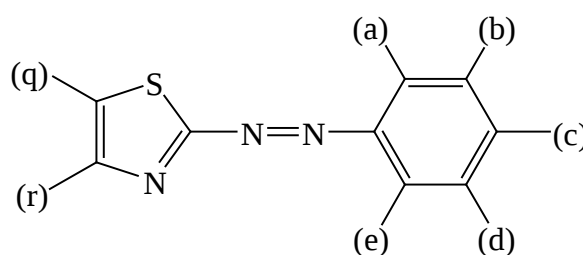
Cobalt is used in magnet steels, stainless steels, alloys, jet turbines, gas turbine generators and electroplating. Cobalt salts are used for the production of brilliant and permanent blue colors in porcelain, glass, pottery, tiles and enamels. Cobalt compounds are used as paint pigments.

Cobalt metal powder is a fire hazard. Evidence indicates that minute quantities of cobalt may be detrimental to higher plant life, particularly in water and sand cultures. Cobalt toxicity is characterized by a chlorosis similar to that induced by lack of iron. Growing cattle can consume up to 50 mg cobalt per 100 lb body weight without ill effects. Sheep can tolerate up to 160 mg daily per 100 lb weight for at least eight weeks without harmful effects. Higher dosages are injurious.

### Thiazolylazodye

Thiazolylazo dyes are easily prepared by the diazotization of 2-aminothiazole and its derivatives. The diazotate formed is so reactive that it has to be coupled with the aromatic substance in cold acidic solution.

General properties of thiazolylazo dyes are red, violet or brownish in their crystalline state, and only a few are readily soluble in water. However, their solubility can be increased by the addition of organic solvent such as ethanol, dimethylformamide and acetone. The general structure of thiazolylazo dye is shown in Figure 1.



**Figure 1** General structure of thiazolylazo dye

Thiazolylazo dyes are sensitive chromogenic reagents in addition to being interesting complexing agents, and have been used as reagents for spectrophotometric

and extraction-photometric determinations of many metal ions. Some of them have also proved to be particularly useful as indicators in complexometric titrations.

4-(2'-thiazolylazo)resorcinol (TAR) is the most widely used reagent, it is soluble in strongly acidic solution, giving a red cation with an absorption maximum at 488 nm, and in strongly alkaline solution, giving a red-violet anion with an absorption maximum at 510 nm. TAR imparts a yellow color and an orange-red color in neutral and dilute acidic and dilute solutions of alkali, respectively (Busev, 1968). The dyes give colored complexes with most metals, stable chelates being formed, especially with some of the transition metals. In acidic and slightly acidic solutions, the metals form complexes with the metal to ligand ratio of 1:1 or a mixture of complexes with ratios 1:1 and 1:2, in alkaline solutions, the equilibrium is usually displaced towards the 1:2 complex (Hovind, 1975).

The complexing reaction of TAR with some of the transition elements is very slow because of the slow substitution of the aqua-complexes of these metals. Thus, TAR reacts slowly with platinum, palladium, gold, rhodium, chromium, osmium, ruthenium and iridium ions (Nickless, 1971).

Some of the reactions for complex formation of thiazolylazo dye lead to very contrasting color changes. Thus palladium(II) forms blue complexes with 4-(5'-sulpho-2'-thiazolylazo)resorcinol (STAR) in highly concentrated sulphuric acid solutions, the color change being greater than that which occurs in weakly acidic solution (Oleinik, 1970).

For a thiazolylazo dye which has an amino group in the *ortho* position relative to the azo group, the metal ion is bonded to the nitrogen of the amino group, the azo group and the hetero atom of the thiazole ring, forming five-membered rings.

In this work, TADAP is prepared by diazotization of 2-aminothiazole and coupling with 2,6-diaminopyridine. The product is recrystallized and used as chelating ligand for determination of cobalt(II).

## Chelating resin

The use of adsorbents for preconcentration of trace elements has received increasing attention in separation and analytical chemistry. In particular, chelating resins and chelating reagent immobilized (adsorbed or chemically bonded) supports have found widespread application for enrichment of aimed metals from a variety of matrix. The imminodiacetate and alkylpolyamine containing chelating resins are commonly employed for removal and preconcentration of trace heavy metals, and macrocyclic hexaketone hexacarboxylic acid, and amidoxime resins have been attempted for collection of uranium in seawater. Silica gel is relatively easy to immobilize chelate ligand. Various chemically bonded gels have been prepared, e.g. , 8-hydroxyquinoline, dithiocarbamates and dimethylglyoxime. Although they are effective preconcentration aids with the fast metal ion exchange kinetics the low swelling and the good thermal stability, preparations are troublesome and kinds of silylation reagent are restricted. Terada et al. developed a variety of adsorbents, which were simply prepared by impregnating chelating reagent on activated silica gel. The gels were successfully used to preconcentrate and determine trace metals in natural waters, e.g., 2-mercaptobenzothiazole-SG for copper(II), cadmium(II), lead(II) and mercury(II), p-dimethylaminobenzilidenerhodanine-SG for gold(III), silver(I) and lead(II), thionalide-SG for palladium(III), arsenic(III) and arsenic(V), and 1-nitroso-2-naphthol for cobalt(II). They also examined silica gel, activated carbon and polytrifluorochloroethylene powder and clarified that silica gel was most useful as a carrier of chelating agents. Although these gels show low adsorption capacities of metal ions, preparations of them can be freely designed according to the purposes (Ueda, 1985).

Silica gel has been modified with chelating group in order to use in many filed of application such as an ion exchanger, liquid chromatography. Of particular interest is the used of these materials as adsorbent of metal ions from dilute solutions. The preparation of chemically modified silica with organic molecules containing nitrogen, sulfur, oxygen and the study of the adsorption of metal ions are great interesting.

Azo compounds containing a hetero ring are useful as the analytical reagents, because their complexing properties are often specific. In the present study, several chelating adsorbents, supported azo dyes on silica gel, were prepared and attempts were made to evaluate their usefulness as a preconcentration aid for metal ions.

In this work, the chelating resin was prepared by using modified silica which was immobilized with 3-(2'-thiazolylazo)-2,6-diaminopyridine (TADAP) for separation of cobalt(II) from aqueous solutions and selectivity of this chelating resin for cobalt(II) were studied.

## LITERATURE REVIEW

### 1. Synthesis of thiazolylazo derivatives and spectrophotometric determination of metal ions

Busev et al. (1968) studied the methods which were given for the synthesis and purification of 5-(2-thiazolylazo)-2,6-diaminopyridine (2,6-TADAP). The maximum absorption wavelengths were given as a function of acidity ( $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  in various concentrations). Molar extinction coefficients were calculated and were given as a function of pH. 2,6-TADAP was not associated over a wide pH range.

Garcia et al. (1982) studied 3-(2'-thiazolylazo)-2,6-diaminopyridine that reacted with palladium(II) in strong  $\text{HClO}_4$  media, to produce a blue 1:1 complex ( $\lambda_{\text{max}} = 665 \text{ nm}$ ,  $\epsilon = 1.37 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), which allowed the spectrophotometric determination of 0.6-4.5 ppm palladium(II). The method was applied to determine small amount of palladium(II) in samples of hydrogenation catalysts.

Gonzalez et al. (1983) studied ionization constants of the 3-(2'-thiazolylazo)-2,6-diaminopyridine. They were determined at  $25^\circ\text{C}$  by a spectrophotometric method as  $\text{pK}_{\text{a}1} = -3.73 \pm 0.03$ ,  $\text{pK}_{\text{a}2} = 1.16 \pm 0.02$  and  $\text{pK}_{\text{a}3} = 4.19 \pm 0.03$ . Formation constant of the complexes with palladium(II) were also be investigated. In the presence of  $\text{Cl}^-$ , three complexes were formed,  $\text{PdHLC l}^{2+}$ ,  $\text{PdHLC l}_2^+$  and  $\text{PdHLC l}_3$ .

Gonzalez et al. (1986) studied the complexation equilibrium between cobalt(III) and 3-(2'-thiazolylazo)-2,6-diaminobenzene (2,6-TADAB) and 3-(2'-thiazolylazo)-2,6-diaminopyridine (2,6-TADAP) spectrophotometrically and determined the protonation constants of the complexes. 2,6-TADAB ( $\epsilon_{580} = 9.5 \pm 104$ ,  $H_0 = 1.86$ ) and 2,6-TADAP ( $\epsilon_{595} = 1.16 \pm 104 \text{ L mol}^{-1} \text{ cm}^{-1}$ ,  $H_0 = 0.98$ ) allowed the determination of 0.024-0.47 and 0.12-2.36 ppm of cobalt(III), respectively. The

method using 2,6-TADAP was applied to the determination of cobalt(III) in low alloy steels and hydrofining catalysts.

Perez et al. (1987) studied the complexation equilibrium between copper(II) and 3-(2'-thiazolylazo)-2,6-diaminopyridine (I) and 3-(4'-methyl-2'-thiazolylazo)-2,6-diaminopyridine (II) spectrophotometrically. The stability constants of the  $\text{CuR}^{2+}$  complexes ( $\log \beta_{101}$ ) were  $3.94 \pm 0.03$  and  $3.98 \pm 0.02$  with I and II, respectively, and those for  $\text{Cu(OH)R}^+$  ( $\log \beta_{111}$ ) were  $13.19 \pm 0.11$  and  $13.14 \pm 0.09$ , respectively, where  $\text{R} = \text{I or II}$ . Both reagents were applied to the spectrophotometric determination of copper(II) in low-alloy steels and Al-base alloys.

Shraydeh et al. (1992) studied the sensitive methods for the determination of trace amounts of cobalt(II) and copper(II) by complexation with 3-(2'-thiazolylazo)-2,6-diaminopyridine (2,6-TADAP). Copper(II) formed a 1:2 violet complex with the reagent having a molar absorptivity of  $1.00 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ , Beer's law was obeyed over the range 0-50.84  $\mu\text{g}$  in the total volume of 10 mL. Cobalt(II) also formed a 1:1 green complex with a molar absorptivity of  $1.07 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and obeying Beer's law over the range 0-23.57  $\mu\text{g}$  in the total volume of 10 mL. The procedure was simple and rapid without any complicate extension steps for copper(II) and without oxidation of cobalt(II) to cobalt(III).

Oxspring et al. (1996) synthesized the chelating agent, 2-(5'-bromo-2'-pyridylazo)-5-diethylaminophenol (PADAP), and found to be a good chromogenic reagent for metal ions. Adsorptive stripping voltammetry (AdSV) is compared to capillary zone electrophoresis (CZE) for the detection and determination of trace concentrations of metal ions (cobalt(II), copper(II), cadmium(II), zinc(II), nickel(II) and lead(II)) as their PADAP chelates. Limits of detection (LODs) for cadmium(II), zinc(II), lead(II) and cobalt(II) were 8.3, 4.1, 3.0 and  $0.5 \times 10^{-8} \text{ M}$ , respectively, using the AdSV method with copper(II) and nickel(II) not giving reproducible cathodic signals as their respective chelates. CZE was performed using  $1 \times 10^{-4} \text{ M}$  PADAP in the run buffer and gave higher LODs than AdSV but better selectivity.

Fan et al. (1998) synthesized the chromogenic reagents, 2-[2-(6-methylbenzothiazolyl)azo]-5-(N-methyl-N-sulfomethyl)aminobenzoic acid (6-Me-BTAMSB), 2-[2-(6-methylbenzothiazolyl)azo]-5-(N-ethyl-N-sulfomethyl)aminobenzoic acid (6-Me-BTAESB) and 2-[2-(6-methylbenzothiazolyl)azo]-5-(N-ethyl-N-carboxymethyl)aminobenzoic acid (6-Me-BTAECB). Their spectrophotometric characteristics were studied. In weak acid medium, they react with nickel(II) to form blue-violet 2:1 complexes, the absorption maxima of which are at 642, 620 and 625 nm with apparent molar absorptivities of  $8.81 \times 10^4$ ,  $8.22 \times 10^4$  and  $1.03 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ , respectively. Beer's law is obeyed over the ranges 0-7, 0-6 and 0-12  $\mu\text{g}/25 \text{ ml}$  nickel(II), respectively.

Bhalotra et al. (1999) used the fourth derivative spectrophotometry for the trace determination of zinc using 1,2-(thiazolylazo)-2-naphthol (TAN) as an analytical reagent and ammonium tetraphenylborate (ATPB) naphthalene as an adsorbent. Zn-TAN was quantitatively retained on ATPB naphthalene in the pH range 6.5-9.5. The calibration plot was linear in the concentration range 0.02-1.4  $\mu\text{g ml}^{-1}$  Zn of DMF solution. The sensitivity of the method as determined from the slope of the calibration plot was  $2.640 (\text{d}^4\text{A}/\text{d}\lambda^4)/(\mu\text{g ml}^{-1})$ . Nine replicate determinations of 5.0  $\mu\text{g}$  of zinc in 5 ml of DMF gave a mean signal height of 2.660 (peak to peak height between  $\lambda_1 = 597 \text{ nm}$  and  $\lambda_2 = 585 \text{ nm}$ ) with a relative standard deviation of 1.1%.

Hanna (1999) studied the complexation of para-Cl-phenylazo-R-acid azo dye with palladium(II) spectrophotometrically. Protonation constant ( $\text{pK}_a$ ) of the ligand was calculated and the stability constants of para-Cl-phenylazo-R-acid ligand with palladium(II) ion was also determined at a constant temperature ( $25.0^\circ\text{C}$ ), where the molar ratio of this complex was 1:1 (metal:ligand) with  $\log \beta_1 = 3.75$ , and 1:2 with  $\log \beta_2 = 8.55$ . Solid complex of para-Cl-phenylazo-R-acid was prepared and characterized on the basis of elemental analysis and FTIR spectral data. A procedure for the spectrophotometric determination of palladium(II) using para-Cl-phenylazo-R-acid as a new azo chromophore was proposed where it was rapid, sensitive and highly specific. Beer's law was obeyed in the range 0.50–10.00 ppm at pH 5.0–6.0 to form a violet–red complex ( $\epsilon = 7.7 \times 10^4 \text{ l}^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$  at  $\lambda_{\text{max}} = 560 \text{ nm}$ ). Metal ions such as

copper(II), chromium(III), lanthanum(III), ytterbium(III), yttrium(III), and rhodium(III) interfered with the complex. Ammonium salt of trimellitic acid such as 1,3,4-benzenetricarboxylic acid was used to precipitate some of the interfering ions and a scheme for separation of palladium(II) from a synthetic mixture similar in composition to platinum ore or deposit was made.

Kompany-Zareh et al. (1999) studied the spectrophotometric method for the determination of copper(II) and nickel(II) by the use of diethyldithiocarbamate (DDTC) as a chelating agent in the presence of aqueous anionic micellar medium of sodium dodecyl sulfate (SDS). A partial least-squares procedure was used to access data obtained from the calibration solutions. The operated method was validated by applying it to the analysis of synthetic mixtures over the concentration ranges 0-286  $\mu\text{mol Cu/ml}$  and 0-619  $\mu\text{mol Ni/ml}$ . The relative errors in determinations were less than 5 % in most cases.

Zareba and Melke (1999) used azo dyes, derivatives of 1,2,4-triazole and pyrocatechine: 3-(3',4'-dihydroxyphenylazo-1')-1,2,4-triazole (TRIAP) and 3-(3',4'-dihydroxyphenylazo-1')-5-mercapto-1,2,4-triazole (METRIAP) for spectrophotometric determination of aluminum(III). In aqueous-methanolic solution at pH 6.20-6.50, aluminum ion formed stabile orange chelates. Molar ratio of L: aluminum was 2:1 (TRIAP) or 3:1 (METRIAP). Other components of these preparations, particularly magnesium(II), did not interfere the determination of aluminium(III). The advantage of the developed method was easy to synthesize the reagent, simple analytical procedure, stability of formed complexes and accuracy of results.

Zhao et al. (1999) studied the synthesis and analytical reactions of a new reagent, 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline (MBTAQ), with cobalt(II) and nickel(II). In the presence of the cationic surfactants cetyltrimethylammonium bromide (CTAB) and borax buffer solution, cobalt(II) and nickel(II) form blue coloured, 1:2 and 1:3 (metal: ligand) complexes with MBTAQ, respectively. The apparent molar absorptivities were  $1.15 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$  for

cobalt(II) and  $1.28 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$  for nickel(II) at 655 and 623 nm. The method obey Beer's law for 0-0.40  $\mu\text{g ml}^{-1}$  of cobalt(II) and 0-0.32  $\mu\text{g ml}^{-1}$  of nickel(II) and detection limit were 0.00050 and 0.00045  $\mu\text{g ml}^{-1}$ .

Toral et al. (2000) studied a second derivative spectrophotometric method that had been developed for the determination of palladium(II) and platinum(IV) in mixtures. The method was based on the formation of the platinum(IV) and palladium(II) complexes with 3-(2-thiazolylazo)-2,6-diaminopyridine, (2,6-TADAP), in the presence of 1.7 M perchloric acid solution, upon heating at 90 °C for 30 min and on the subsequent direct derivative spectrophotometric measurement. The zero-crossing approach and the graphic method were used for determination of platinum(IV) and palladium(II), respectively. Each analyte was determined in the presence of one another in the ranges of  $8.9 \times 10^{-7}$  to  $3.1 \times 10^{-5}$  M for platinum(IV) and  $4.6 \times 10^{-7}$  to  $6.8 \times 10^{-5}$  M, for palladium(II). The detection limits achieved ( $3\sigma$ ) were found to be  $2.7 \times 10^{-7}$  M of platinum(IV) and  $1.4 \times 10^{-7}$  M of palladium(II). The relative standard deviations were in all instances less than 1.0%. This work was also included a study of effect of interferences and the application of the proposed method in synthetic mixtures.

Amin et al. (2002) studied the complexation of yttrium(III) with 5-(4'-chlorophenylazo)-6-hydroxypyrimidine-2,4-dione (I), 5-(2'-bromophenylazo)-6-hydroxypyrimidine-2,4-dione (II), 5-(2',4'-dimethylphenylazo)-6-hydroxypyrimidine-2,4-dione (III), 5-(4'-nitro-2',6'-dichlorophenylazo)-6-hydroxypyrimidine-2,4-dione (IV), 5-(2'-methyl-4'-hydroxyphenylazo)-6-hydroxypyrimidine-2,4-dione (V). The complex formation was completed spontaneously in buffer solution and the resulting complex was stable for at least 3 h after dilution. Under the optimum conditions employed, the molar absorptivities were found to be  $1.60 \times 10^4$ ,  $1.29 \times 10^4$ ,  $1.96 \times 10^4$ ,  $1.45 \times 10^4$  and  $1.21 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  and the molar ratios were (1:1) and (1:2) (M:L). The linear ranges were found within 95  $\mu\text{g}$  of yttrium(III) in 25 ml solution. One of the characteristics of the complex was its high tolerance for calcium and hence a method of separation and enrichment of amounts of yttrium(III) by using calcium

oxalate precipitation was developed and applied to measure yttrium(III) in nickel-base alloys.

Hashem et al. (2002) studied the solution properties of nickel(II) complex with 4-(2'-benzo-thiazolylazo) salicylic acid (BTAS) by zero-order absorption spectrophotometry in 40 % (v/v) ethanol at 20°C. The equilibria that exist in solution were established and the basic characteristics of complexes formed were determined. A new direct spectrophotometric method for the determination of trace amounts of the nickel(II) was proposed based on the formation of the nickel(II) (BTAS) complex at pH 7.0. The absorption maximum and molar absorptivity were 525 nm and  $0.6 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ , respectively. The use of first-derivative spectrophotometry eliminated the interference of iron(III) and enabled the simultaneous determination of nickel(II) and iron(III) using BTAS. Quantitative determination of nickel(II) and iron(III) were possible in the range 0.59-7.08 and 2.1-8.4  $\mu\text{g ml}^{-1}$ , respectively with a relative standard deviation of 0.5%.

Salazar and Toral (2004) synthesized 3-[2'-thiazolylazo]-2,6-diaminopyridine or 2,6-TADAP and used as chromophore reagent for the determination of metals of the platinum group. In this work, a study on stability of the 2,6-TADAP, a synergetic action of the temperature, the reaction time and the acidity of the medium were also be investigated. According to spectral behavior it could be postulated that 2,6-TADAP ligand suffers structural changes, having as consequence the formation of another azo compound. Besides, the mechanism of decomposition and characterization of the formed compound was also included. The characteristic chemical of new azo compound was appropriate for the development of analytic methods for the determination of metals belonging to the platinum group, using the new ligand called 3-[N,N-ethyl-met-azo]-2,6-diaminopyridine or 2,6-DAPEMA.

## **2. Preparation of chelating resin for separation of metal ions**

Nakayama et al. (1982) prepared a new chelate-forming resin bearing -SH and azo groups from a common anion-exchange resin by treatment with

azothiopyrinedisulfonic acid (I). The I-treated resin was very stable and highly effective for the collection of mercury(II), copper(II) and cadmium(II) by the batch and column methods. In the column method, the amount of mercury(II) in solution could be reduced to  $<0.5 \mu\text{g/l}$ . The mercury(II) adsorbed could be eluted with thiourea solution, and the resin could be used repeated, especially for the treatment of wastewater.

Ueda et al. (1985) synthesized the chelating adsorbents, heterocyclic azo dyes supported on silica gel, and investigated their adsorption behavior toward metal ions. The 1-(2-pyridylazo)-2-naphthol (PAN)-SG and 2-(2'-thiazolylazo)-p-cresol (TAC)-SG show greater affinity for uranyl(II) and zirconyl(II), compared with the other metal ions like copper(II), cadmium(II), iron(II), iron(III) and alkaline earths. Trace uranyl(II) can be quantitatively retained on the column of the gels at neutral pH region and flow rate 3-4 ml/min. The uranyl(II) retained was easily eluted from the column bed with a mixture of acetone and nitric acid (9:1 v/v) and determined by spectrophotometry using Arsenazo-III. Matrix components in seawater did not interfere and the spiked recovery of uranyl(II) in artificial seawater was found to be average 98.6%, with the relative standard deviation of 1.08%. Both gels were applied to the determination of uranium in seawater with satisfactory results.

Mao et al. (1986) studied the determination of trace uranium in wastewater by using spectrophotometric method. A polystyrene-based macroporous resin containing PAR was used for separation and enrichment of uranium from wastewater from uranite mining with a recovery of  $>98\%$ . uranyl(II) was quantitatively adsorbed from the wastewater at a pH of 5.5 in the presence of  $1.2 \times 10^{-6}$  M EDTA and eluted with 1 N HCl. The preparation of the polystyrene-azo-PAR resin was discussed.

Saxena et al. (1994) synthesized a very stable chelating resin matrix by covalently linking Alizarin Red-S with the benzene ring of the polymer Amberlite XAD-2 through an  $-\text{N}=\text{N}-$  group. The chelating resin was used for the preconcentration of zinc(II), cadmium(II), nickel(II) and lead(II) from aqueous solution. The optimum pH for the adsorption of zinc(II) and cadmium(II) were 5-6,

for nickel(II) and lead(II) were 3-4 and 6, respectively. Zinc(II), cadmium(II), nickel(II) and lead(II) were eluted from the chelating resin by 4 M hydrochloric acid, 1 M nitric acid, 4 M hydrochloric acid and 3 to 4 M nitric acid, respectively. The adsorption capacities of the resin were 511, 124, 135 and 306  $\mu\text{g/g}$  of the resin for zinc(II), cadmium(II), nickel(II) and lead(II), respectively.

Lemos et al. (1998) used polyurethane foam modified by 2-(2'-benzothiazolylazo)-2-p-cresol (B-TAC) as an adsorbent for determination of cadmium(II) trace levels. It was found that pH had effect on the adsorption of cadmium(II) on B-TAC. The adsorption of cadmium(II) by B-TAC was investigated within the pH range of 6.50 to 9.25. It was found that the maximum adsorption of cadmium(II) was achieved at pH 9 in the ammonium buffer solution. Cadmium(II) was eluted from the column by using hydrochloric acid at various concentrations as eluents. The results showed that 0.1 M hydrochloric acid was the most suitable eluent for desorption of cadmium(II) from B-TAC.

Kumar et al. (2000) synthesized a stable chelating resin matrix by covalently linking o-aminophenol (o-AP) with the benzene ring of the polystyrene-divinylbenzene resin, Amberlite XAD-2, through a  $-\text{N}=\text{N}-$  group. It was used to preconcentrate copper(II), cadmium(II), cobalt(II), nickel(II), zinc(II) and lead(II), prior to their determination by flame atomic absorption spectrometry. The optimum pH values for quantitative sorption of copper(II), cadmium(II), cobalt(II), nickel(II), zinc(II) and lead(II) were 6.2-7.4, 5.6-7.2, 5.6-9.0, 6.0-9.0, 5.7-7.0 and 5.0-6.0, respectively. These metals are desorbed (recovery 91-98%) with 4 M nitric acid. The sorption capacity of the resin is 3.37, 3.42, 3.29, 3.24, 2.94 and 3.32  $\text{mg of metal g}^{-1}$  of resin, respectively, for copper(II), cadmium(II), cobalt(II), nickel(II), zinc(II) and lead(II).

Krysztalkiewicz et al. (2002) studied the adsorption of several organic dyes on a modified silica surface. For this purpose, ethylene glycol (EG)-silica was applied, precipitated from sodium metasilicate solution using carbon dioxide in presence of ethylene glycol. In order to promote their interaction with dyes, the silica surface was

modified using silane coupling agents with the amino functional group. Technique of conducting the adsorption process was discussed. Studies on morphology and microstructure were performed employing scanning electron microscopy (SEM). Particle size distribution was also examined using the technique of dynamic light scattering. The SEM micrographs and particle size distributions showed that highly uniform pigments can be obtained employing EG-silica as a core. Studies on elution of dyes from the silica surface demonstrated that, in general, stable pigments were obtained.

Tawari and Singh (2002) prepared four chelating matrices by coupling Amberlite XAD-2 with chromotropic acid (AXAD-2-CA or 1), pyrocatechol (AXAD-2-PC or 2) and thiosalicylic acid (AXAD-2-TSA or 3) and impregnation of Amberlite XAD-7 with xylenol orange (AXAD-7-XO or 4). All the four resins quantitatively adsorbed lead(II) at pH 3-8 when the flow rate was maintained between 2 and 10 ml min<sup>-1</sup>. Nitric acid (0.5-4.0 M) eluted lead(II) from all the chelating resins. The adsorption capacity was in the range 16.0-186.0  $\mu\text{mol g}^{-1}$ . The limit of detection and limit of quantification found in ranges 2.44-7.87 and 2.76-8.64 ng ml<sup>-1</sup>, respectively.

Barbette et al. (2004) synthesized the new modified silica gels, namely N-tripropionate (or N-triacetate)-substituted tetraazamacrocycles-bound silica gels, for the extraction of uranium(VI). The effect of the nature of the ligand, the pH and the temperature was studied both in batch experiments as well as in continuous extraction. These silica gels were better than a commercially available acid-type chelating resin for the extraction of uranium(VI). The results showed that the total removal of uranium(VI) from a contaminated solution can be achieved by using a column packed with such tetraazamacrocycles-bound silica gels.

Esteves et al. (2005) prepared a new hydroxypyrimidinone-functionalized silica, (HOPY-PrN)-Si, with high affinity for hard metal ions. The new chelating matrix was obtained by coupling a 1-hydroxy-2-(1H)-pyrimidinone derivative, HOPY-PrN, to an epoxy-activated silica. It showed good stability at neutral and acidic conditions and high sequestering capacity for hard metal ions, namely iron(III) and

aluminium(III). However, the presented silica-gel derivative was considerably less expensive and also gave support to its potential interest as a adsorbent of traces hard toxic metal ions from water streams or even from physiological fluids.

Hassanien and Abou-El-Sherbini (2005) prepared the aminopropylsilica gel (APSG) by linking silica gel with aminopropyltrimethoxysilane. The APSG was reacted subsequently with morin yielding morin-bonded silica gel (morin-APSG). Morin-APSG was found to be highly stable in common organic solvents, acidic medium (<2 M hydrochloric acid and nitric acid) or alkaline medium up to pH 8. The separation and preconcentration of silver(I), gold(III), palladium(II), platinum(II) and rhodium(III) from aqueous medium using morin-APGS were studied. The optimum pH values for the separation of silver(I), gold(III), palladium(III), platinum(II) and rhodium(III) on the adsorbent were 5.7, 2.2, 3.7, 3.7 and 6.8, giving rise to separation efficiencies of 43.9, 85.9, 97.7, 60.9 and 91.0 %, respectively, where the activity was found to be >90 % in the presence of acetate ion. The ion adsorption capacity of morin-APSG towards copper (II) at pH 5.5 was found to be 0.249 mmol g<sup>-1</sup> where the adsorption capacities of silver(I) and palladium(III) were 0.087 and 0.121 mmol g<sup>-1</sup> and 0.222 and 0.241 mmol g<sup>-1</sup> at pH 2.2 and 5.7, respectively. Complete elution of the adsorbed metal ions was carried out using 10 ml (0.5 M hydrochloric acid + 0.01 M thiourea) in case of gold(III), palladium(III), platinum(II) and rhodium(III) and 10 ml 0.5 M nitric acid in case of silver(I).

Jesionowski et al. (2005) studied the physicochemical analysis on silicas precipitated according to a novel method, in an emulsion system. Substrates for the process involved solutions of sodium metasilicate and sulphuric acid while the organic phase consisted of cyclohexane and non-ionic emulsifiers. The silicas were used to obtain hybrid structures of the formed inorganic pigments. For this purpose, the adsorption of organic dyes on the silica surface was preceded by modification of the surface with silane coupling agent containing amine groups. Stable pigments were obtained on silica core, the surface of which was modified with N-2-(aminoethyl)-3-aminopropyltrimethoxysilane. Particles of the obtained pigment manifested a spherical shape and particle size distribution proved that no agglomerate structures

were presented. High stability of the obtained pigments proved that the organic dye was chemically bound to the modified silica surface.

Madrakian et al. (2005) synthesized a new modified silica gel using 2,4,6-trimorpholino-1,3,5-triazin. The modified silica gel was used for separation, preconcentration and determination of silver ion in natural water by atomic absorption spectrometry (AAS). This new bonded silica gel was used as an effective adsorbent for the solid-phase extraction (SPE) of silver ion from aqueous solutions. Experimental conditions for effective adsorption of trace levels of silver ion were optimized with respect to different experimental parameters in column process. Common coexisting ions did not interfere with the separation and determination of silver at pH 3.5 so that silver ion completely adsorbed on the column. The accuracy of the method was estimated by using spring and tap water samples that were spiked with different amounts of silver ion. The adsorption isotherm of silver ion was obtained. The capacity of the adsorbent at optimum conditions found to be 384  $\mu\text{g}$  of silver per gram of adsorbent.

Ngeontae et al. (2006) synthesized silica gel which chemically bonded with aminothioamidoanthraquinone. The metal adsorption properties of the modified silica were studied towards lead(II), copper(II), nickel(II), cobalt(II) and cadmium(II). For batch method, the optimum pH ranges for lead(II), copper(II) and cadmium(II) extraction were  $>3$  but for nickel(II) and cobalt(II) extraction were  $>4$ . The contact times to reach the equilibrium were less than 10 min. The adsorption isotherm fitted the Langmuir's model showed the maximum adsorption capacities of 0.56, 0.30, 0.15, 0.12 and 0.067 mmol/g for lead(II), copper(II), nickel(II), cobalt(II) and cadmium(II), respectively. In the flow system, a column packed modified silica at 20 mg for lead(II) and copper(II), 50 mg for cadmium(II), 60 mg for cobalt(II), nickel(II) was studied at a flow rate of 4 and 2.5 ml/min for nickel(II). The adsorbed metals were quantitatively eluted by 1 % nitric acid. The application of this modified silica gel to preconcentration of pond water, tap water and drinking water gave high accuracy and precision (% R.S.D.  $<9$ ).

## MATERIALS AND METHODS

### Materials

#### 1. Apparatus

Absorbance measurements were carried out on a Perkin Elmer Lamda 35 UV-Vis spectrophotometer. Perkin Elmer 1100B Atomic absorption spectrophotometer was used for the quantitative determination of cobalt(II). The instrument was operated under air-acetylene flame with analytical wavelength at 240.7 nm. Infrared spectra ( $4000\text{--}200\text{ cm}^{-1}$ ) were obtained by a Perkin Elmer system 2000 Fourier transform infrared spectrometer. Nuclear magnetic resonance spectra were recorded at 400 MHz on a Bruker Advance DPX-400. An elemental analyzer was performed with a Perkin Elmer series II CHNS/O analyzer 2400. The pH values were measured by using an Inolab level 1-pH meter.

#### 2. Reagents

- 2-aminobenzothiazole ( $\text{C}_7\text{H}_6\text{N}_2\text{S}$ , Lab. grade, Fluka, Buchs, Switzerland)
- Sodium nitrite ( $\text{NaNO}_2$ , Lab. grade, Merck, Darmstadt, Germany)
- 2,6-diaminopyridine ( $\text{C}_5\text{H}_7\text{N}_3$ , Lab grade, Acros organics, New Jersey, U.S.A.)
- Sodium acetate trihydrate ( $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ , Lab. grade, BDH, Poole, England)
- Cobalt standard for atomic absorption 1000 mg/l ( $\text{Co}(\text{NO}_3)_2$ , AR. grade, Carlo Erba, Milan, Italy)
- Iron standard for atomic absorption 1000 mg/l ( $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ , AR. grade, Carlo Erba, Milan, Italy)
- Nickel standard for atomic absorption 1000 mg/l ( $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ , AR. grade, Carlo Erba, Milan, Italy)

- Cadmium standard for atomic absorption 1000 mg/l (AR. grade, Carlo Erba, Milan, Italy)
- Lead standard for atomic absorption 1000 mg/l ( $\text{Pb}(\text{NO}_3)_2$ , AR. grade, Carlo Erba, Milan, Italy)
- Potassium hydrogen phosphate ( $\text{K}_2\text{HPO}_4$ , Lab. grade, Fisher scientific company, U.S.A.)
- Thiourea ( $\text{H}_2\text{NCSNH}_2$ , AR. grade, Merck, Darmstadt, Germany)
- Ethylenediamine tetraacetic acid ( $\text{C}_8\text{H}_{16}\text{N}_2\text{O}_8$ , AR. grade, Ajax chemicals, N.S.W., Australia)
- Sodium hydroxide ( $\text{NaOH}$ , AR. grade, Merck, Darmstadt, Germany)
- Sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ , AR. grade, Merck, Darmstadt, Germany)
- Sodium phosphate ( $\text{Na}_3\text{PO}_4$ , AR. grade, J.T. Baker Chemicals, Deventer, Holland)
- Sodium oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ , AR. grade, Merck, Darmstadt, Germany)
- Potassium thiocyanate ( $\text{KSCN}$ , AR. grade, J.T. Baker, Phillipsburg, NJ, U.S.A.)
- Potassium bromide ( $\text{KBr}$ , AR. grade, Merck, Darmstadt, Germany)
- Potassium iodide ( $\text{KI}$ , AR. grade, Merck, Darmstadt, Germany)
- Citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ , AR. grade, APS Finechem, Seven Hills, Australia)
- Boric acid ( $\text{H}_3\text{BO}_3$ , AR. grade, Fisher Chemicals, Leicestershire. UK)
- Nitric acid ( $\text{HNO}_3$ , Lab. grade, Carlo Erba, Rodano, Milan, Italy)
- Perchloric acid ( $\text{HClO}_4$ , Lab. grade, Lab Scan, Bangkok, Thailand)
- Hydrochloric acid ( $\text{HCl}$ , Lab. grade, Lab Scan, Bangkok, Thailand)
- Dimethylsulfoxide, D-6 ( $\text{C}_2\text{D}_3\text{OS}$ , AR. grade, Merck, Darmstadt, Germany)
- Ethyl alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ , AR. grade, Mallinckrodt, St. Louis, Missouri, U.S.A.)
- Silica gel ( $\text{SiO}_2$ , Lab. grade, Merck, Darmstadt, Germany)
- (3-chloropropyl)trimethoxysilane ( $\text{C}_6\text{H}_{15}\text{ClO}_3\text{Si}$ , AR. grade, Fluka, UK)
- Deionized water

## Methods

### 1. Synthesis of 3-(2'-thiazolylazo)-2,6-diaminopyridine (TADAP)

A gram of 2-aminothiazole was dissolved in 16 ml of 6 M hydrochloric acid and cooled in an ice-bath. Sodium nitrite (0.70 g) was dissolved in a small amount of water. Nitrite solution was slowly poured into the 2-aminothiazole solution while stirring with a glass rod under low temperature (-5 to 0 °C). The solution of diazonium salt was slowly poured while stirring into a well cooled solution of 2,6-diaminopyridine (1.0 g) in 40 ml of 4 M hydrochloric acid. The mixture was stirred in the ice-bath for 1 hour and then 0.001 M sodium hydroxide solution was added into the mixture until pH 6 was reached. A red precipitate began to settle immediately. The solution was filtered and the precipitated was washed with water and air-dried to give 3-(2'-thiazolylazo)-2,6-diaminopyridine (TADAP). The crude product was purified by recrystallization with a mixture of ethanol-water (1:3) to give red needle-shaped crystal with melting point of 209-210 °C. The resultant product was characterized by FTIR, <sup>1</sup>H NMR, MS and elemental analysis.

### 2. Preparation of solutions

#### 2.1 Preparation of universal buffer solutions

Universal buffer solutions used in this work were prepared by mixing of mixture of 0.20 M boric acid and 0.05 M citric acid (1:1) with 0.10 M Na<sub>3</sub>PO<sub>4</sub> at various ratio as shown in Table2.

**Table 2** The preparation of universal buffer solutions at pH 3.0 to 11.0

| pH   | Mixture of 0.20 M boric acid and 0.05 M citric acid (1:1) (ml) | 0.10 M Na <sub>3</sub> PO <sub>4</sub> (ml) |
|------|----------------------------------------------------------------|---------------------------------------------|
| 3.0  | 176                                                            | 24                                          |
| 4.0  | 155                                                            | 45                                          |
| 5.0  | 134                                                            | 66                                          |
| 6.0  | 118                                                            | 82                                          |
| 7.0  | 99                                                             | 101                                         |
| 8.0  | 85                                                             | 115                                         |
| 9.0  | 69                                                             | 131                                         |
| 10.0 | 54                                                             | 146                                         |
| 11.0 | 44                                                             | 156                                         |

### 2.2 Preparation of $1.0 \times 10^{-3}$ M TADAP

For the preparation of  $1.0 \times 10^{-3}$  M, 0.0055 g of TADAP was dissolved and made up to 25.00 ml by 0.10 M HClO<sub>4</sub> in volumetric flask.

### 2.3 Preparation of $1.0 \times 10^{-3}$ M cobalt(II) solutions

For the preparation of  $1.0 \times 10^{-3}$  M cobalt(II), 1.47 ml of standard solution of cobalt nitrate (1000 ppm) was added in a 25.00 ml volumetric flask and diluted to the marked by deionized water.

## 3. Complex formation between TADAP and cobalt(II)

TADAP is thiazolylazo dye, which gives color complex with many metals especially with transition metals. The reaction of TADAP with cobalt(II) at various pH was investigated in order to determine the suitable pH for studying on the formation of complex between cobalt(II) and TADAP. The following procedure for

formation of complex was used in this work. Pipetted 0.50 ml of  $1.0 \times 10^{-3}$  M TADAP into 25.00 ml volumetric flasks and then 0.50 ml of  $1.0 \times 10^{-3}$  M cobalt(II) ions solution in buffer solution (pH range 3.0 to 11.0) was pipetted into previous volumetric flasks. After 90 minutes, complex between cobalt(II) and TADAP was studied by spectrophotometric method. The results are shown in Figures 5 to 7.

#### **4. Stoichiometric determination of complex between TADAP and cobalt(II) by continuous variation method.**

From the studying on the complex formation in the previous section, the suitable pH for studying on the stoichiometric determination of cobalt(II) complex was at pH 9.0, 10.0 and 11.0.

Pipetted 0.00, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90 and 1.00 ml of  $1.0 \times 10^{-3}$  M cobalt(II) into each of eleven 25.00 ml volumetric flasks. Then 1.00, 0.90, 0.80, 0.70, 0.60, 0.50, 0.40, 0.30, 0.20 and 0.10 ml of  $1.0 \times 10^{-3}$  M TADAP were pipetted into each volumetric flasks, respectively. The solutions were diluted to mark with universal buffer solution. After 90 minutes, the absorbance of the solutions were measured by UV-Vis spectrophotometer at 598 nm. The result at pH 10 is shown in Figure 10.

#### **5. Stability of complex between TADAP and cobalt(II)**

The stability of complex between TADAP and cobalt(II) was observed by measuring the absorbance at wavelength 598 nm in universal buffer solution of pH 10.0 at every five minutes over a period of 3 hours. The result is shown in Figure 11.

## **6. Determination for stability constant of complexes between TADAP and cobalt(II)**

The Benesi-Hildebrand's equation used to determine the stability constant of complex between TADAP and cobalt(II). The cobalt(II) complex solution was prepared by mixing various amount of TADAP solution into a constant volume of  $8 \times 10^{-6}$  M cobalt(II) solution. The concentration of TADAP was varied between  $4 \times 10^{-6}$  M and  $2.4 \times 10^{-5}$  M. The series of complex solution were prepared in universal buffer solution of pH 10.0. The absorbances of the complex solutions were measured by UV-Vis spectrophotometer at the wavelength 598 nm. The calculation of stability constant between cobalt(II) and TADAP is shown in Appendix A.

## **7. Structural determination of complex between TADAP and cobalt(II)**

The complex was prepared by mixing  $1.0 \times 10^{-3}$  M TADAP solution with  $1.0 \times 10^{-3}$  M cobalt(II) solution (2:1) at pH 10.0. The precipitate of the complex was taken at room temperature and then filtered off and washed with distilled water. Finally, the precipitate of complex was dried at room temperature under low pressure and studied by using FTIR spectrophotometer,  $^1\text{H}$ -NMR and elemental analyzer.

## **8. Determination of linear range and detection limit of complex between TADAP and cobalt(II)**

### **8.1 Linear range**

Pipetted 0.10, 0.20, 0.30, 0.40, 0.50, 0.70, 0.90, 1.10, 1.30 and 1.50 ml of  $1.0 \times 10^{-3}$  M TADAP into each ten 25.00 ml volumetric flask and then 0.10 ml of  $1.0 \times 10^{-3}$  M cobalt(II) was pipetted into each ten 25.00 ml volumetric flask and made up to 25.00 ml by universal buffer solution of pH 10.0. After 90 minutes the absorbance of the solutions were measured by UV-Vis spectrophotometer of 598 nm.

Pipetted 0.50 ml of  $1.0 \times 10^{-3}$  M TADAP into ten 25.00 ml volumetric flask. And then, pipetted 0.025, 0.050, 0.075, 0.100, 0.125, 0.150, 0.175, 0.20, 0.225 and 0.250 ml of  $1.0 \times 10^{-3}$  M cobalt(II) into each ten 25.00 ml volumetric flask. The solutions were made up to 25.00 ml by universal buffer solution of pH 10.0. After 90 minutes, the absorbances of the solutions were measured by UV-Vis spectrophotometer at 598 nm. The result is shown in Figure 14.

## 8.2 Detection limit

The limit of detection of cobalt(II) as complex between TADAP and cobalt(II) was examined by linear calibration graph. Series of complex solution were prepared over a concentration range of  $2.0 \times 10^{-6}$  M to  $1.2 \times 10^{-5}$  M of cobalt(II). Pipetted 0.50 ml of  $1.0 \times 10^{-3}$  M TADAP into six 25.00 ml volumetric flasks and mixed with 0.025, 0.050, 0.075, 0.10, 0.125 and 0.150 ml of  $1.0 \times 10^{-3}$  M cobalt(II), respectively. The solutions were made up to 25.00 ml by universal buffer solution of pH 10.0. After 90 minutes, the absorbance of the solutions were measured by UV-Vis spectrophotometer at 598 nm. The result is shown in Figure 15.

## 9. Investigation of interfering cations and anions for complex formation between TADAP and cobalt(II)

### 9.1 Cations interference

The degree of interference of five cations (cadmium(II), sodium(I), nickel(II), calcium(II) and iron(III)) on the complex formation between TADAP and cobalt(II) were investigated. Series of complex solution were prepared by mixing 0.50 ml of  $1.0 \times 10^{-3}$  M TADAP with 0.10 ml of  $1.0 \times 10^{-3}$  M cobalt(II) in the presence of cations at various concentration ratios to cobalt(II) (cobalt(II):interfering cation was 1:1, 1:25, 1:50, 1:75 and 1:100 respectively). Each solution was made up to volume with universal buffer solution of pH 10.0 in 25.00 ml volumetric flask. After 90 minutes, the absorbance of the complex solutions were measured against reagent blank by UV-Vis spectrophotometer at 598 nm. The presence of cations that

caused change of absorbance in range of 95% confidential was accepted as non-significant interfering effect. The result is shown in Table 6.

### 9.2 Anions interference

The degree of interference of nine anions (iodide, EDTA, oxalate, thiocyanate, thiourea, cyanide, phosphate, bromide and acetate ions) on the complex formation between TADAP and cobalt(II) were investigated. Series of complex solution were prepared by mixing 0.50 ml of  $1.0 \times 10^{-3}$  M TADAP with 0.10 ml of  $1.0 \times 10^{-3}$  M cobalt(II) in the presence of anions at various concentration ratios to cobalt(II) (cobalt(II):interfering anion was 1:1, 1:25, 1:50, 1:75 and 1:100). Each solution was made up to volume with universal buffer solution of pH 10.0 in 25.00 ml volumetric flask. After 90 minutes, the absorbance of the complex solutions were measured against reagent blank by UV-Vis spectrophotometer at 598 nm. The presence of anions that caused change of absorbance in range of 95% confidential was accepted as non-significant interfering effect. The results are shown in Table 6.

### 9.3 Masking of interfering cations

The masking efficiency of several complexing agents such as EDTA, oxalate, thiourea, thiocyanate and iodide were examined in order to eliminate the effect from interfering metal ions. Series of complex solution were prepared by mixing 0.50 ml of  $1.0 \times 10^{-3}$  M TADAP with 0.10 ml of  $1.0 \times 10^{-3}$  M cobalt(II) in the presence of interfering metal ions at ratio cobalt(II):metal ion, 1:25. Masking agent was added to the complex by various ratio to cobalt(II) (cobalt(II):masking agent was 1:25, 1:50 and 1:100). Each solution was made up to volume with universal buffer solution of pH 10.0 in 25.00 ml volumetric flask. After 90 minutes, the absorbance of the complex solutions were measured against reagent blank by UV-Vis spectrophotometer at 598 nm. The presence of masking agent that caused change of absorbance in range of 95% confidence was accepted as non-significant interfering effect. The results are shown in Table 7.

## 10. The determination of cobalt(II) in synthetic solutions

TADAP was used as analytical reagent for determination of cobalt(II) by spectrophotometric method. Synthetic mixture solutions of cobalt(II) and interfering metal ions were prepared by mixing aliquots of  $1.0 \times 10^{-3}$  M of cobalt(II) with various concentration of each metal ion. The first series, the molar concentration ratio of cobalt(II): nickel(II) was 100:1, which was prepared by pipetted 0.275 ml of  $1.0 \times 10^{-3}$  M cobalt(II) and 0.275 ml of  $1.0 \times 10^{-5}$  M nickel(II) solution. Then, the 1.50 ml of  $1.0 \times 10^{-3}$  M TADAP was added into solution and diluted to 25.00 ml by universal buffer solution of pH 10.0. The second series, the molar concentration ratio of cobalt(II):cadmium(II) was 100:1. The final concentration of cobalt(II) in each series was  $1.1 \times 10^{-5}$  M. The synthetic solutions were determined by UV-Vis spectrophotometer and the results were compared with the quantity of cobalt(II) from the complexing solution between  $1.1 \times 10^{-5}$  M cobalt(II) and TADAP.

## 11. Preparation of 3-(2'-thiazolylazo)-2,6-diaminopyridine resin (Si-TADAP)

Silica gel (50g) suspended in 200 ml of dried toluene was refluxed and mechanically stirred under nitrogen atmosphere for 2 hours. To this suspension, 20 ml of chloropropyltriethoxysilane was added drop wise and the mixture was under reflux for 24 hours. The solid was filtered and washed with ethanol. This modified silica gel was dried in vacuum at room temperature. Seven and half grams of the modified silica gel was suspended in 100 ml of dried toluene, under reflux while being mechanically stirred with 1.0 g of TADAP for 12 hours. The immobilized silica gel, namely Si-TADAP, was filtered off and washed with 0.50 M hydrochloric acid, 0.50 M sodium hydroxide and distilled deionized water until the filtrate was colorless. The Si-TADAP was dried at room temperature at low pressure condition. The resultant product was characterized by FTIR and elemental analysis as shown in Figure 17, 18 and 19 and Table 11 and 12.

## 12. Determination of capacity for the adsorption of cobalt(II) by Si-TADAP

The adsorption of cobalt(II) was studied under static condition. To determine the capacity of Si-TADAP, the influence of various parameters such as pH, initial concentration of metal ion and shaking time were optimized under static condition by using batch equilibrium experiment.

The experiment conditions for studying on the influence of various parameters on the adsorption of cobalt(II) on Si-TADAP were as follows;

**Effect of pH:** Capacity of Si-TADAP was determined at the pH from 3.0 to 9.0. The pH of the solution in each experiment was adjusted by universal buffer solutions. Fifty milligrams of Si-TADAP was equilibrated with 10 ppm cobalt(II) solution, which were prepared in universal buffer solution at pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0. Then the mixture was shaken for 3 hours. After the mixture were filtered, the filtrates were determined for cobalt(II) by atomic absorption spectrophotometer. The results are shown in Figure 20.

**Effect of concentration of cobalt(II):** 10, 25, 50, 75, 100, 125 and 150 ppm cobalt(II) solution were prepared in universal buffer of pH 5.0. Fifty milligrams of Si-TADAP was equilibrated with 10.0 ml of cobalt(II) solution at various concentrations. Then the mixture were shaken for 3 hours. After the mixture were filtered, the filtrates were determined for cobalt(II) by atomic absorption spectrophotometer. The results are shown in Figure 21.

**Effect of shaking time:** Fifty milligrams of Si-TADAP was equilibrated with 10.0 ml of 50 ppm cobalt(II) solution in universal buffer of pH 5.0. Then the mixture were shaken for 15, 30, 45, 60, 120, 180 and 240 minutes, respectively. After the mixture were filtered, the filtrates were determined for cobalt(II) by atomic absorption spectrophotometer. The results are shown in Figure 22.

### **13. Desorption of cobalt(II) on Si-TADAP**

Fifty milligram of Si-TADAP loaded with 10.0 ml of 50 ppm of cobalt(II) solution was shaken for 2 hours. Then the loaded resin was filtered off, washed with double distilled water and air-dried. The loaded resin was shaken individually in 10.0 ml of 7 eluents, namely, sodium acetate, EDTA, hydrochloric acid, thiourea, nitric acid, oxalate and potassiumhydrogenphosphate. After the shaking period for 2 hours, the mixtures were filtered and the filtrates were analyzed for cobalt(II) by atomic absorption spectrophotometer. The results are shown in Table 13.

### **14. Efficiency of Si-TADAP on the adsorption of cobalt(II)**

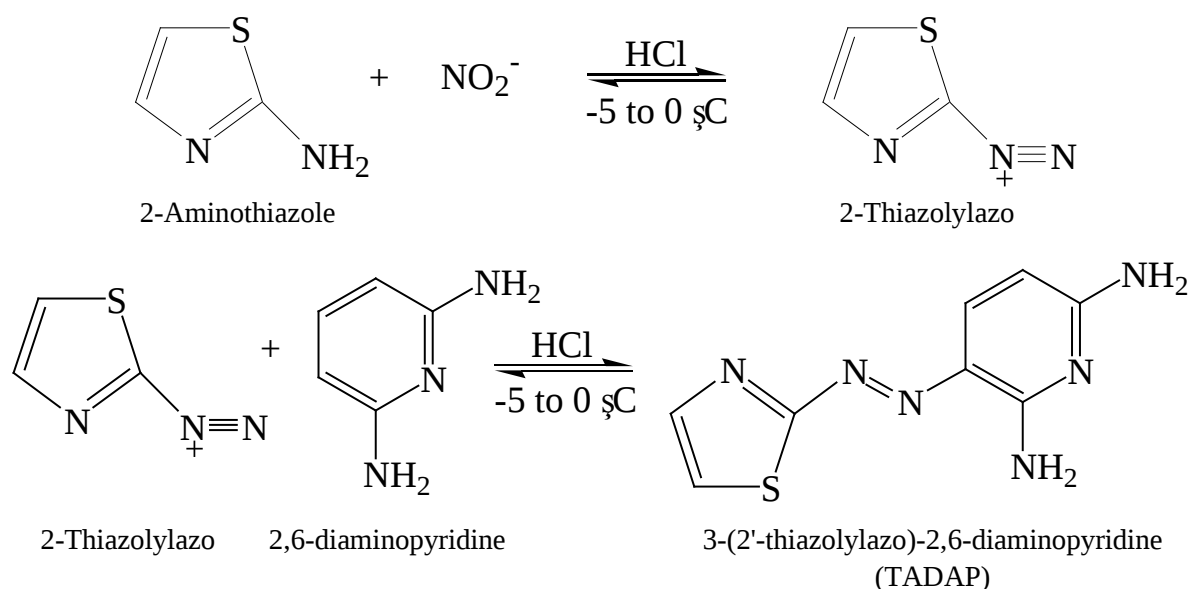
Fifty milligrams of Si-TADAP loaded with 10.0 ml of 50 ppm of cobalt(II) solution was shaken for 2 hours. Then the loaded resin was filtered off, washed with distilled water and air-dried. The cobalt(II) on the Si-TADAP was desorped by using 0.30 M  $\text{KH}_2\text{PO}_4$  as eluent at the shaking time of 2 hours. Then the desorped Si-TADAP was reused for the sorption of cobalt(II). The efficiency for sorption of cobalt(II) was determined by atomic absorption spectrophotometer. The results are shown in Figure 23.

## RESULTS AND DISCUSSION

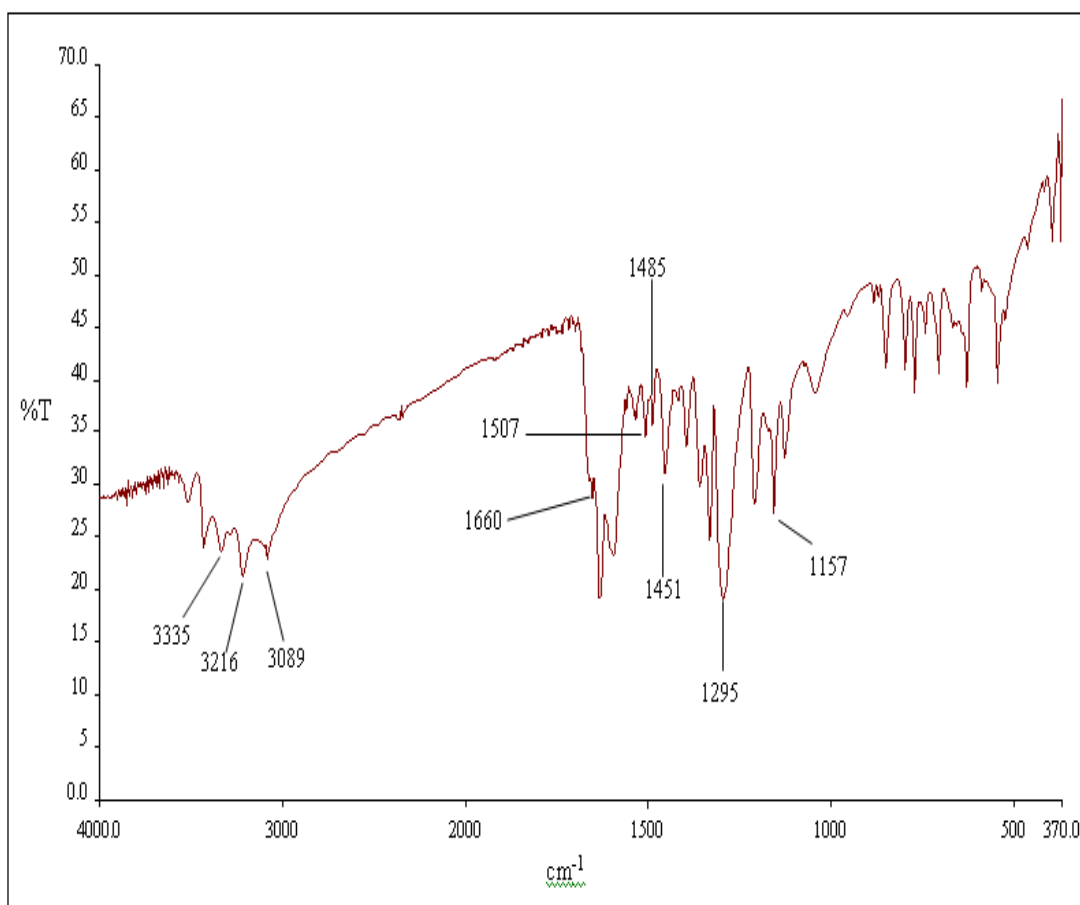
### 1. Synthesis of 3-(2'-thiazolylazo)-2,6-diaminopyridine (TADAP)

The synthesis pathway of 3-(2'-thiazolylazo)-2,6-diaminopyridine (TADAP) is shown in Figure 2. TADAP was synthesized by diazotization of 2-aminothiazole in hydrochloric acid at -5 to 0 °C, then coupling with 2,6-diaminopyridine in hydrochloric acid at the same temperature. Finally, the crude product of TADAP was precipitated with  $1 \times 10^{-3}$  M sodium hydroxide solution. The crude product was purified by recrystallization from ethanol-water (3:1) solution, which gave TADAP as red needle crystal with melting point of 209-210 °C and 50.77 % yield.

The red needle shaped crystalline of TADAP was characterized by FTIR,  $^1\text{H}$  NMR and elemental analysis. The results are shown in Figure 3, 4 and Table 3. The solution of TADAP in aqueous solution gave red color with the maximum absorption at 480 nm.

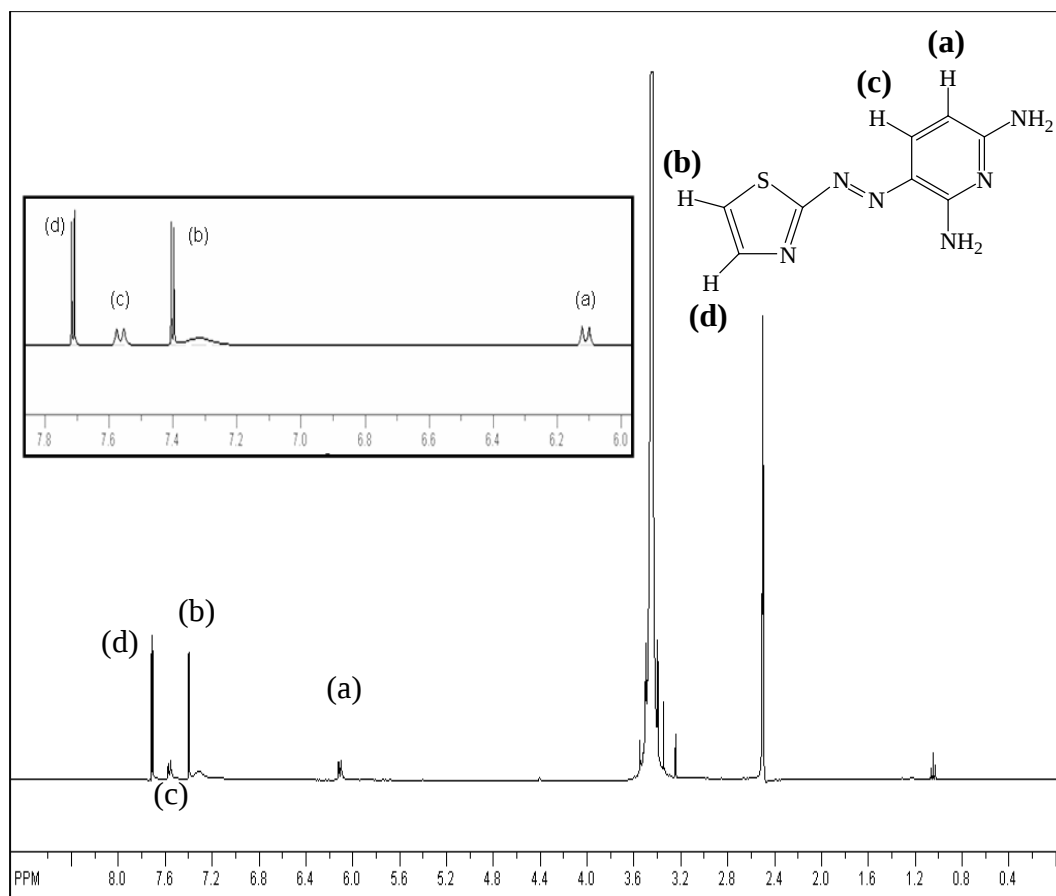


**Figure 2** Synthesis pathway of 3-(2'-thiazolylazo)-2,6-diaminopyridine (TADAP).



**Figure 3** IR spectrum of 3-(2'-thiazolylazo)-2,6-diaminopyridine (TADAP).

The infrared spectrum (KBr :  $\text{cm}^{-1}$ ) was as followed : 3335, 3218 (w, N-H stretch), 3089 (w, C-H stretch aromatic), 1660 (s, C=N stretch), 1630 (s, N-H bend aromatic), 1507 (m, C=C stretch aromatic), 1451 (m, N=N stretch), 1295 (s, C-N stretch) and 1157 (m, C-S stretch).



**Figure 4**  $^1\text{H}$  NMR spectrum of 3-(2'-thiazolylazo)-2,6-diaminopyridine (TADAP).

The  $^1\text{H}$  NMR spectrum ( $\text{DMSO-d}_6$ , 400 MHz) was as follow:  $\delta$  6.113 (1H, d,  $\text{H}_a$ ), 7.401 (1H, d,  $\text{H}_b$ ), 7.572 (1H, d,  $\text{H}_c$ ) and 7.714 (1H, d,  $\text{H}_d$ ).

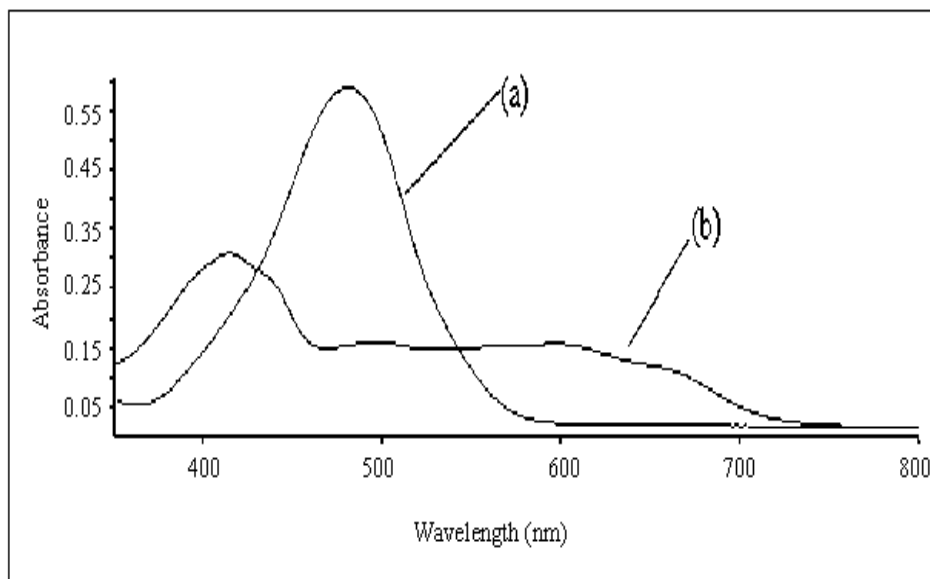
**Table 3** The elemental analysis of 3-(2'-thiazolylazo)-2,6-diaminopyridine (TADAP)

| Element | Theoretical value | Experimental value | % Error |
|---------|-------------------|--------------------|---------|
| C       | 43.64%            | 43.80%             | 0.367%  |
| H       | 3.661%            | 3.792%             | 3.578%  |
| N       | 38.16%            | 38.45%             | 0.760%  |
| S       | 14.56%            | 14.78%             | 1.511%  |

The results of IR spectrum,  $^1\text{H}$  NMR spectrum and elemental analysis indicated that the synthesized product was TADAP.

## 2. Complex formation between TADAP and cobalt(II)

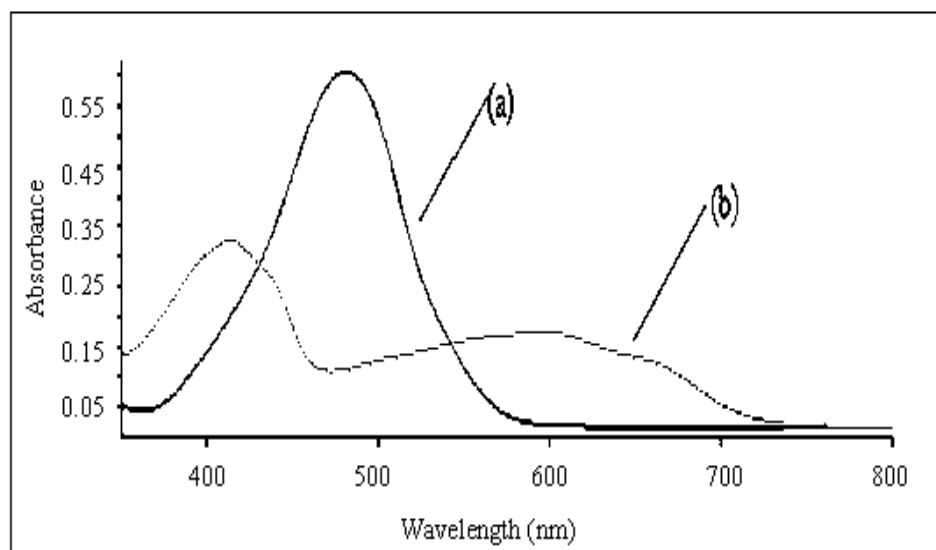
The absorption spectrum of TADAP and cobalt(II)-TADAP complex were studied in the visible region. The azo compound displays mainly a broad band in the visible region ( $\lambda = 480$  nm) which was assigned as  $n$  to  $\pi^*$  transition within the azo linkage influenced by intramolecular charge transfer. From the results showed that TADAP could form complexes with cobalt(II) at ranging from 9.0 to 11.0. The cobalt(II) complex gave a green color. The results are shown in Figure 5 to 7 and Table 4.



**Figure 5** Absorption spectra of TADAP and cobalt(II)-TADAP complex at pH 9.

(a) TADAP

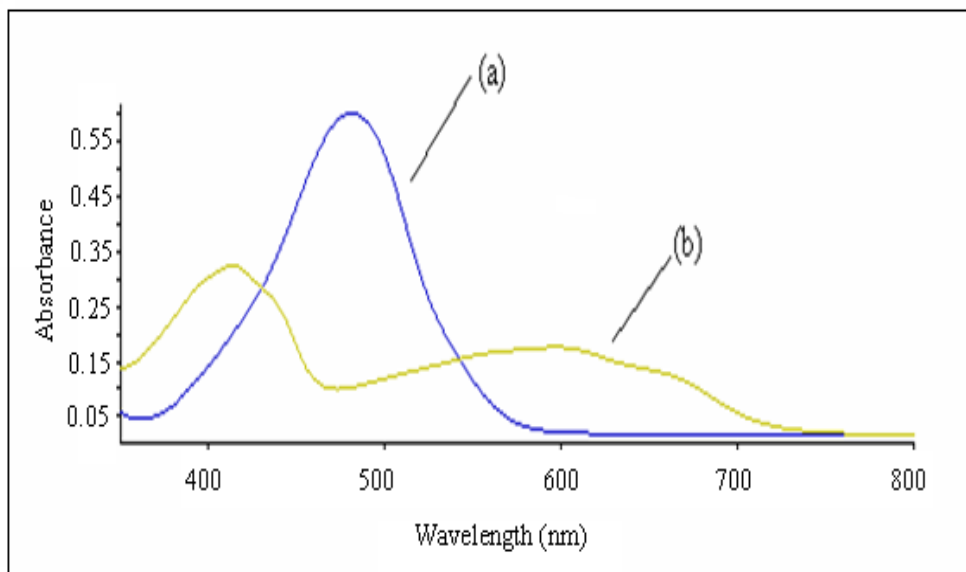
(b) Complex of cobalt(II)-TADAP



**Figure 6** Absorption spectra of TADAP and cobalt(II)-TADAP complex at pH 10.

(a) TADAP

(b) Complex of cobalt(II)-TADAP



**Figure 7** Absorption spectra of TADAP and cobalt(II)-TADAP complex at pH 11.

(a) TADAP

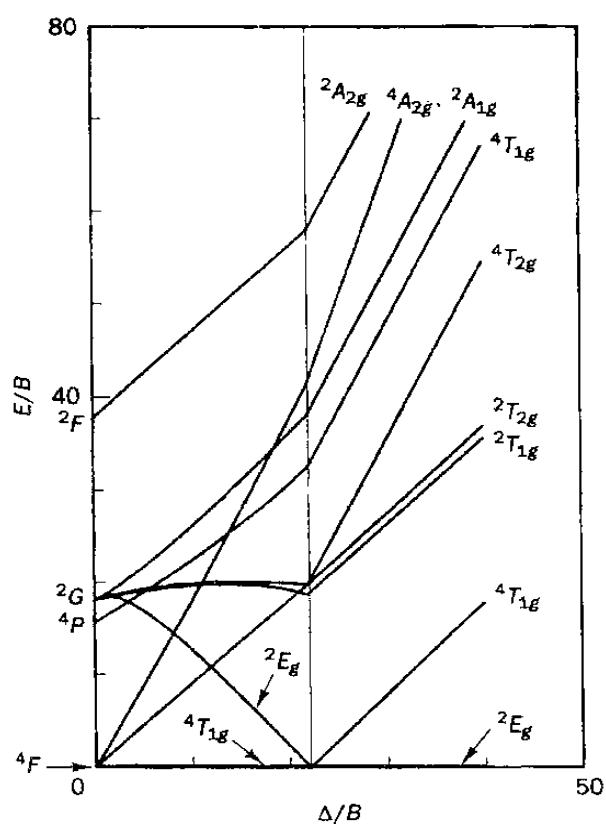
(b) Complex of cobalt(II)-TADAP

**Table 4** Complex formation between cobalt(II) and TADAP at pH 9.0-11.0

| pH   | Color of TADAP solution | Color of cobalt(II)-<br>TADAP complex<br>solution | $\lambda_{\max}$ |
|------|-------------------------|---------------------------------------------------|------------------|
| 9.0  | Orange                  | Green                                             | 598              |
| 10.0 | Orange                  | Green                                             | 598              |
| 11.0 | Orange                  | Green                                             | 598              |

Tanabe-Sugano diagram was used for the interpretation of electronic spectra of the complex. Cobalt(II) is metal ion which has  $d^7$  configuration, so the Tanabe-Sugano diagram of  $d^7$  configuration as shown in Figure 8 was used for the interpretation. The following transitions are expected:

| <u>Spin allowed</u>                  | <u>Spin forbidden</u>                    |
|--------------------------------------|------------------------------------------|
| ${}^2E_g \longrightarrow {}^2T_{1g}$ | ${}^2E_g \longrightarrow {}^4T_{1g}$     |
| ${}^2E_g \longrightarrow {}^2T_{2g}$ | ${}^2E_g \longrightarrow {}^4T_{2g}$     |
| ${}^2E_g \longrightarrow {}^2A_{1g}$ | ${}^2E_g \longrightarrow {}^4T_{1g} (P)$ |
| ${}^2E_g \longrightarrow {}^2A_{2g}$ | ${}^2E_g \longrightarrow {}^4A_{2g}$     |

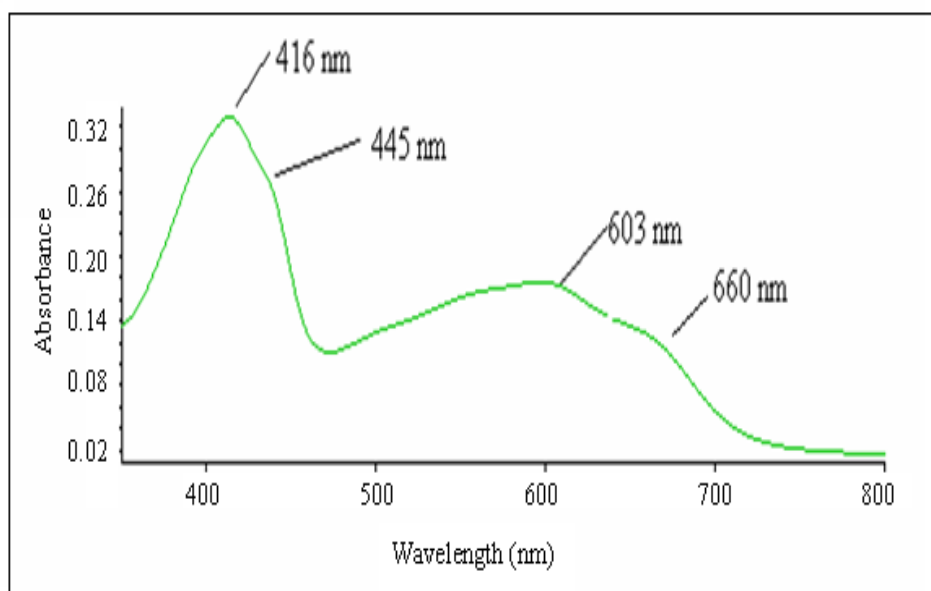


**Figure 8** Tanabe-Sugano diagram of  $d^7$  configuration

Source: Shriver (1999)

The character of the complex's spectrum was matched to the prediction when TADAP acted as the strong field ligand. The absorption spectrum for the spin allowed d-d transition of complex show four band at 660, 603, 445 and 416 nm as shown in Figure 9. These bands were assigned as  ${}^2E_g \longrightarrow {}^2T_{1g}$ ,  ${}^2E_g \longrightarrow {}^2T_{2g}$ ,  ${}^2E_g \longrightarrow {}^2A_{1g}$  and  ${}^2E_g \longrightarrow {}^2A_{2g}$  transition, respectively. For TADAP as the strong field ligand, the

first peak at 416 nm was closely overlapped with the second peak at 445 nm and the third peak at 603 nm was also closely overlapped with the fourth peak at 660 nm.

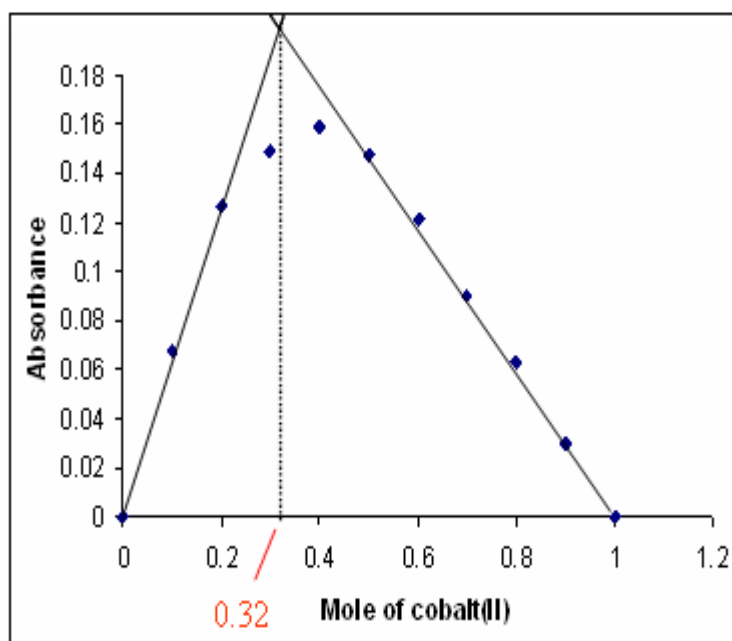


**Figure 9** Absorption spectrum of cobalt(II)-TADAP complex.

### **3. Stoichiometric determination of complex between TADAP and cobalt(II) by continuous variation method**

Stoichiometric determination of complex between TADAP and cobalt(II) at pH 9.0 to 11.0 were performed by continuous variation method (Job's method).

The result from the stoichiometric determination of complex between cobalt(II) and TADAP at pH 10.0 is shown in Figure 10. The maximum absorption of the complex was occurred at 598 nm. Therefore, this wavelength was chosen as the wavelength for studying on the formation of cobalt(II) complex.



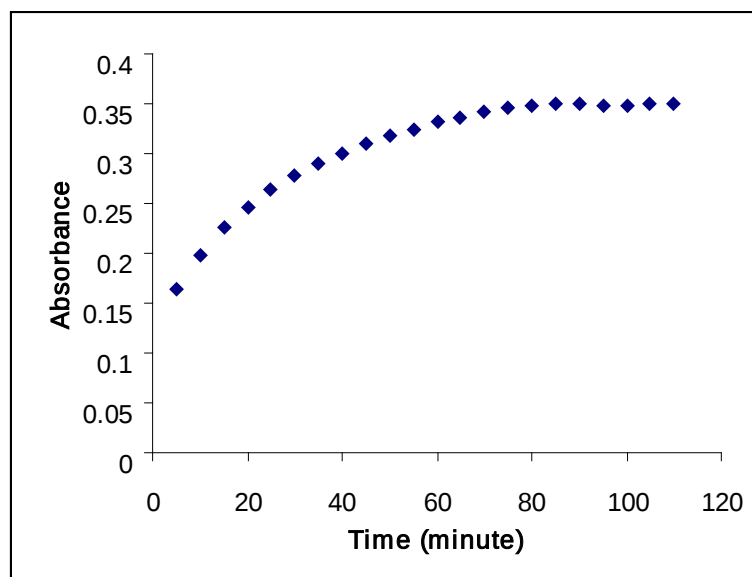
**Figure 10** Job's plot of complex between cobalt(II) and TADAP at pH10.

From Figure 10, the stoichiometry of complex between cobalt(II) and TADAP was verified to be 1:2 (cobalt(II):TADAP) by applying the Job's method. The stoichiometry of complex between cobalt(II) and TADAP at pH 9.0 to pH 11.0 was also at the ratio of 1:2 (cobalt(II):TADAP).

#### 4. Stability of complex between TADAP and cobalt(II)

The stability of complex between cobalt(II) and TADAP at pH 10.0 was studied. From Figure 11, the result shows that TADAP formed complex with cobalt(II) which remained constant after 90 minutes. Thus, the complex was measured after 90 minutes.

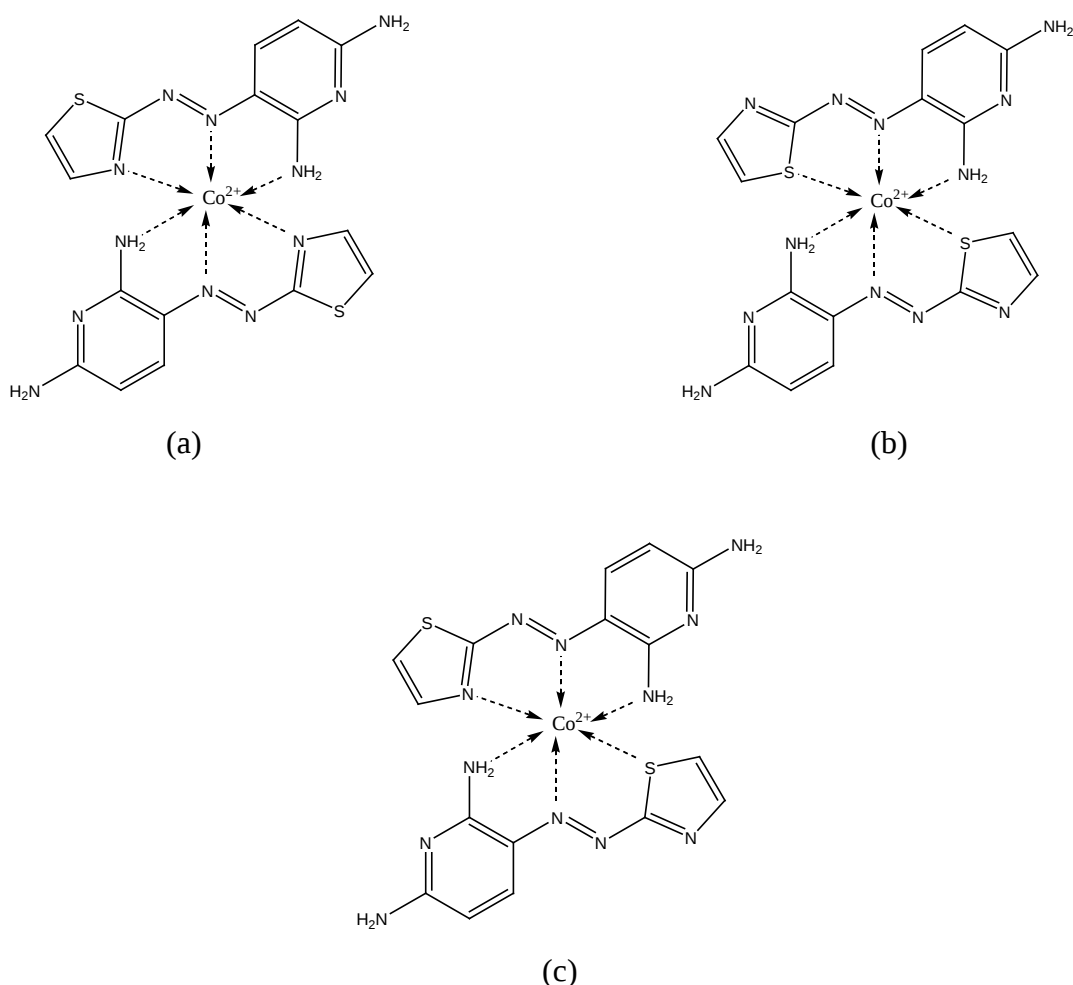
From the stoichiometry of complex, the stability constant was calculated by Benesi-Hilderbrand method as shown in Appendix A. The stability constant was  $1.86 \times 10^{10}$  and molar extinction coefficient was  $1.52 \times 10^4 \text{ l}^{-1}\text{mol}^{-1}\text{cm}^{-1}$ .



**Figure 11** Relationship between absorbance of cobalt(II)-TADAP complex and time.

## 5. Structural determination of complex between TADAP and cobalt(II)

TADAP is a polydentate ligand which can form complex with metal ions by using nitrogen and sulfur as donor atom. Cobalt(II) is transition metal which is the characteristic of the borderline acid (Shriver, 1999). Therefore, TADAP might act as chelating ligand with three probable formula of complexes formed as shown in Figure 12.

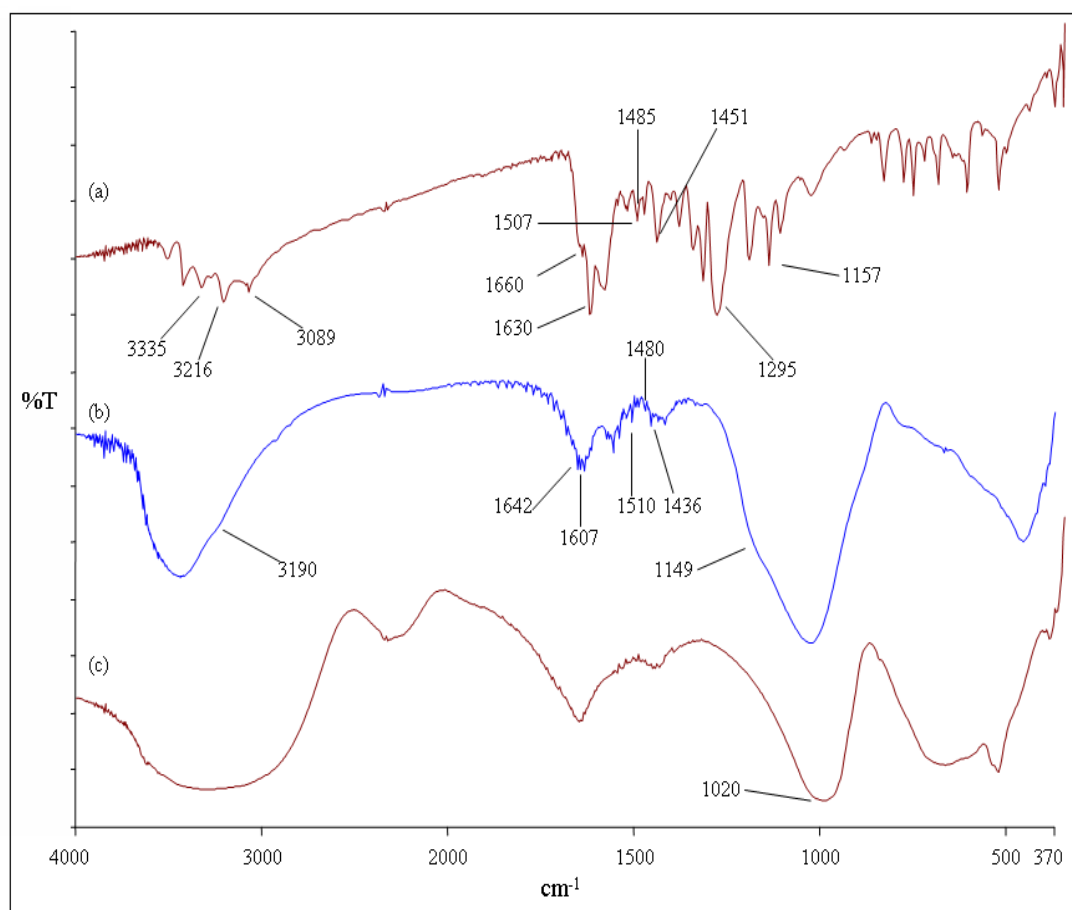


**Figure 12** Postulated structures of complex between cobalt(II) and TADAP.

- a) Six atoms of nitrogen are donor atoms.
- b) Four atoms of nitrogen and two atoms of sulfur are donor atoms.
- c) Five atoms of nitrogen and an atom of sulfur are donor atoms.

Theoretically, IR spectrum of the complex can be used to indicate the donor atoms of ligands for bonding with metal ions by the decreasing of wavenumber due to the decreasing of the bond order of the donor atom. The results from the infrared spectra of TADAP and cobalt(II)-TADAP complex are shown in Figure 13 and Table 5. For the complex, the peak assigned for N-H stretching at 3335 and 3216 were shifted to 3190  $\text{cm}^{-1}$ , N=N stretching was shifted from 1451  $\text{cm}^{-1}$  to 1436  $\text{cm}^{-1}$ , the peak assigned for C=N stretching was shifted from 1660  $\text{cm}^{-1}$  to 1642  $\text{cm}^{-1}$  and the peak assigned for C-S stretching was shifted from 1157  $\text{cm}^{-1}$  to 1149  $\text{cm}^{-1}$ . The peak

assigned for N-H bending was also shifted from  $1630\text{ cm}^{-1}$  to  $1607\text{ cm}^{-1}$ . The characteristic intensity for the primary amine of this peak was also changed to the character for the secondary amine. This may indicated the bonding between the nitrogen atom in amine with the cobalt(II). Therefore, TADAP might acted as a tridentate ligand by using nitrogen atom of  $\text{-NH}_2$ , nitrogen atom of  $\text{N=N}$  and nitrogen or sulfur atom in thiazolylazo ring as donor atoms. The postulated structure of the complex could still be the three of structures that shown in Figure 12. Nevertheless, from the IR spectrum of the complex, there was a very strong peak at  $1020\text{ cm}^{-1}$  of P-O stretching. Therefore, this complex should has a phosphate ion as the counter ion and the molecular formula of the complex should be  $[\text{Co}(\text{TADAP})_2]_3.(\text{PO}_4^{3-})_2$ .



**Figure 13** IR spectra of (a) TADAP, (b) cobalt(II)-TADAP complex and (c)  $\text{Na}_3\text{PO}_4$

**Table 5** Data from the IR spectra of TADAP and cobalt(II)-TADAP complex

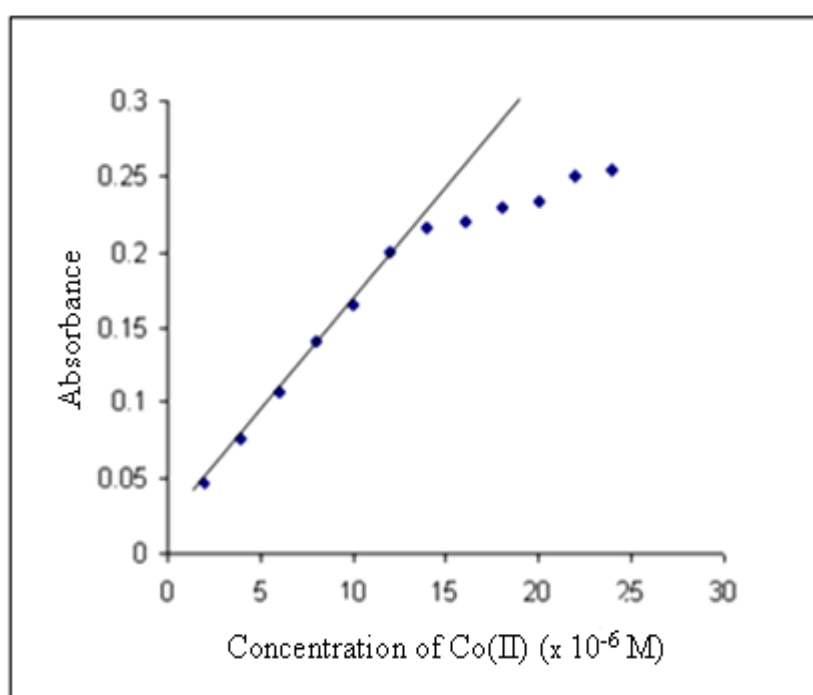
| TADAP                             |                      | Cobalt(II)-TADAP complex          |                      |
|-----------------------------------|----------------------|-----------------------------------|----------------------|
| Wavenumber<br>(cm <sup>-1</sup> ) | Functional group     | Wavenumber<br>(cm <sup>-1</sup> ) | Functional group     |
| 3335 and 3216 (w)                 | N-H stretch          | 3190 (w)                          | N-H stretch          |
| 3089 (w)                          | C-H stretch aromatic | -                                 | C-H stretch aromatic |
| 1660 (s)                          | C=N stretch          | 1642 (s)                          | C=N stretch          |
| 1630 (s)                          | N-H bend aromatic    | 1607 (w)                          | N-H bend aromatic    |
| 1507 and 1485 (m)                 | C=C stretch          | 1510 and 1480 (m)                 | C=C stretch          |
| 1451 (m)                          | N=N stretch          | 1436 (m)                          | N=N stretch          |
| 1295 (s)                          | C-N stretch          | 1229 (s)                          | C-N stretch          |
| 1157 (m)                          | C-S stretch          | 1140 (m)                          | C-S stretch          |
|                                   |                      | 1020 (s)                          | P-O stretch          |

<sup>1</sup>H NMR spectrum of the complex may also use to indicate the donor atoms of ligand for bonding with metal ions. Generally, the chemical shift of the proton close to the donor atoms is decreased due to the increasing of electron density (shielded) of that proton. However, the result from the <sup>1</sup>H NMR spectrum of cobalt(II)-TADAP complex did not show any significant peaks. This may be because the solubility of cobalt(II)-TADAP complex is very low in solvents such as DMSO-d<sub>6</sub> and CDCl<sub>3</sub>. However, this should be investigated in the future work.

By using hyperchem 7.5, the formation energy of cobalt(II)-TADAP complexes in three structures as shown in Figure 12 were calculated. It was found that the formation energy of structure 12 (a) was 83.04 kcal/mol, structure 12 (b) was 67.79 kcal/mol and structure 12 (c) was 92.72 kcal/mol. From the formation energies of three complexes this may be conclude that the most possible structure of cobalt(II)-TADAP complex was structure 12 (b). However, this is a calculation from a basic program which may not give a very high accurate results. To get higher accurate results, Gaussian 03 should be used for the calculation in the future work.

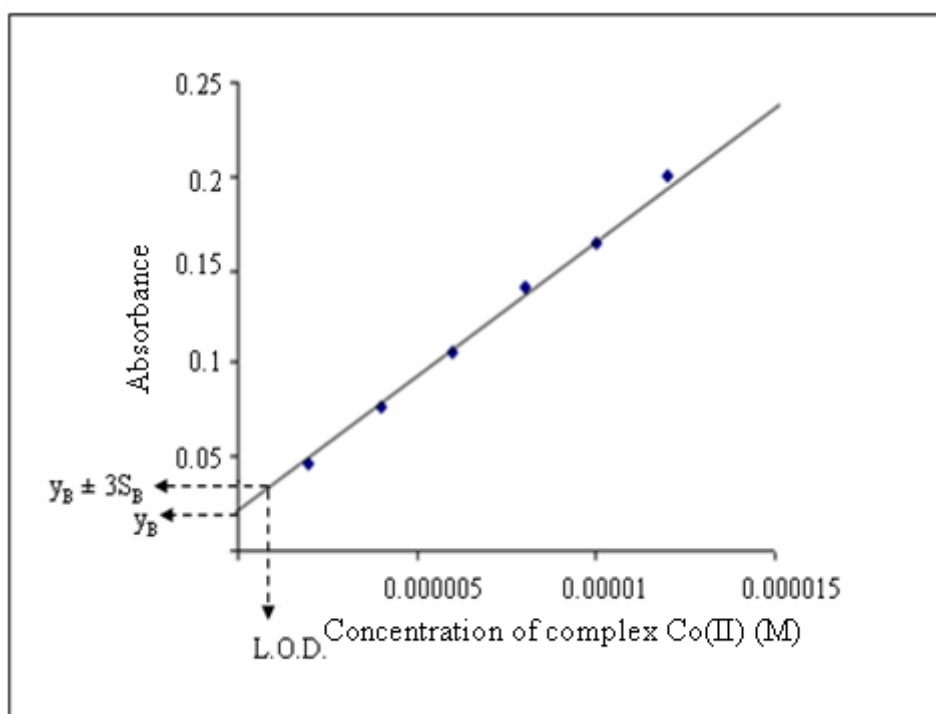
## 6. Determination of linear range and limit of detection of complex between TADAP and cobalt(II)

The linear range and limit of detection of complex between cobalt(II) and TADAP were studied and shown in Figure 14. The increasing in the absorbance of complex were deviated from Beer's law when the concentration of cobalt(II) was higher than  $1.2 \times 10^{-5}$  M.



**Figure 14** Relationship of the absorbance of complex between cobalt(II) and TADAP by increasing concentration of cobalt(II) in excess TADAP solution.

To determine the limit of detection, the calibration curve of complex between cobalt(II) and TADAP was prepared. The relationship between absorbance and concentration of complex were plotted (Figure 15). The intercept ( $y_B$ ) could be observed from calibration curve. The limit of detection, calculated from  $y_B \pm 3S_B$  (99% confidence), was  $5.25 \times 10^{-7}$  M. The calculation for the limit of detection is shown in Appendix B (Miller, 2000).



**Figure 15** Relationship between absorbance and concentration of complex between cobalt(II) and TADAP.

## 7. Investigation of interfering cation and anions for complex formation between TADAP and cobalt(II)

### 7.1 Interfering cations and anions

The effect of interfering cations and anions for the analysis of cobalt(II) were studied. For the interference study, some metal ions were selected due to their usage in the industrial related to cobalt(II). The effect of anions on the analysis of cobalt(II) was also studied. The anions which did not interfere with the analysis of cobalt(II) were used as masking agent for interfering metal ions.

In this study, the complex solution between cobalt(II) and TADAP was prepared and measured the absorbance by UV-Vis spectrophotometer at 598 nm. The experiments were carried out at five replicates. The average absorbance and standard deviation values of five replicates of cobalt(II) were calculated. Therefore, the

analysis concentration of cobalt(II) could accepted in the range of  $5.78 \times 10^{-7}$ - $1.51 \times 10^{-6}$  (95% confidence).

When the interfering cations and anions at various concentration were added into the complex solution between cobalt(II) and TADAP, the change in the absorbance of solution comparing to the pure complex could indicated the effect of cations and anions on the analysis of cobalt(II). The cation or anions would regard to have the interfering effect when the analysis absorbance of complex solutions were out of acceptable range. The results are shown in Table 6.

**Table 6** Spectrophotometric determination of cobalt(II) using TADAP as analytical reagent in the presence of interfering species (+ = Interfere, - = Not interfere)

| Interference species        | Molar ratio of Cobalt(II): Interference species |      |      |      |       |
|-----------------------------|-------------------------------------------------|------|------|------|-------|
|                             | 1:1                                             | 1:25 | 1:50 | 1:75 | 1:100 |
| $\text{Cd}^{2+}$            | -                                               | +    | +    | +    | +     |
| $\text{Na}^+$               | -                                               | -    | -    | -    | -     |
| $\text{Ni}^{2+}$            | -                                               | -    | -    | +    | +     |
| $\text{Ca}^{2+}$            | +                                               | +    | +    | +    | +     |
| $\text{Fe}^{3+}$            | -                                               | -    | -    | -    | +     |
| $\text{I}^-$                | -                                               | -    | -    | -    | -     |
| EDTA                        | -                                               | +    | +    | +    | +     |
| $\text{C}_2\text{O}_4^{2-}$ | -                                               | -    | +    | +    | +     |
| $\text{SCN}^-$              | +                                               | +    | +    | +    | +     |
| Thiourea                    | +                                               | +    | +    | +    | +     |
| $\text{CN}^-$               | -                                               | -    | +    | +    | +     |
| $\text{H}_2\text{PO}_4^-$   | +                                               | +    | +    | +    | +     |
| $\text{Br}^-$               | -                                               | -    | -    | -    | -     |
| $\text{CH}_3\text{COO}^-$   | +                                               | +    | +    | +    | +     |

According to the hard and soft acids and bases theory, the interactions of Lewis acids and bases containing elements drawn from throughout the periodic table to consider at two main classes of substance (hard and soft). The two classes were identified by the opposite order of strengths (as measured by the stability constant,  $K_{stab}$ , for the formation of the complex) which they form complexes with halide ion bases:

Hard acids bond in the order:  $I^- < Br^- < Cl^- < F^-$

Soft acids bond in the order:  $F^- < Cl^- < Br^- < I^-$

The classification of Lewis acids and bases was shown in Table 7. Hard and soft acids and bases were identified by the trends in stabilities of the complexes they form; hard acids tend to bind to hard bases and soft acids tend to bind to soft bases.

**Table 7** The classification of Lewis acids and based

| Hard                                   | Borderline                        | Soft                                             |
|----------------------------------------|-----------------------------------|--------------------------------------------------|
| Acids $H^+$ , $Li^+$ , $Na^+$ , $K^+$  | $Fe^{2+}$ , $Co^{2+}$ , $Ni^{2+}$ | $Cu^{2+}$ , $Ag^+$ , $Au^{3+}$ , $Tl^+$ , $Hg^+$ |
| $Be^{2+}$ , $Mg^{2+}$ , $Ca^{2+}$      | $Cu^{2+}$ , $Zn^{2+}$ , $Pb^{2+}$ | $Pd^{2+}$ , $Cd^{2+}$ , $Pt^{2+}$ , $Hg^{2+}$    |
| $Cr^{2+}$ , $Cr^{3+}$ , $Al^{3+}$      |                                   |                                                  |
| Bases $F^-$ , $OH^-$ , $H_2O$ , $NH_3$ | $NO_2^-$ , $SO_3^{2-}$ , $Br^-$   | $H^-$ , $R^-$ , $CN^-$ , $CO$ , $I^-$            |
| $CO_3^{2-}$ , $NO_3^-$ , $O^{2-}$      | $N_3^-$ , $N_2$                   | $SCN^-$ , $R_3P$ , $C_6H_6$                      |
| $SO_4^{2-}$ , $PO_4^{3-}$ , $ClO_4^-$  | $C_6H_5N$ , $SCN^-$               | $R_2S$                                           |

Source: Shriver (1999)

From Table 6, Calcium ion was the most interfering for the analysis of cobalt(II) may be because calcium ion could form ion pair with phosphate ion in buffur solution. Cadmium(II), nickel(II) and iron(III) interfered the analysis of cobalt(II) may be because cadmium(II) was characterized as soft acid and nickel(II) and iron(III) were characterized as borderline acids which could form complex well with TADAP. Sodium ion did not interfere the analysis because this cation was the s-block metal ion.

For anions, thiocyanide, thiourea and cyanide ion interfered the analysis of cobalt(II) may be because these anions were characterized as borderline bases which could form complex with borderline acid such as cobalt(II). EDTA, oxalate ion and acetate ion also interfered the analysis of cobalt(II) may be because these anions could form complex with cobalt(II) by chelate effect so the stability constants of complex were increased (The chelate effect is the greater stability of a complex containing a coordinated polydentate ligand compared with a complex containing the equivalent number of similar monodentate ligands.). As iodide and bromide are soft base then they might not interfere with the analysis of cobalt(II). Thus, they might be used as masking agent to reduce the interfering metal ions.

## 7.2 Masking of interfering cations

For the studied of masking agents, the cobalt(II) complexes which had the ratio of 1:25 (cobalt(II):cations) were prepared. The selected anions were added in cobalt(II) complex solution to use as masking agent. The results are shown in Table 8.

**Table 8** Masking of interfering cation for the analysis of cobalt(II) by TADAP

(+ = Interfere, - = Not interfere)

| Complex solution | Ratio of<br>Cobalt(II):cation:masking agent | Masking agent  |                 |
|------------------|---------------------------------------------|----------------|-----------------|
|                  |                                             | I <sup>-</sup> | Cl <sup>-</sup> |
| Cobalt(II)       | 1:25:25                                     | +              | +               |
| +                | 1:25:50                                     | +              | +               |
| Calcium(II)      | 1:25:100                                    | +              | +               |
| Cobalt(II)       | 1:25:25                                     | +              | +               |
| +                | 1:25:50                                     | -              | -               |
| Cadmium(II)      | 1:25:100                                    | -              | -               |

From Table 8, iodide and chloride ion could mask the interfering effect from cadmium(II). Cadmium(II) was characterized as soft acid which could form complex

with soft bases such as these anions. For others cations, iodide ion could not used as the masking agent.

### 8. Determination of cobalt(II) in synthetic solution by TADAP

TADAP was used for the determination of quantity of cobalt(II) by spectrophotometric method. The results from this method were compared with the results from atomic absorption spectroscopy. Cobalt(II) in various synthetic solution were determined in the presence of interfering metal ions (nickel(II) and cadmium(II) because cobalt(II) is byproduct of nickel(II) production (Shriver, 1999)) by 1% v/v.

**Table 9** Determination of cobalt(II) in synthetic solutions

| Synthetic solutions      | Concentration of Cobalt(II) (M) | Spectrophotometric method |         | Atomic absorption spectroscopic method |         |
|--------------------------|---------------------------------|---------------------------|---------|----------------------------------------|---------|
|                          |                                 | Cobalt(II)                |         | Cobalt(II)                             |         |
|                          |                                 | found (M)                 | % Error | found (M)                              | % Error |
| Cobalt(II)               | $2 \times 10^{-6}$              | $2.48 \times 10^{-6}$     | 24.00   | $2.35 \times 10^{-6}$                  | 17.50   |
|                          | $7 \times 10^{-6}$              | $7.84 \times 10^{-6}$     | 12.00   | $7.75 \times 10^{-6}$                  | 10.71   |
|                          | $1.1 \times 10^{-5}$            | $1.07 \times 10^{-5}$     | 2.73    | $1.12 \times 10^{-5}$                  | 1.82    |
| Cobalt(II) + Nickel(II)  | $2 \times 10^{-6}$              | $2.51 \times 10^{-6}$     | 25.50   | $2.48 \times 10^{-6}$                  | 24.00   |
|                          | $7 \times 10^{-6}$              | $7.75 \times 10^{-6}$     | 10.71   | $7.59 \times 10^{-6}$                  | 8.43    |
|                          | $1.1 \times 10^{-5}$            | $1.16 \times 10^{-5}$     | 5.45    | $1.16 \times 10^{-5}$                  | 5.45    |
| Cobalt(II) + Cadmium(II) | $2 \times 10^{-6}$              | $2.55 \times 10^{-6}$     | 27.50   | $2.58 \times 10^{-6}$                  | 29.00   |
|                          | $7 \times 10^{-6}$              | $7.90 \times 10^{-6}$     | 12.86   | $7.79 \times 10^{-6}$                  | 11.28   |
|                          | $1.1 \times 10^{-5}$            | $1.05 \times 10^{-5}$     | 4.54    | $1.11 \times 10^{-5}$                  | 0.91    |

From Table 9, the results of determination of cobalt(II) in both methods were very similar. It was found that, these interference metal ions effected on the determination when the concentration of cobalt(II) was lower than  $1.1 \times 10^{-5}$  M.

**Table 10** Comparison of two methods for determination of cobalt(II) in synthetic solution

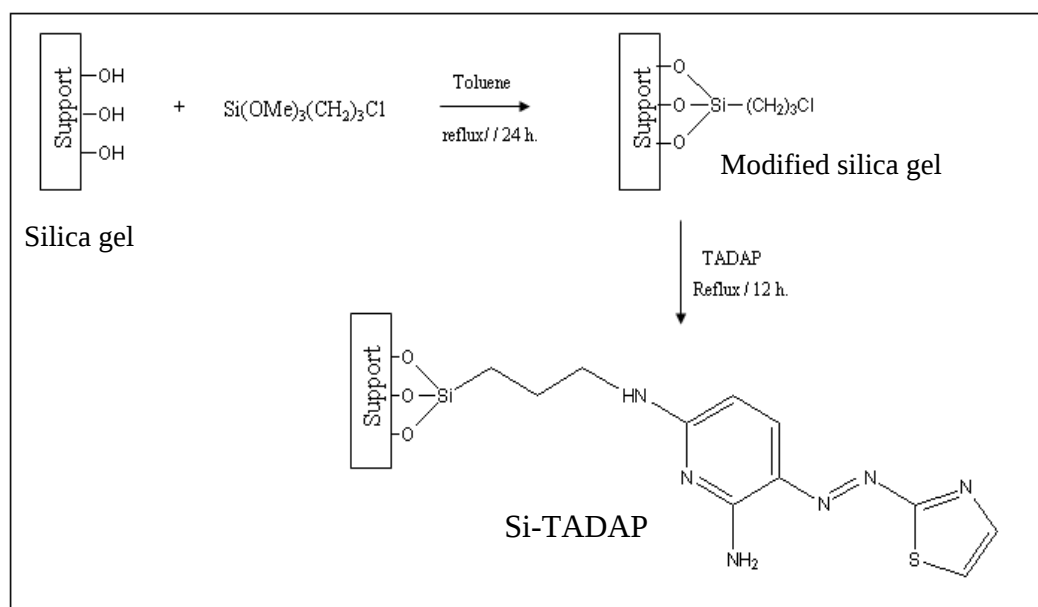
| Synthetic solutions | Concentration (M)    | Spectrophotometric method | Atomic absorption spectroscopic method | $ t $ |
|---------------------|----------------------|---------------------------|----------------------------------------|-------|
|                     |                      | Cobalt(II) found (M)      | Cobalt(II) found (M)                   |       |
| Cobalt(II)          | $2 \times 10^{-6}$   | $2.48 \times 10^{-6}$     | $2.35 \times 10^{-6}$                  | 1.7   |
|                     | $7 \times 10^{-6}$   | $7.84 \times 10^{-6}$     | $7.75 \times 10^{-6}$                  | 0.95  |
|                     | $1.1 \times 10^{-5}$ | $1.07 \times 10^{-5}$     | $1.12 \times 10^{-5}$                  | 1.46  |
| Cobalt(II)          | $2 \times 10^{-6}$   | $2.51 \times 10^{-6}$     | $2.48 \times 10^{-6}$                  | 0.29  |
| +                   | $7 \times 10^{-6}$   | $7.75 \times 10^{-6}$     | $7.59 \times 10^{-6}$                  | 1.56  |
| Nickel(II)          | $1.1 \times 10^{-5}$ | $1.16 \times 10^{-5}$     | $1.16 \times 10^{-5}$                  | 0     |
| Cobalt(II)          | $2 \times 10^{-6}$   | $2.55 \times 10^{-6}$     | $2.58 \times 10^{-6}$                  | 0.22  |
| +                   | $7 \times 10^{-6}$   | $7.90 \times 10^{-6}$     | $7.79 \times 10^{-6}$                  | 1.05  |
| Cadmium(II)         | $1.1 \times 10^{-5}$ | $1.05 \times 10^{-5}$     | $1.11 \times 10^{-5}$                  | 1.44  |

The Table 10 shows the comparison of two methods at various concentration of cobalt(II). There were 4 degrees of freedom so the critical value was  $t_4 = 2.78$  ( $P = 0.05$ ). The observed values of  $|t|$  were less than the critical value so the developing method did not give significantly different results for the determination of

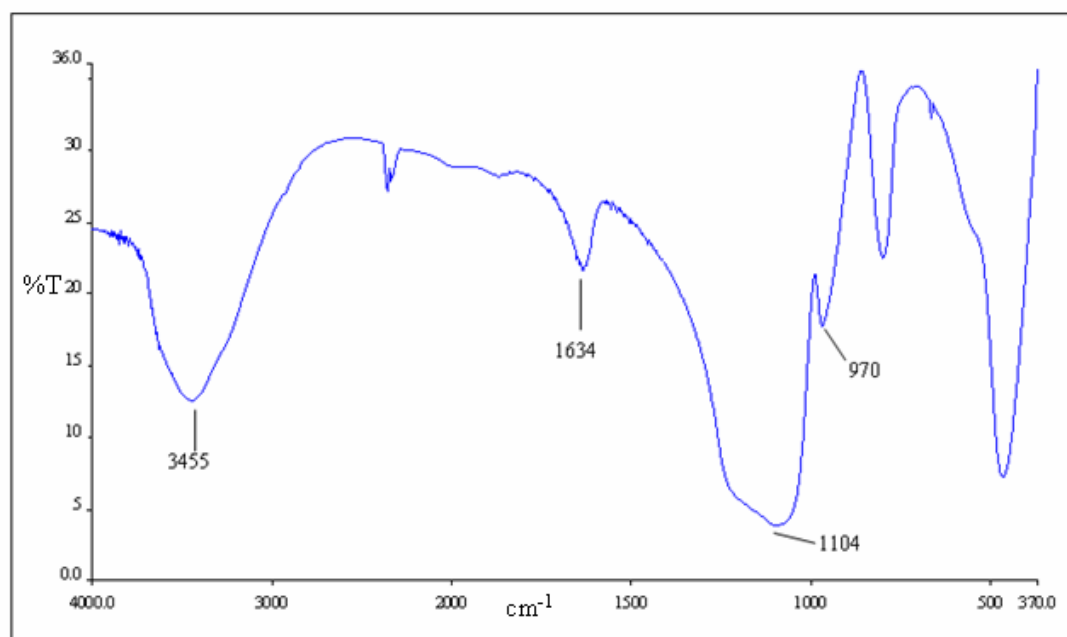
cobalt(II) from the atomic absorption spectroscopy which generally used as the reference method.

### 9. Preparation of 3-(2'-thiazolylazo)-2,6-diaminopyridine resin (Si-TADAP)

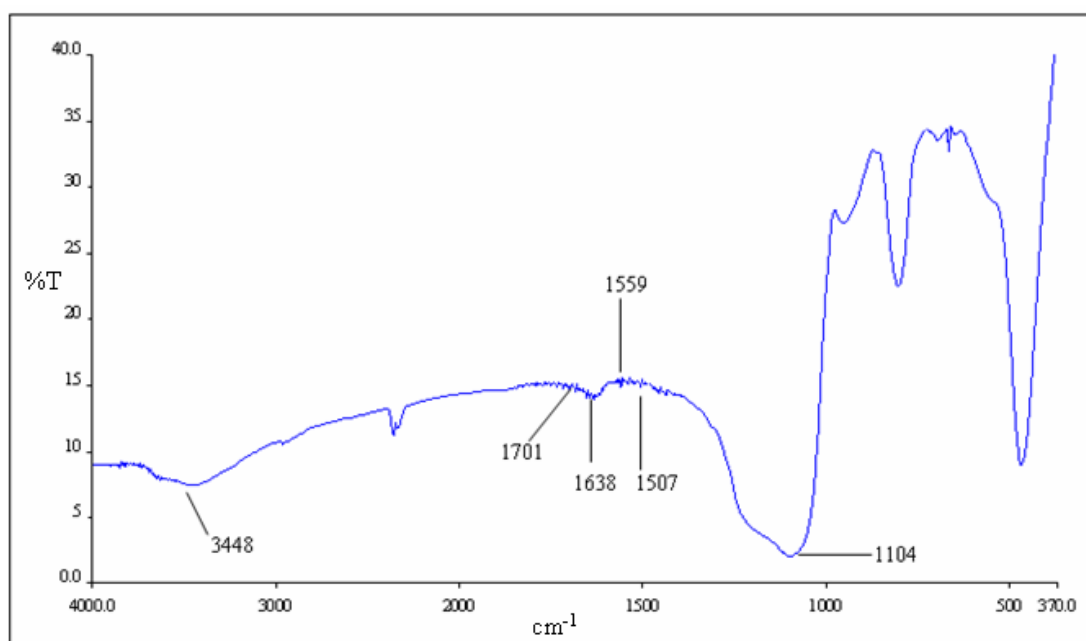
Figure 16 shows the pathway of synthesis Si-TADAP. The resin was characterized by FTIR and elemental analysis. The results are shown in Figure 17, 18 and 19 and Table 11 and 12.



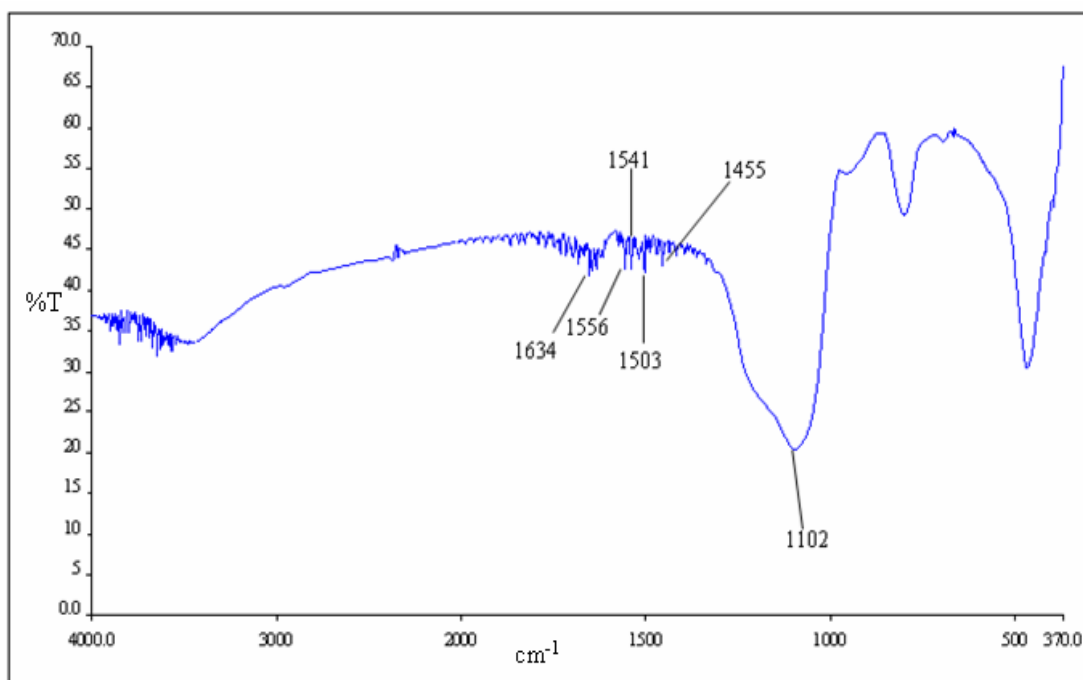
**Figure 16** Synthesis pathway of 3-(2'-thiazolylazo)-2,6-diaminopyridine resin (Si-TADAP)



**Figure 17** IR spectrum of silica gel



**Figure 18** IR spectrum of modified silica gel



**Figure 19** IR spectrum of Si-TADAP

From Figure 18, the IR spectrum of the modified silica gel shows some extra peaks, in the range of  $1500\text{--}1800\text{ cm}^{-1}$ , comparing to the IR spectrum of pure silica gel (see Figure 17). These extra peaks are assigned for the C-C and C-H bonds for the hydrocarbon compound. Thus, (3-chloropropyl)trimethoxysilane was immobilized on silica gel. From Figure 19, Si-TADAP had the peaks assigned for C=C bond at  $1503\text{ cm}^{-1}$ , N-H bend aromatic at  $1634\text{ cm}^{-1}$  and N=N bond at  $1455\text{ cm}^{-1}$ . This is proved that the modified silica gel is contained TADAP.

**Table 11** The elemental analysis of modified silica gel

| Element | Value (%) |
|---------|-----------|
| C       | 4.620     |
| H       | 1.033     |
| N       | 0.023     |
| S       | 0.039     |

**Table 12** The elemental analysis of Si-TADAP

| Element | Value (%) |
|---------|-----------|
| C       | 5.043     |
| H       | 1.067     |
| N       | 0.272     |
| S       | 0.122     |

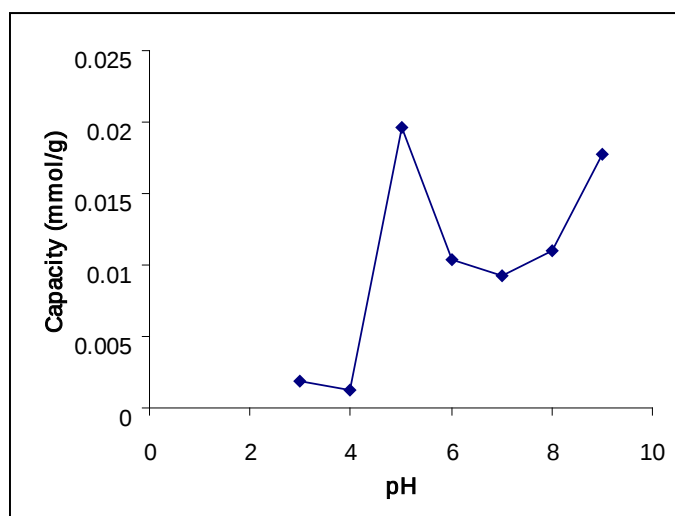
From Table 11, the percentage of carbon atom was 4.620 %. It proved that (3-chloropropyl)trimethoxysilane was modified on silica gel with the capacity at 12.71 mg/g. From Table 12, the percentage of nitrogen and sulfur atoms in Si-TADAP was increase from the immobilized silica gel. Therefore, the modified silica gel was contained TADAP, namely Si-TADAP. From the elemental analysis, Si-TADAP contained TADAP at capacity of 0.82 mg/g.

#### **10. Determination of capacity for the adsorption of cobalt(II) by Si-TADAP**

To determine the capacity for the adsorption of metal ion on the Si-TADAP, the influence of various parameter such as pH, initial concentration of metal ion and shaking time were optimized by using batch equilibrium experiment.

##### **(1) Effect of pH**

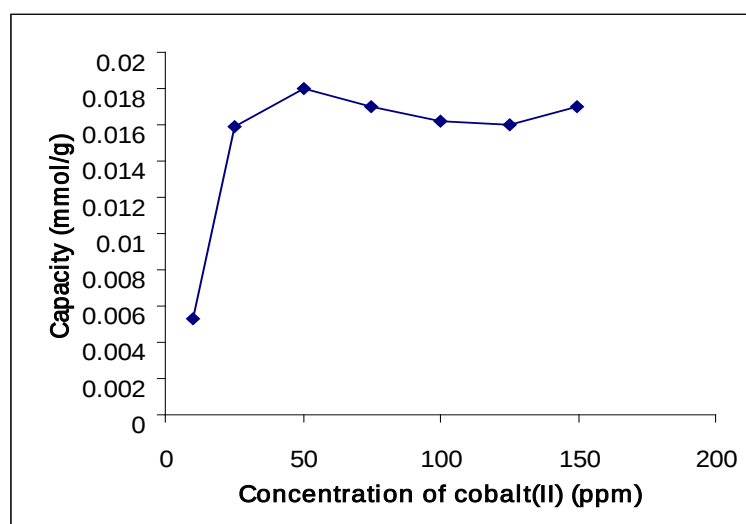
The capacity of Si-TADAP at pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 were 0.0019, 0.0013, 0.0196, 0.0104, 0.0092, 0.0110 and 0.0178 mmol/g, respectively as shown in Figure 20. It was found that the highest capacity for the adsorption of Si-TADAP to cobalt(II) was obtained at pH 5.0.



**Figure 20** Effect of pH on the adsorption of cobalt(II) by Si-TADAP

(2) Effect of initial concentration of cobalt(II)

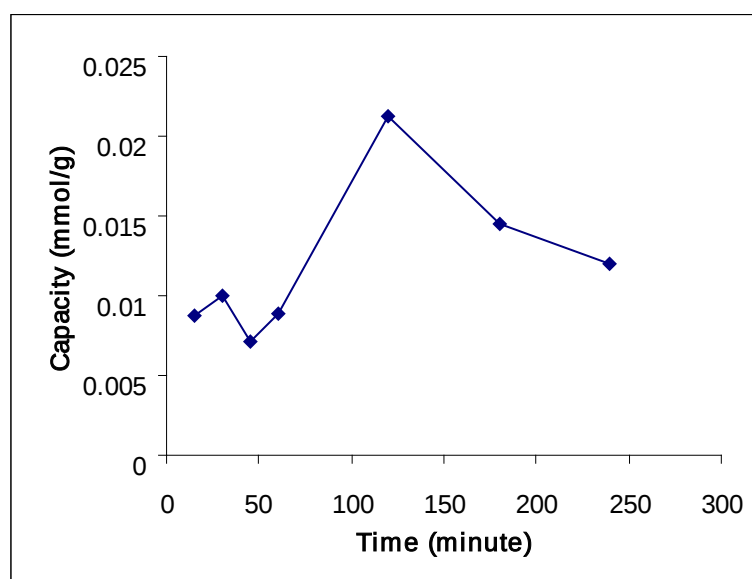
Figure 21 indicated that the initial concentration of cobalt(II) had affect on the adsorption of cobalt(II) by Si-TADAP. The capacity of Si-TADAP for cobalt(II) reached maximum when the concentration of cobalt(II) was 50 ppm.



**Figure 21** Effect of initial concentration of cobalt(II) on the adsorption of the cobalt(II) by Si-TADAP

### (3) Effect of shaking time

The capacity of Si-TADAP for the adsorption of cobalt(II) as a function of shaking time is shown in Figure 22. It was found that the adsorption of cobalt(II) on Si-TADAP increased with increasing shaking time up to 2 hours, which the capacity of Si-TADAP was almost constant.



**Figure 22** Effect of shaking time on the adsorption of cobalt(II) by Si-TADAP

From the results, the capacity of Si-TADAP of cobalt(II) at the optimum condition (pH 5.0, shaking time 2 hours and initial concentration of cobalt(II) 50 ppm) was 0.0213 mmol/g which equivalent to 1.255 mg/g.

## 11. Desorption of cobalt(II) on Si-TADAP

In batch equilibrium experiment, the desorption of cobalt(II) from Si-TADAP by various eluents were examined. The results are shown in Table 13. It was suggested that 0.30 M  $\text{KH}_2\text{PO}_4$  can be used as eluent for the desorption of cobalt(II) from Si-TADAP.

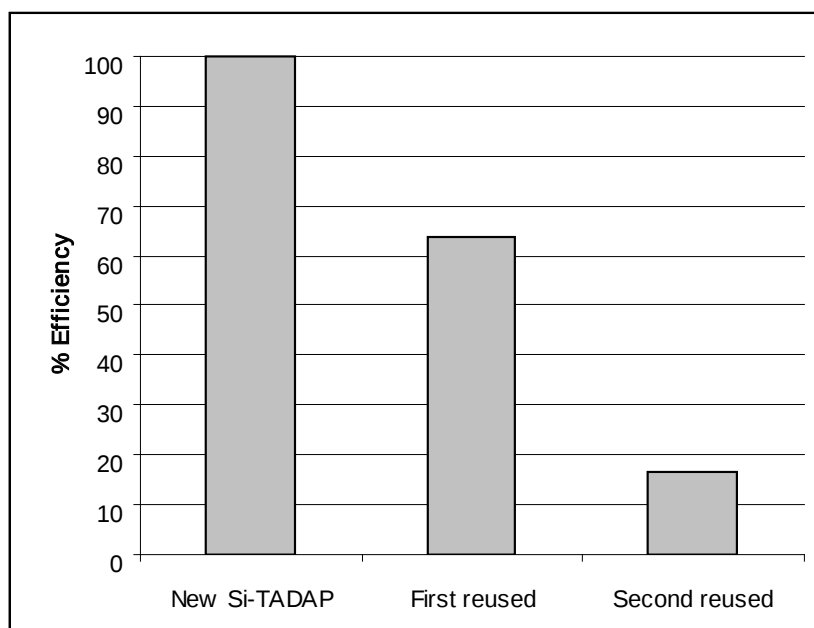
**Table 13** % Desorption of cobalt(II) from Si-TADAP by various eluents

| Eluent                                | % Desorption of cobalt(II) |
|---------------------------------------|----------------------------|
| 0.1 M CH <sub>3</sub> COONa           | 49.31                      |
| 0.5 M CH <sub>3</sub> COONa           | 21.28                      |
| 0.1 M EDTA                            | 2.39                       |
| 0.2 M EDTA                            | 4.36                       |
| 0.25 M HCl                            | 1.26                       |
| 0.5 M HCl                             | 3.15                       |
| 0.1 M KH <sub>2</sub> PO <sub>4</sub> | 68.65                      |
| 0.2 M KH <sub>2</sub> PO <sub>4</sub> | 74.00                      |
| 0.3 M KH <sub>2</sub> PO <sub>4</sub> | 79.50                      |

## 12. Efficiency of Si-TADAP on the adsorption of cobalt(II)

The efficiency of Si-TADAP for adsorption of cobalt(II) was determined by batch equilibrium experiment. As shown in figure 23, % Efficiency of first and second reused of Si-TADAP was 63.58 % and 16.67 %, respectively.

Account for the low adsorption efficiency of the reused Si-TADAP, the used Si-TADAP was digested with nitric acid and the solution was determined for the cobalt(II) by atomic absorption spectrophotometer. It was found that some cobalt(II) still adsorbed on Si-TADAP. Thus, the efficiency of the reused Si-TADAP decreased due to the undesorbed cobalt(II) in the resin. To increase the efficient of the reused Si-TADAP, the new eluent need to be investigated for further study.



**Figure 23** % Efficiency of Si-TADAP for the adsorption of cobalt(II)

## CONCLUSION

3-(2'-thiazolylazo)-2,6-diaminopyridine (TADAP) was synthesized and characterized. The complex formation between cobalt(II) and TADAP was studied. Cobalt(II) could form complex with TADAP in universal buffer solution ranging from pH 9.0 to 11.0. The wavelength which gave the maximum different in absorbance between cobalt(II) complex and TADAP was 598 nm. The ratio of cobalt(II):TADAP was 1:2. The structure of complex between cobalt(II) and TADAP was determined by FT-IR,  $^1\text{H}$ -NMR and elemental analysis which was proved that TADAP acts as tridentate ligand. The stability constant of complex between cobalt(II) and TADAP was determined by Benesi-Hildebrand's equation. From the optimum condition of cobalt(II) complex in universal buffer solution of pH 10, the stability constants was  $1.86 \times 10^{10}$ . This may be concluded that the complex between TADAP and cobalt(II) was fairly stable.

TADAP could be applied as the analytical reagent for the analysis of cobalt(II) by spectrophotometric method. The linear range of the method was  $2.0 \times 10^{-6}$  to  $1.2 \times 10^{-5}$  M with the molar extinction coefficient of  $1.52 \times 10^4 \text{ l}^{-1}\text{mol}^{-1}\text{cm}^{-1}$ . The interfering effect on the analysis of cobalt(II) of various metal ions such as cadmium(II), iron(III), nickel(II), sodium and calcium(II) were studied. Iodide and chloride ion were proved to be effective masking reagent for cadmium(II).

A modified silica gel containing 3-(2'-thiazolylazo)-2,6-diaminopyridine (Si-TADAP) was developed for selective sorption of cobalt(II) from aqueous solutions. The capacity of Si-TADAP of cobalt(II) at the optimum condition was 0.0213 mmol/g which equivalent to 1.255 mg/g. Seventy nine percents of cobalt(II) in the loaded Si-TADAP was successfully eluted by 0.3 M  $\text{KH}_2\text{PO}_4$ .

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## **APPENDIX**

## APPENDIX A

### Calculation of stability constant by Benesi-Hildebrand equation

For the example of the determination of stability constant,  $K$ , of complex between cobalt(II) and TADAP in universal buffer solution of pH 10, the Benesi-Hildebrand equation was applied from equilibrium reaction of complex.



The equilibrium constant for the above reaction is defined by the equation

$$\begin{aligned}
 K &= \frac{[ML_2]}{([M]-[ML_2])([L]-2[ML_2])^2} \quad \text{0} \\
 &= \frac{[ML_2]}{([M]-[ML_2])[L]^2} \\
 [M] - [ML_2] &= \frac{[ML_2]}{K[L]^2} \\
 [M] &= \frac{[ML_2] + K[L]^2[ML_2]}{K[L]^2} \\
 [ML_2] &= \frac{[M]}{\frac{1}{K[L]^2} + 1} \quad \text{----- (2)}
 \end{aligned}$$

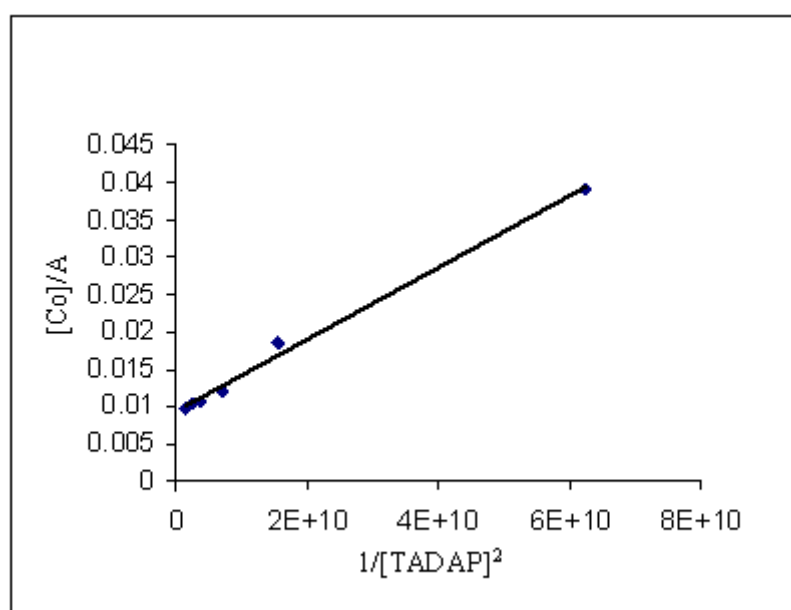
From Beer's law, the true molar extinction coefficient,  $\epsilon_0$ , of the complex at the wavelength of maximum absorption will then be given by the equation

$$\epsilon_0 = A/cb = (\log I_0/I)/[ML_2]b \quad \text{----- (3)}$$

The  $[ML_2]$  can be eliminate between equation 2 and 3, rearrange the resulting equation, and obtain the relation

$$[M]b/(\log I_0/I) = \frac{1}{K \cdot \epsilon_0 \cdot [L]^2} + \frac{1}{\epsilon_0} \text{ ----- (4)}$$

Which is “Benesi-Hildebrand equation” in the form of linear equation,  $y = mx + c$ . In experiment of complex between cobalt(II) and TADAP, the relationship of  $1/[L]^2$  and  $[M]/(\log I_0/I)$  is shown in Appendix Figure A1.



**Appendix Figure A1** The relationship of  $1/[L]^2$  and  $[M]/(\log I_0/I)$  of complex between cobalt(II) and TADAP.

The stability constant of complex was obtained from the slope.

$$\text{Slope} = 1/\epsilon_0 K = 5 \times 10^{-13} \text{ ----- (5)}$$

$$\text{Intercept} = 1/\epsilon = 0.0093 \text{ ----- (6)}$$

Combine (5) and (6);  $K = \text{intercept/slope} = 1.86 \times 10^{10}$

## APPENDIX B

### Calculation of limit of detection

**Appendix Table B1** Calibration curve of complex between cobalt(II) and TADAP

| Concentration of<br>cobalt(II) complex<br>(mol/l) | Absorbance ( $y_i$ ) | Signal from<br>regression line<br>$\hat{y} = 15215x + 0.016$ | y-residuals                     |
|---------------------------------------------------|----------------------|--------------------------------------------------------------|---------------------------------|
| $2 \times 10^{-6}$                                | 0.046                | 0.0464                                                       | $4.410 \times 10^{-10}$         |
| $4 \times 10^{-6}$                                | 0.077                | 0.0769                                                       | $9.216 \times 10^{-9}$          |
| $6 \times 10^{-6}$                                | 0.106                | 0.1073                                                       | $5.329 \times 10^{-7}$          |
| $8 \times 10^{-6}$                                | 0.141                | 0.1377                                                       | $1.043 \times 10^{-5}$          |
| $10 \times 10^{-6}$                               | 0.164                | 0.1681                                                       | $1.521 \times 10^{-5}$          |
| $12 \times 10^{-6}$                               | 0.200                | 0.1986                                                       | $2.161 \times 10^{-6}$          |
|                                                   |                      |                                                              | $\Sigma = 2.834 \times 10^{-5}$ |

$$\begin{aligned}
 \text{SD} &= \sqrt{\frac{\sum [y_i - \hat{y}]^2}{n-2}} \\
 &= 2.662 \times 10^{-3}
 \end{aligned}$$

$$\begin{aligned}
 \text{LOD signal} &= y_B + 3S_B \\
 &= y_{\text{intercept}} + 3 \text{ SD} \\
 &= 0.016 + 3(2.662 \times 10^{-3}) \\
 &= 0.0240
 \end{aligned}$$

LOD signal was transformed to LOD value by equation of regression line.

$$\begin{aligned}
 \hat{y} &= (15215x) + 0.016 \\
 0.024 &= (15215x) + 0.016 \\
 x &= 5.249 \times 10^{-7} \quad \text{mol/l}
 \end{aligned}$$

Limit of detection for complex between cobalt(II) and TADAP is  $5.249 \times 10^{-7}$  mol/l.

## APPENDIX C

### Calculation of the percentage of elements of TADAP

Molecular formula of TADAP is  $C_8H_8N_6S$ . From molecular weight of TADAP (220.254 g/mol), the percentage of elements of TADAP can be determined as followed:

$$\begin{aligned}\text{Percentage of carbon} &= \frac{\text{number of carbon} \times \text{atomic weight of carbon}}{\text{Molecular weight of TADAP}} \times 100 \\ &= \frac{8 \times 12.011}{220.254} \times 100 \\ &= 43.64\%\end{aligned}$$

$$\begin{aligned}\text{Percentage of hydrogen} &= \frac{\text{number of hydrogen} \times \text{atomic weight of hydrogen}}{\text{Molecular weight of TADAP}} \times 100 \\ &= \frac{8 \times 1.008}{220.254} \times 100 \\ &= 3.66\%\end{aligned}$$

$$\begin{aligned}\text{Percentage of nitrogen} &= \frac{\text{number of nitrogen} \times \text{atomic weight of nitrogen}}{\text{Molecular weight of TADAP}} \times 100 \\ &= \frac{6 \times 14.007}{220.254} \times 100 \\ &= 38.16\%\end{aligned}$$

$$\begin{aligned}\text{Percentage of sulfur} &= \frac{\text{number of sulfur} \times \text{atomic weight of sulfur}}{\text{Molecular weight of TADAP}} \times 100 \\ &= \frac{1 \times 32.066}{220.254} \times 100 \\ &= 14.56\%\end{aligned}$$