

## SEPARATION OF LEAD AND COBALT IONS FROM SOLUTION BY 2-(2'-THIAZOLYLAZO)-P-CRESOL CHELATING RESIN

### INTRODUCTION

Cobalt is a grayish lustrous metal. It is brittle, hard, transition metal with magnetic properties similar to those of iron. 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 30.0 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,  $\text{CoAs}_2$ , cobaltite,  $\text{CoAsS}$ , and linnaeite,  $\text{Co}_3\text{S}_4$ .

Cobalt is used in magnet steels, stainless steels, alloys, jet turbines, gas turbine generators and electroplating because of its appearance, hardness, and resistance to oxidation. 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-60, an artificial isotope, is an important  $\gamma$ -ray source, and is extensively used as a tracer and a radiotherapeutic agent. Single compact sources of  $^{60}\text{Co}$  are readily available.

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.

**Table 1** Some properties of cobalt and lead

Property	Cobalt	Lead
Atomic number	27	82
Number of naturally occurring isotopes	1	4
Atomic weight	58.933	207.2
Electronic configuration	[Ar] 3d <sup>7</sup> 4s <sup>2</sup>	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>
Electronegativity	1.7	1.6
Melting point / °C	1495	327.5
Boiling point / °C	2927	1749
Thermal conductivity / W m <sup>-1</sup> K <sup>-1</sup>	100	35
Density (20 °C) / g cm <sup>-3</sup>	8.9	11.34
Electrical resistivity (20 °C) / μΩ cm	6	21

Source: Greenwood (1997)

Lead is a bluish-white lustrous metal. The properties of lead are shown in Table 1. Lead is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air.

Lead is found in nature sparingly. It is present in ores such as galena (lead sulfide, PbS), anglesite (lead sulfate, PbSO<sub>4</sub>), minim (a form of lead oxide with formula Pb<sub>3</sub>O<sub>4</sub>), cerussite (lead carbonate, PbCO<sub>3</sub>) and other minerals. Galena is the most important source.

Lead is widely used in alloys, cable covering, plumbing, ammunition, storage batteries, paints, solder, containing corrosive liquids and insecticides. The oxide of lead is used in producing fine "crystal glass" and "flint glass" with a high refractive index for achromatic lenses. Tetraethyl lead (PbEt<sub>4</sub>), antiknock additive substance, is still used in some grades of petrol (gasoline) and is responsible for a considerable portion of the lead found in the biosphere. It is being phased out in many countries on

environmental grounds. Typical symptoms of lead poisoning are cholic, anaemia, headaches, convulsions, chronic nephritis of kidneys, brain damage and central nervous-system disorders. It acts by complexing with oxo-groups in enzymes and affects virtually all steps in the process of haem synthesis and porphyrin metabolism.

From the hazard of cobalt and lead, it is important to separate these elements from aqueous solutions.

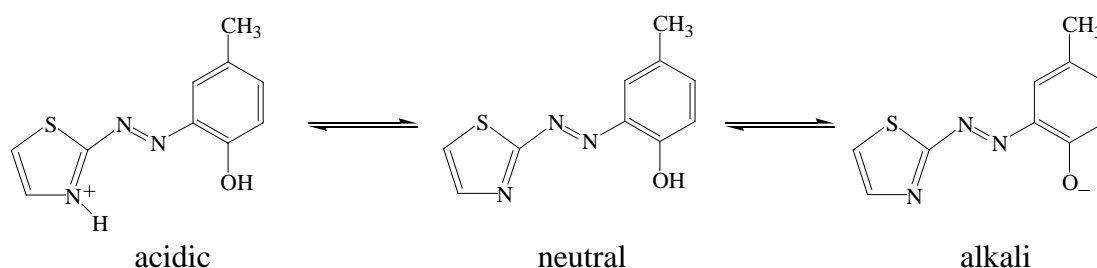
Thiazolylazo dyes and its derivatives can be used as sensitive chromogenic reagents, complexing agents, reagents for spectrophotometric and extraction-photometric determination of many metal ions (Jensen, 1960). These compounds are easily prepared by diazotisation of 2-aminothiazole and then coupling the reactive diazotate formed with phenolic substances.

Many procedures for determination, preconcentration and separation of several metals have been developed which usually involved with various materials for the adsorption such as polyurethane foam loaded with TAC collected copper, cobalt, nickel, zinc and cadmium (Tanaka, 1982), heterocyclic azo dyes supported on silica gel was used as a chelating resin for adsorption of uranium (Ueda, 1985), Amberlite XAD resin was used for the preconcentration of zinc(II), cadmium(II), nickel(II) and lead(II) from aqueous solutions (Saxena, 1994).

Chloromethylated polystyrene divinylbenzene loaded with 3,5-methylpyrazole was used for the adsorption of metal ions (Myasoedova, 1976). It was used because of its good physical and chemical properties such as porosity, high surface area, durability and purity.

In this work, 2-(2'-thiazolylazo)-p-cresol (TAC) which is derivative of thiazolylazophenol was prepared and used as chelating ligand for cobalt(II) and lead(II).

TAC is soluble in acidic and neutral solution, giving yellow color with a maximum absorption at 372 nm and in strongly alkali solution, giving red color with a maximum absorption at 532 nm. These hypsochromic (blue shift) and bathochromic (red shift) shifts are due to protonation and ionization, respectively.



**Figure 1** Chemical structure of 2-(2'-thiazolylazo)-p-cresol (TAC) in acidic, neutral and alkali solution.

Source: Hovind (1975)

The complexation of TAC with cobalt(II) and lead(II) were determined by using continuous variation method in acidic and alkali solutions.

The chelating resin was prepared by using chloromethylated polystyrene divinylbenzene which was immobilized with 2-(2'-thiazolylazo)-p-cresol (TAC) for separation of cobalt(II) and lead(II) from aqueous solutions and selectivity of this chelating resin for cobalt(II) and lead(II) were studied.

## LITERATURE REVIEWS

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

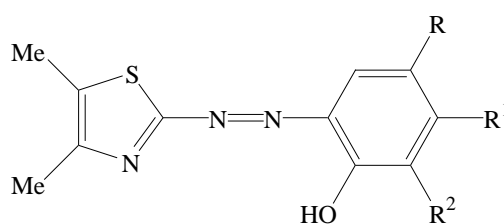
Kaneniwa (1959) synthesized 2-(2'-thiazolylazo)-p-cresol (TAC) by diazotisation of 2-aminothiazole and then coupling with p-cresol. The crude product was recrystallized in ethanol to give TAC as brown needles, melting point of 131-132 °C. The 0.1% methanolic solution of TAC became yellow to pink at pH 7.0-9.0. The following compounds were similarly prepared and their change of color according to pH studied [appearance, m.p., change of color (pH interval) given]: thiazolylazo-resorcinol (TAR), red needles, 218-219 °C, yellow to deep orange (4.2-6.2) and deep orange to red (8.2-10.2); thiazolylazo- $\beta$ -naphthol ( $\beta$ -TAN), brown red needles, 140-141 °C, orange to pink (8.2-10.0); thiazolylazo- $\alpha$ -naphthol ( $\alpha$ -TAN), brown red needles, 185-186 °C, slightly red to violet (5.4-7.4). These compounds formed chelate complexes with Cu(II), Co(II) and Ni(II) to give red, violet, and blue solutions, respectively.

Jensen (1960) synthesized 1-(2'-thiazolylazo)- $\beta$ -naphthol-6-sulphonic acid (TAN-6-S), 2-(2'-thiazolylazo)-p-cresol (TAC), 6-(2'-thiazolylazo)-resorcinol (TAR), 6-(2'-thiazolylazo)-orcinol (TAO) and 6-(2'-thiazolylazo)-1-oxy-3-dimethylamino-benzene (TAM) which could be used as complexometric metal indicator. These azo dyes were prepared by diazotisation of 2-aminothiazole and then coupling with  $\beta$ -naphthol-6-sulphonic acid, p-cresol, resorcinol, orcinol and m-dimethylamino-phenol, respectively. The compounds were investigated for their properties as metal indicators for Th(V), La(III), UO<sub>2</sub>(II), Pb(II), Hg(II), Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Mg(II) and Ca(II).

Komarek et al. (1979) studied the usefulness of several azo dyes for the extraction concentration of traces of Cu(II), Ni(II), Co(II), Cd(II), and Zn(II) in iso-BuCOMe and for their final determination by atomic absorption spectrophotometry

with an acetylene-air flame or using a graphite atomizer. The azo dyes: 1-(2-pyridylazo)-2-naphthol, 2-(2-pyridylazo)-1-naphthol (I), 2-(2-benzothiazolylazo)-1-naphthol, 2-(2-quinolylazo)-1-naphthol, 1-(2-thiazolylazo)-2-naphthol, 2-(2-thiazolylazo)-4-methylphenol and 2-(2-thiazolylazo)-4-methoxyphenol were studied. Procedures for determination of metals in salt solutions, potable waters and metallic aluminium were given. By using electrothermal atomization on graphite, the detection limits were 2.54, 2.47, 2.64, 0.045, and 0.13  $\mu\text{g/ml}$  for Cu(II), Ni(II), Co(II), Cd(II), and Zn(II), respectively. Atomic absorption spectrophotometry was also useful in the study of extraction equilibria, and for finding the optimum extraction conditions for these elements by heterocyclic azo dyes.

Fumiaki et al. (1982) synthesized ligands I ( $R = \text{Me, Et, Ph, Cl, } R^1 = R^2 = \text{H; } R = \text{Me, } R^1 = \text{H, } R^2 = \text{OMe, Me; } R = R^2 = \text{H, } R^1 = \text{NMe}_2$ ) by azo coupling of the diazonium salt and the appropriate phenol and their acid dissociation constants were studied. The complexes of I with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) were prepared and their formation constants were determined. These complexes had enhanced stability over the analogs without Me substitution of the thiazole ring.



ligands I

Feng (1984) studied the complex formation reaction of Co(III) with 2-(2-thiazolylazo)-5-(diethylamino)phenol and a method was developed for the spectrophotometric determination of trace of cobalt. The composition of the 1:2 metal-ligand complex was determined by Job's method and by the molar ratio method. The complex had an apparent stability constant of  $4.78 \times 10^{10}$  and a molar absorptivity of  $7.69 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Beer's law was obeyed for 0-0.8  $\mu\text{g Co/ml}$ .

Interferences by various anions and cations were studied. The method was applied to the determination of trace cobalt in natural water.

Rathaiah and Eshwar (1985) studied the complexation between Pb(II) and 1-(2'-thiazolylazo)-2-naphthol in faintly acidic media (pH 6.1-6.7), which formed a reddish brown chelate solution in MeOH-H<sub>2</sub>O mixtures. The 1:1 complex exhibited maximum absorbance at 575-580 nm in 40% MeOH, was stable for 36 hours, adhered to Beer's law for Pb(II) concentration of 0.2-6.0 µg/ml, had formation constant (log K) of 5.30, and molar absorptivity  $1.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The method was applied for the determination of lead content in an alloy.

Gandhi et al. (1990) synthesized three thiazolylazo dyes; 5-(2-thiazolylazo)-2,4-dihydroxybenzoid acid (TARK), 2-(2-thiazolylazo)-p-cresol (TAC) and 1-(2-thiazolylazo)-2-naphthol (TAN). They had been investigated as reagents for the spot detection, ring oven identification and ring colorimetric detection of Cd(II), Pb(II) and Zn(II). It was found that TAC was the most sensitive reagent for Cd(II), Pb(II) and Zn(II).

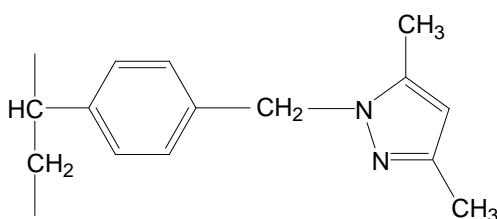
Ferreira et al. (1991) studied the reaction between Pb(II) and 2-(2-thiazolylazo)-p-cresol (TAC) in the presence of Tergitol NPX (4 mg/ml). At pH 9.0-10.0, an intensely colored complex was given which was stable for at least 4 hours. The composition of the complex was 1:2 (Pb(II):TAC) and the log of the formation constant was  $11.92 \pm 0.40$ . Beer's law was obeyed up to 6.0 µg/ml of Pb(II) at 650 nm. The apparent molar absorptivity at 650 nm was  $2.07 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and the detection limit was obtained as 10.0 µg/ml of Pb(II). The method was applied to the determination of Pb(II) in copper-base alloy.

Masoud et al. (1995) studied the electronic absorption spectra of thiazolylazo compounds in presence of different solvents. The pK-values of these compounds were evaluated spectrophotometrically and pH-metrically and laid in the range of 4.30-8.92. The position of the spectral bands and their intensities were pH-dependent, with the presence of different isobestic points. The modes of ionization were assigned. The

formation constants of the Co(II), Ni(II) and Cu(II) complexes were evaluated. The mechanisms of hydration and solvation of thiazolylazo compounds in dioxane were discussed.

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

Myasoedova et al. (1976) synthesized chelating adsorbent containing pyrazole groups as substituent by aminating chloromethylated polystyrene divinylbenzene copolymers with 3,5-methylpyrazole. The structure of this chelating resin can be depicted as;



The adsorption of metal ions, which interacted with the pyrazole groups of the adsorbent, depended on the solution acidity and the concentration of other elements.

Nakayama et al. (1982) prepared a new chelate-forming resin bearing -SH and azo groups from a common anion-exchange resin by treatment with azothiopyrine disulfonic acid (I). The I-treated resin was very stable and highly effective for the collection of Hg (II) by the batch and column methods and for adsorption of copper and cadmium. In the column method, the amount of Hg (II) in solution could be reduced to <0.5 µg/L. The Hg(II) adsorbed could be eluted with thiourea solution, and the resin could be used repeatedly, especially for the treatment of wastewater.

Tanaka et al. (1982) studied polyurethane foam which loaded with  $\text{Bu}_3\text{PO}_4$  solution of 2-(2-thiazolylazo)-4-mephenol (TAC) collected several metal ions, as Cu(II), Ni(II), Co(II), Zn(II), and Cd(II), by immersing it in the sample solution, and the color of the foam changes from yellow to green and greenish brown. The color intensity of the foam was proportional to the metal concentration. When the foam (1 cm x 1 cm x 1 cm, TAC: 0.5 mg,  $\text{Bu}_3\text{PO}_4$  0.05 ml) was immersed for 5 min in 2 ml of the sample solution buffered at pH 8.3 with  $\text{NH}_4\text{NO}_3\text{-NH}_3$  solution, the detection



limit and absorption maximum wavelength were as follow; Cu(II) 0.5 ppm, 615 nm, Ni(II) 0.2 ppm, 615 nm, Co(II) 0.2 ppm, 586 nm, Zn(II) 1 ppm, 598 nm, and Cd(II) 2 ppm, 598 nm. The proposed method was applied to the determination of the metal ion concentration in wastewater of plating industry.

Grote and Kettrup (1985) synthesized the ion-exchange resins containing S-bonded dithizone and dehydrodithizone as functional groups. The adsorption of noble metals and base metals on the ion-exchange resins were investigated. The reaction of dehydrodithizone with chloromethylated polystyrene yielded the ion-exchanger, P-TD. The tetrazolium groups on P-TD were reduced to produce a chelating resin, P-D, which contained S-bonded dithizone as the functional group. These sorbents were used for adsorption of platinum group metal ions and Au(III). The distribution coefficients as function of acidity were also studied. The desorption of precious metal ions such as Au(III), Pd(II), Pt(IV), Ru(III), Rh(III), Os(III), Ir(II) and Ir(IV) from the P-D and P-TD ion-exchange resins were studied by various eluents (6 M hydrochloric acid, 2 M perchloric acid, ammonium nitrate, sodium thiocyanate and thiourea). The P-D ion-exchange loaded with precious metal ions was eluted with 4 M hydrochloric acid for eluting the Ru(III), Rh(III) and Ir(V). Then the sorbed species of Au(III) and Pd(II) were eluted with 10 ml of 5% thiourea in 0.1 M hydrochloric acid. For P-TD, Pd(II) and Pt(IV) were eluted satisfactorily by thiourea in the absence of Ir(IV). Then the loaded resin was eluted with 0.5 M thiocyanate which desorped Os(IV) and 50% of Ir(IV). The P-D chelating resin was selective for separation of Pd(II) and Au(III). P-D chelating resin was unsuitable for cyclic procedures whereas the P-TD anion-exchanger was able to regenerate and utilize for selective separation of Pd(II), Pt(IV), Os(IV) and Au(III).

Ueda et al. (1985) synthesized the chelating adsorbents, heterocyclic azo dyes supported on silica gel, and investigated their adsorption behavior toward metal ions. 1-(2-Pyridylazo)-2-naphthol-silica gel and 2-(2-thiazolylazo)-p-cresol-silica gel show greater affinity for  $\text{UO}_2^{2+}$  and  $\text{ZrO}^{2+}$  than for other metal ions like Cu(II), Cd(II), Fe(II), Fe(III), and the alkali earths. Trace  $\text{UO}_2^{2+}$  could be quantitatively retained on gel columns in the neutral pH region and at flow-rate 3-4 ml/min. The  $\text{UO}_2^{2+}$  retained

was easily eluted from the column bed by 9:1 (v/v) Me<sub>2</sub>CO-HNO<sub>3</sub> determined by spectrophotometry using Arsenazo-III. Matrix components in seawater did not interfere, and the spiked recovery of UO<sub>2</sub><sup>2+</sup> in artificial seawater averaged 98.6%, with a 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%. UO<sub>2</sub><sup>2+</sup> was quantitatively sorbed from the wastewater at a pH of 5.5 in the presence of 1.2x10<sup>-6</sup> M EDTA and eluted with 1 N HCl. The preparation of the polystyrene-azo-PAR resin was discussed.

Pesavento et al. (1988) studied two sulfonated azo-dyes, which had a N-donor atom in the diazo group and were known to complex heavy metal ions in aqueous solution. They were sorbed by a strong- base anion- exchange resin (Dowex 1-X8) simply by ion-exchange. The resin containing the dyes behaved like a chelating resin, able to sorbed Cu(II) and Ni(II) from aqueous solution, under proper conditions. The acidity, ionic compound, volume of the aqueous solution and the amount and nature of the sorbed ligand were the factors which determined the fraction of metal ion sorbed when the batch technique was used.

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 -N=N- group. The chelating resin was used for the preconcentration of Zn(II), Cd(II), Ni(II) and Pb(II) from aqueous solution. The optimum pH for the adsorption of Zn(II) and Cd(II) were 5-6, for Ni(II) and Pb(II) were 3-4 and 6, respectively. Zn(II), Cd(II), Ni(II) and Pb(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 µg/g of the resin for Zn(II), Cd(II), Ni(II) and Pb(II), respectively.

Lim et al. (1996) synthesized the new chelating resins, XAD-2, 4, 16-TAC and XAD-2, 4, 16-TAO by reacting Amberlite XAD-2, XAD-4, and XAD-16 macroreticular resins with 2-(2-thiazolylazo)-p-cresol (TAC) and 4-(2-thiazolylazo)-orcinol (TAO) as functional groups and were characterized by elemental analysis and FTIR spectrophotometry. The content of functional group in chelating resin was 0.60 mmol/g in XAD-16-TAC and 0.68 mmol/g in XAD-16-TAO, respectively. The chelating resins were stable in acidic and alkali solution and can be reused over 10 times. The adsorption behaviors of some metal ions on two chelating resins were studied by batch method. For the optimum conditions of adsorption, the time required for equilibrium was about 1 hour and the optimum pH was 5. In the presence of anions such as  $\text{SO}_4^{2-}$  and  $\text{CH}_3\text{COO}^-$ , the adsorption of U(VI) ion was slightly reduced but other anions such as  $\text{Cl}^-$  and  $\text{NO}_3^-$  revealed no interference effect. Also, adsorption capacity of U(VI) ion was decreased by addition of  $\text{CO}_3^{2-}$  ion because of complex formation of  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ , but alkali metals and alkali earth metals including Na(I), K(I), Mg(II), and Ca(II) were not affected by the adsorption extent. Masking agent, NTA showed better separation efficiency of U(VI) ion from coexisting metal ions such as Th(IV), Zr(IV), Hf(IV), Cu(II), Cd(II), Pb(II), Ni(II), Zn(II) and Mn(II) than EDTA and CDTA.

Chattopadhyay et al. (1997) prepared a new chelating resin incorporating imidazolylazo groups into a matrix of polystyrene divinylbenzene. The exchange capacity of the resin for the ions Hg(II), Ag(I), and Pb(II) as a function of pH was determined. The resin exhibited no affinity to alkali, or alkali earth metals. Hg(II) in trace quantities was very effectively removed from river water spiked with Hg(II) at the usual pH of natural waters.

Lemos et al. (1998) used polyurethane foam modified by 2-(2'-benzothiazolylazo)-2-p-cresol (B-TAC) as a sorbent for determination of Cd(II) trace levels. It was found that pH had effect on the adsorption of Cd(II) on B-TAC. The adsorption of Cd(II) by B-TAC had been investigated within the pH range of 6.50 to 9.25. It was found that the maximum adsorption of Cd(II) was achieved at pH 9.0 in the ammonium buffer solution. Cd(II) was eluted from the column by using hydrochloric

acid at various concentrations. The results showed that 0.1 M hydrochloric acid was the most suitable eluent for desorption Cd(II) from B-TAC.

Ferreira and De Brito (1999) studied an analytical procedure for the determination of trace cobalt in saline matrixes by ICP-AES, using a column containing Amberlite XAD-2 resin loaded with 2-(2-thiazolylazo)-p-cresol (TAC) for the steps of preconcentration and separation. This method did not require toxic chloroform as an eluent.

Kim et al. (2000) studied polystyrene-divinylbenzene-2-(2-thiazolylazo)-p-cresol, which could absorb metal ions, specially uranium ion, and work as a ligand of metal for forming chelate with metal to isolate the metal. The compound was manufactured by the following steps of: (1) nitration of polystyrene-divinylbenzene copolymer; (2) amination of nitro compound; (3) diazotisation of aminated polystyrene-divinylbenzene copolymer; (4) reaction of diazotized polystyrene-divinylbenzene copolymer with thiazolylazo-p-cresol.

Lee et al. (2000) synthesized two chelating resins, XAD-16-TAC and XAD-16-TAO by Amberlite XAD-16 macroreticular resin with 2-(2-thiazolylazo)-p-cresol (TAC) and 4-(2-thiazolylazo)-orcinol (TAO) as functional groups. The adsorption behavior of Zr(IV), Th(IV) and U(VI) with two chelating resins were examined with respect to the effect of pH and masking agent by batch method. It was found that the optimum pH was at 5-6, and the two chelating resins showed good separation efficiency of Zr(IV) and Th(IV) by using  $\text{NH}_4\text{F}$  as a masking agent. Characteristics of desorption were studied with 0.1-2.0 M  $\text{HNO}_3$  as desorption reagent. 2 M  $\text{HNO}_3$  showed high desorption efficiency to most of metal ions except Zr(IV). XAD-16-TAC resin was applied for the separation and preconcentration of trace Zr(IV) from mixed metal ions. Also Th(IV) ion could be successfully separated from U(VI) and Zr(IV) ion by using XAD-16-TAO resin.

Lemos et al. (2002) studied an online enrichment flow system, which was developed to determine trace amounts of cobalt in seawater samples. It was based on

the chemical adsorption of cobalt(II) ions onto a mini-column packed with Amberlite XAD-2 resin loaded with TAC reagent. After cobalt preconcentration, the analyte was eluted by 0.50 M nitric acid solution and determined directly by flame atomic absorption spectrometry (FAAS). A preconcentration factor of 87 in 15 ml of sample (3 min preconcentration time) was achieved by using the time-based technique. The detection limit was 0.13  $\mu\text{g/l}$  and the precision (evaluated as the relative standard deviation) reached values within the range of 7.0-1.4% in cobalt solutions varying from 0.50 to 10  $\mu\text{g/l}$  concentration, respectively. Chemical and flow variables as well as concomitant were studied in the developed procedure. The method was tolerant to other ions usually presence in the analyzed samples. The proposed procedure was successfully applied for the determination of cobalt in a certified reference material. The recoveries of cobalt in samples of natural waters, measured by standard addition technique, demonstrated that the proposed procedure had also a good accuracy.

Mondal and Das (2002) studied chloromethylated polystyrene divinylbenzene, which was functionalized through -NH-CH<sub>2</sub>- bond with bis-(2-aminophenyl)disulfide. The resulting chelating resin was characterized by elemental analysis, IR spectra and metal ion capacity. The sorption capacities for both As (III) and As (V) were determined using batch technique and they show a strong sorption at pH 4.5. The effects of the presence of co-existing ions were examined. The concentration of each of the arsenic species was determined by HG-AAS. The sorption and desorption cycles were examined using a column packed with the resin without any loss of column performance which indicated the possibility for its reuse. The developed column technique was used for the removal of arsenic species from natural water.

Rerkpalin (2003) synthesized 2-(2'-thiazolylazo)-p-cresol (TAC) and studied properties and application of TAC. The complexation of TAC with Cu(II) and Cd(II) were studied. TAC could form green complex with Cu(II) at pH 3.0, 5.0 and 7.0 and red-violet complex at pH 10.0. The color of Cd(II)-TAC complex is yellow at pH 7.0, violet at pH 7.5 and 8.0 and red-violet complex at pH 9.0. The ratio of Cu(II):TAC and Cd(II):TAC in their complex are 1:1 in acidic and alkali condition. The chelating resin (P-TAC) was prepared. The ability of P-TAC for adsorption of Cu(II) and Cd(II)

had been studied by batch equilibrium and column experiment. Cu(II) and Cd(II) on P-TAC were successively eluted by 2 M hydrochloric acid and 1 M nitric acid, respectively. P-TAC was used to separate Cu(II) and Cd(II) from synthetic waste solution.

## MATERIALS AND METHODS

### Materials

#### 1. Apparatus

Absorbance measurements were carried out on a Jasco model 7800 UV-Vis spectrophotometer. Perkin Elmer 1100B and Perkin Elmer (Analyst 800) Atomic absorption spectrophotometers were used for the quantitative determination of cobalt(II) and lead(II). The instrument was operated under air-acetylene flame with analytical wavelengths at 240.7 nm and 283.3 nm for cobalt(II) and lead(II), respectively. Infrared spectra ( $4000\text{-}200\text{ cm}^{-1}$ ) were obtained by a Perkin Elmer system 2000 Fourier transform infrared spectrometer. All absorption was reported in wave number ( $\text{cm}^{-1}$ ). Nuclear magnetic spectra were recorded at 400 MHz on a Bruker Advance DPX-400. An elemental analysis of TAC was performed with a Perkin Elmer series II CHNS/O analyzer 2400. Mass spectrum of TAC was obtained from HPLC/MS (Agilent 1100). The pH values were measured by using an inoLab level 1-pH meter.

#### 2. Reagents

All reagents were analytical grade, except 2-aminothiazole (Merck, Darmstadt, Germany) and p-cresol (M&B, Degenhamt, England) were laboratory grade. Double distilled deionized water was used for the preparation of solutions. Chloromethylated polystyrene divinylbenzene (Fluka, Steinheim, Switzerland) consists of cross linked with 1% DVB, 200-400 mesh. Standard solution of cobalt(II) and lead(II) for atomic absorption spectrophotometry were prepared by dilution of  $1000\text{ mg L}^{-1}$  stock standard solution (Carlo Erba, Milan, Italy).

## Methods

### 1. Preparation of solutions

#### 1.1 Preparation of buffer solutions

Buffer solutions used in this work were prepared by mixing various reagents as stated in Table 2.

**Table 2** The buffer solutions at pH range from 3.0 to 10.0 which were prepared and used in this work.

pH	Buffer system
3	0.1 M CH <sub>3</sub> COOH (98.23 ml) and 0.1 M CH <sub>3</sub> COONa (1.77 ml)
4	0.1 M CH <sub>3</sub> COOH (64.75 ml) and 0.1 M CH <sub>3</sub> COONa (36.25 ml)
5	0.1 M CH <sub>3</sub> COOH (35.70 ml) and 0.1 M CH <sub>3</sub> COONa (64.30 ml) 0.1 M KHP (50.00 ml) and 0.1 M NaOH (22.60 ml)
6	0.1 M CH <sub>3</sub> COOH (5.26 ml) and 0.1 M CH <sub>3</sub> COONa (94.74 ml) 0.1 M KHP (50.00 ml) and 0.1 M NaOH (44.20 ml)
7	0.1 M NaH <sub>2</sub> PO <sub>4</sub> (62.00 ml) and 0.1 M Na <sub>2</sub> HPO <sub>4</sub> (38.00 ml) 0.1 M KH <sub>2</sub> PO <sub>4</sub> (50.00 ml) and 0.1 M NaOH (29.10 ml) 0.1 M tris(hydroxymethyl)aminomethane (50.00 ml) and 0.1 M HCl (46.60 ml)
8	0.1 M NH <sub>4</sub> OH (5.26 ml) and 0.1 M NH <sub>4</sub> Cl (94.74 ml) 0.1 M KH <sub>2</sub> PO <sub>4</sub> (50.00 ml) and 0.1 M NaOH (46.70 ml) 0.1 M tris(hydroxymethyl)aminomethane (50.00 ml) and 0.1 M HCl (29.20 ml)
9	0.1 M NH <sub>4</sub> OH (35.71 ml) and 0.1 M NH <sub>4</sub> Cl (64.29 ml) 0.1 M tris(hydroxymethyl)aminomethane (50.00 ml) and 0.1 M HCl (5.70 ml) 0.1 M NaHCO <sub>3</sub> (65.80 ml) and 0.1 M Na <sub>2</sub> CO <sub>3</sub> (34.20 ml)
10	0.1 M NH <sub>4</sub> OH (84.75 ml) and 0.1 M NH <sub>4</sub> Cl (15.25 ml) 0.1 M tris(hydroxymethyl)aminomethane (50.00 ml) and 0.1 M HCl (3.80 ml) 0.1 M NaHCO <sub>3</sub> (27.27 ml) and 0.1 M Na <sub>2</sub> CO <sub>3</sub> (72.73 ml)



## 1.2 Preparation of universal buffer solutions

Universal buffer solutions used in this work were prepared by mixing the 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 ratios as stated in Table 3.

**Table 3** The universal buffer solutions at pH range from 3.0 to 11.0 which were prepared and used in this work.

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	176	24
4	155	45
5	134	66
6	118	82
7	99	101
8	85	115
9	69	131
10	54	146
11	44	156

## 1.3 Preparation of $1 \times 10^{-3}$ M and $2 \times 10^{-4}$ M TAC

For the preparation of  $1 \times 10^{-3}$  M, 0.0219 g of TAC was dissolved and made up to 100 ml by 95% ethanol in volumetric flask.

Solutions of  $2 \times 10^{-4}$  M TAC at various pH were prepared by diluting  $1 \times 10^{-3}$  M TAC in volumetric flask with various buffer solutions as stated in Table 2.

#### 1.4 Preparation of $1 \times 10^{-3}$ M and $2 \times 10^{-4}$ M cobalt(II) solutions

For the preparation of  $1 \times 10^{-3}$  M cobalt(II), 5.89 ml of standard solution of cobalt nitrate (1000 ppm) was added in a 100 ml volumetric flask and diluted to the marked by 0.1 M  $\text{HNO}_3$ . Solutions of  $2 \times 10^{-4}$  M cobalt(II) at various pH were prepared by diluting  $1 \times 10^{-3}$  M cobalt(II) in volumetric flask with various buffer solutions as stated in Table 2.

#### 1.5 Preparation of $1 \times 10^{-3}$ M and $2 \times 10^{-4}$ M lead(II) solutions

For the preparation of  $1 \times 10^{-3}$  M lead(II), 20.70 ml of standard solution of lead nitrate (1000 ppm) was added in a 100 ml volumetric flask and diluted to the marked by 0.1 M  $\text{HNO}_3$ . Solutions of  $2 \times 10^{-4}$  M lead(II) at various pH were prepared by diluting  $1 \times 10^{-3}$  M lead(II) in volumetric flask with various buffer solutions as stated in Table 2.

## 2. Synthesis of 2-(2'-thiazolylazo)-p-cresol (TAC)

Two grams of 2-aminothiazole was dissolved in 20 ml of 6 M hydrochloric acid and cooled in an ice-bath. Sodium nitrate (1.40 g) was dissolved in a small amount of water. After the crushed ice was added to both solutions, 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 p-cresol in 50 ml of 4 M hydrochloric acid. The mixture was left in the ice-bath for 1 hour and then 40% w/v of sodium acetate solution was added into the mixture until pH 5.0 was reached. A brown precipitate began to settle immediately. The solution was filtered and the precipitated was washed with water and air-dried to give 2-(2'-thiazolylazo)-p-cresol (TAC). The crude product was purified by recrystallization with a mixture of ethanol-water (1:1) to give brown needles-shaped crystals with melting point of 131-132 °C. The resultant product was characterized by FTIR,  $^1\text{H}$  NMR, MS and elemental analysis.

### **3. Determination of the acid dissociation constant ( $pK_a$ ) of 2-(2'-thiazolylazo)-p-cresol (TAC)**

One millilitre of  $1 \times 10^{-3}$  M TAC solution was added into each of nine 25 ml volumetric flasks and then made up volume by universal buffer solutions at pH 3.0-11.0 (shown in Table 3). The absorbance of the solution was measured by UV-Vis spectrophotometer at 350-800 nm. The  $pK_a$  of the -OH group of TAC was determined by two different methods: the half height method and the limiting absorbance method (Masoud, 2003). The calculation is shown in Appendix C.

### **4. Structural determination of complex between 2-(2'-thiazolylazo)-p-cresol (TAC) and cobalt(II) and between TAC and lead(II)**

The mixture between  $1 \times 10^{-3}$  M TAC solution and  $1 \times 10^{-3}$  M cobalt(II) solution and the mixture between  $1 \times 10^{-3}$  M TAC solution and  $1 \times 10^{-3}$  M lead(II) solution (1:1) were prepared at pH 8.0. The precipitate was taken at room temperature and then filtered off and washed with double distilled deionized water. Finally, the precipitate of complexes were dried at room temperature under low pressure and studied by using FTIR spectrophotometer, nuclear magnetic resonance spectrometer.

### **5. Complex formation between 2-(2'-thiazolylazo)-p-cresol (TAC) and cobalt(II) and between TAC and lead(II)**

2-(2'-thiazolylazo)-p-cresol (TAC) is thiazolylazo dye, which gives color complex with most metals especially with transition metals. The reaction of TAC with cobalt(II) and lead(II) at various pH were investigated in order to determine the appropriate pH for studying on the formation of complex between cobalt(II) and TAC and between lead(II) and TAC. The effect of the buffer was also investigated. The following procedure for formation of complex was used in this work. Pipetted 5.0 ml of  $2.0 \times 10^{-4}$  M metal ions in buffer solution (pH range 3.0 to 10.0) into 25 ml volumetric flasks and then 5.0 ml of  $2.0 \times 10^{-4}$  M TAC solution in buffer solution (pH range 3.0 to 10.0) were pipetted into the previous volumetric flasks. After that,

complex solutions were diluted to the mark with buffer solutions. The formation of complex between cobalt(II) and TAC and between lead(II) and TAC were studied by spectrophotometric method. The results are shown in Figures 17 to 24.

## **6. Stoichiometric determination of complex between 2-(2'-thiazolylazo)-p-cresol (TAC) and cobalt(II) and between TAC and lead(II) by continuous variation method**

From the studying on the complex formation in the previous section(5), the appropriate pH for studying on the stoichiometric determination of cobalt(II) complex were pH 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 and for lead(II) complex were pH 6.5, 7.0, 8.0 and 9.0.

### **6.1 Stoichiometric determination of complex between 2-(2'-thiazolylazo)-p-cresol (TAC) and cobalt(II)**

Pipetted 0.00, 1.00, 2.00, 3.00, 4.00, 5.00, 6.00, 7.00, 8.00, 9.00 and 10.00 ml of  $2.0 \times 10^{-4}$  M cobalt(II) in acetate buffer solution at pH 5.0 into each of eleven 25 ml volumetric flasks. Then 10.00, 9.00, 8.00, 7.00, 6.00, 5.00, 4.00, 3.00, 2.00, 1.00 and 0.00 ml of  $2.0 \times 10^{-4}$  M 2-(2'-thiazolylazo)-p-cresol (TAC) in acetate buffer solution at pH 5.0 were pipetted into each volumetric flasks, respectively. After that, the solution were diluted to the mark with acetate buffer solution at pH 5.0. The stoichiometric determination of the complex at pH 6.0, 7.0, 8.0, 9.0 and 10.0 were also studied by using the same method as described above. The buffer solutions used in this study were stated in Table 2. The absorbance of the solutions were measured by UV-Vis spectrophotometer at 585 nm for acidic and neutral condition, and at 610 nm for basic condition. The results are shown in Figures 25 to 40.

## 6.2 Stoichiometric determination of complex between 2-(2'-thiazolylazo)-p-cresol (TAC) and lead(II)

Pipetted 0.00, 1.00, 2.00, 3.00, 4.00, 5.00, 6.00, 7.00, 8.00, 9.00 and 10.00 ml of  $2.0 \times 10^{-4}$  M lead(II) in acetate buffer solution at pH 6.5 into each of eleven 25 ml volumetric flasks. Then 10.00, 9.00, 8.00, 7.00, 6.00, 5.00, 4.00, 3.00, 2.00, 1.00 and 0.00 ml of  $2.0 \times 10^{-4}$  M 2-(2'-thiazolylazo)-p-cresol (TAC) in acetate buffer solution at pH 6.5 were pipetted into each volumetric flasks, respectively. After that, the solution were diluted to the mark with acetate buffer solution at pH 6.5. The stoichiometric determination of the complex at pH 7.0, 8.0 and 9.0 were also studied by using the same method as described above. The buffer solutions used in this study were stated in Table 2. The absorbance of the solutions were measured by UV-Vis spectrophotometer at 595 nm for acidic and neutral condition, and at 615 nm for basic condition. The results are shown in Figures 42 and 43.

## 7. Preparation of 2-(2'-thiazolylazo)-p-cresol resin (P-TAC)

The experimental conditions for studying on the influence of solvent and shaking time on the preparation of P-TAC were as followed;

Effect of solvent : Solvents used for the preparation of P-TAC were dimethylformamide, diethylamine, triethylamine and the mixture of dimethylformamide and triethylamine (1:1). The procedure for preparation of P-TAC was as followed; fifty milligrams of chloromethylated polystyrene divinylbenzene was activated in 5.0 ml of each solvent at 50 °C for 3 hours. Then solution of TAC (0.02 g of TAC was dissolved in 5.0 ml of each solvent) was added into each flask. The flasks were shaken at room temperature for 72 hours. The resulting P-TAC was filtered off and washed with 0.5 M hydrochloric acid, 0.5 M sodium hydroxide and double distilled deionized water, respectively. It was then extracted in a soxhlet extractor with ethanol for 48 hours and washed with double distilled deionized water until the filtrate was colorless. The P-TAC was dried at room temperature at low pressure condition. The dried P-TAC was used to study on the influence of solvent on the

preparation of P-TAC. The procedure for determination of capacity for cobalt(II) of P-TAC was as followed; Fifty milligrams of P-TAC, which was prepared in each solvent, was equilibrated with 10.00 ml of 100 ppm of cobalt(II) solution at pH 7.0. Then the mixtures were shaken for 3 hours and filtered. The filtrates were determined for cobalt(II) and lead(II) by atomic absorption spectrophotometer. The results are shown in Table 10.

Effect of shaking time : the shaking time was varied from 12 to 96 hours (12, 24, 48, 72 and 96 hours) by using the previous procedure. In addition, the mixture solvent of dimethylformamide and triethylamine (1:1) was used in the preparation of P-TAC. The results are shown in Figure 45.

As the effect of solvent and shaking time had been optimized, therefore the procedure for the preparation of P-TAC was recommended. Firstly, by 0.50 g of chloromethylated polystyrene divinylbenzene was activated in 5.0 ml of the mixture solvent of dimethylformamide and triethylamine (1:1) at 50 °C for 3 hours. Then 0.02 g of TAC, which was dissolved in 5.0 ml of the mixture solvent, was added into the flask. The flask was shaken at room temperature for 72 hours and the P-TAC was filtered off and washed with 0.5 M hydrochloric acid, 0.5 M sodium hydroxide and double distilled deionized water, respectively. It was then extracted in a soxhlet extractor with ethanol for 48 hours and washed with double distilled deionized water until the filtrate was colorless. The P-TAC was dried at room temperature at low pressure condition.

## **8. Determination of the sorption capacity of cobalt(II) and lead(II) by P-TAC**

The sorption of cobalt(II) and lead(II) were studied under static and dynamic conditions. To determine the capacity of P-TAC, 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, whereas the effect of flow rate was studied under dynamic condition by using column equilibrium experiment.

## 8.1 Optimization of parameters for the maximum adsorption of cobalt(II) on P-TAC

### 8.1.1 Batch equilibrium experiment

The experiment conditions for studying on the influence of various parameters on the sorption of cobalt(II) on P-TAC were as followed;

Effect of pH : Capacity of P-TAC was determined in the pH range from 3.0 to 7.0. The pH of the solution in each experiment was adjusted by buffer solutions. Fifty milligrams of P-TAC was equilibrated with 10.0 ml of 150 ppm cobalt(II) solution, which were prepared in buffer solution at pH 3.0, 4.0, 5.0, 6.0 and 7.0. Then the mixtures were shaken for 4 hours. After the mixture were filtered, the filtrates were determined for cobalt(II) by atomic absorption spectrophotometer. The results are shown in Figure 46.

Effect of concentration of cobalt(II) : 10, 25, 50, 100, 150 and 200 ppm cobalt(II) solution were prepared in acetate buffer at pH 7.0. Fifty milligrams of P-TAC was equilibrated with 10.0 ml of cobalt(II) solution at various concentration. Then the mixtures were shaken for 4 hours. After the mixture were filtered, the filtrates were determined for cobalt(II) by atomic absorption spectrophotometer. The results are shown in Figure 47.

Effect of shaking time : Fifty milligrams of P-TAC was equilibrated with 10.0 ml of 150 ppm cobalt(II) solution in acetate buffer at pH 7.0. Then the mixtures were shaken for 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.0 hours, respectively. After the mixtures were filtered, the filtrates were determined for cobalt(II) by atomic absorption spectrophotometer. The results are shown in Figure 48.

As the results of optimization study shown above, the following procedure could be recommended. Fifty milligrams of P-TAC was equilibrated with

10.0 ml of 150 ppm cobalt(II) solution in acetate buffer at pH 7.0. Then the mixtures were shaken for 4 hours. After the mixtures were filtered, the filtrates were determined for cobalt(II) by atomic absorption spectrophotometer.

### 8.1.2 Column equilibrium experiment

The studying method of the column equilibrium experiment in the effect of flow rate for sorption of cobalt(II) on P-TAC was as followed;

Effect of the flow rate : The effect of flow rate on the sorption of cobalt(II) on P-TAC was studied at the flow rate of 0.50, 0.33 and 0.25 ml min<sup>-1</sup>. The procedure to determine the capacity of P-TAC was as followed; A glass column with 1.0 cm diameter was filled with 0.30 g of P-TAC to gave a bed height of about 1.0 cm. Then acetate buffer solution at pH 7.0 was passed through this column. Then 200 ml of 10 ppm cobalt(II) in acetate buffer solution at the pH 7.0 was passed through the column at flow rate of 0.5 ml min<sup>-1</sup> until the concentration of cobalt(II) in the effluent was the same as the feed solution. Fractions (1.0 ml) of the effluent were determined for cobalt(II) by the atomic absorption spectrophotometer. The capacity of P-TAC was determined from breakthrough curve. The capacity of P-TAC at flow rate of 0.33 and 0.25 ml min<sup>-1</sup> were determined by using the same method as described above. The results are shown in Figures 49 and 51.

## 8.2 Optimization of parameters for the maximum adsorption of lead(II) on P-TAC

### 8.2.1 Batch equilibrium experiment

The experiment conditions for studying on the influence of various parameters on the sorption of lead(II) on P-TAC were as followed;

Effect of pH : Capacity of P-TAC was determined in the pH range from 3.0 to 6.0. The pH of the solution in each experiment was adjusted by buffer



solutions. Fifty milligrams of P-TAC was equilibrated with 10.0 ml of 100 ppm lead(II) solution, which were prepared in buffer solution at pH 3.0, 4.0, 5.0, 5.5 and 6.0. Then the mixtures were shaken for 24 hours. After the mixtures were filtered, the filtrates were determined for lead(II) by atomic absorption spectrophotometer. The results are shown in Figure 52.

Effect of concentration of lead(II) : 10, 25, 50, 75, 100 and 150 ppm lead(II) solution were prepared in acetate buffer at pH 5.5. Fifty milligrams of P-TAC was equilibrated with 10.0 ml of lead(II) solution at various concentrations. Then the mixtures were shaken for 24 hours. After the mixtures were filtered, the filtrates were determined for lead(II) by atomic absorption spectrophotometer. The results are shown in Figure 53.

Effect of shaking time : Fifty milligrams of P-TAC was equilibrated with 10.0 ml of 150 ppm lead(II) solution in acetate buffer at pH 5.5. Then the mixtures were shaken for 1, 2, 4, 8, 12, 16, 20, 24, 28 and 32 hours, respectively. After the mixtures were filtered, the filtrates were determined for lead(II) by atomic absorption spectrophotometer. The results are shown in Figure 54.

As the results of optimization study shown above the following procedure could be recommended. Fifty milligrams of P-TAC was equilibrated with 10.0 ml of 100 ppm lead(II) solution in acetate buffer at pH 5.5. Then the mixtures were shaken for 24 hours. After the mixtures were filtered, the filtrates were determined for lead(II) by atomic absorption spectrophotometer.

### 8.2.2 Column equilibrium experiment

The studying method of the column equilibrium experiment in the effect of flow rate for sorption of lead(II) on P-TAC was as follow;

Effect of the flow rate : The effect of flow rate on the sorption of lead(II) on P-TAC was studied at the flow rate of 0.50, 0.33 and 0.25 ml min<sup>-1</sup>. The

procedure to determine the capacity of P-TAC was as followed; A glass column of 1.0 cm inner diameter was filled with 0.30 g of P-TAC to gave a bed height of about 1.0 cm. Then acetate buffer solution at pH 5.5 was passed through this column. Then 200 ml of 20 ppm lead(II) in acetate buffer solution at the pH 5.5 was passed through the column at flow rate of  $0.5 \text{ ml min}^{-1}$  until the concentration of lead(II) in the effluent were the same as the feed solution. Fractions (1.0 ml) of the effluents were determined for lead(II) by atomic absorption spectrophotometer. The capacity of P-TAC was determined from breakthrough curve. The capacity of P-TAC at flow rate of 0.33 and  $0.25 \text{ ml min}^{-1}$  were determined by using the same method as described above. The results are shown in Figures 55 to 57.

### **9. Desorption of cobalt(II) and lead(II) on P-TAC**

Fifty milligram of P-TAC loaded with 10.0 ml of 150 ppm of cobalt(II) solution was shaken for 4 hours and fifty milligram of P-TAC loaded with 10.0 ml of 100 ppm of lead(II) solution was shaken for 10 minutes. 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 10 eluents, namely, ammonia solution, perchloric acid, hydrochloric acid, nitric acid, potassium thiocyanate, acethylacetone, citric acid, EDTA, 1,10-phenanthroline and thiourea. After the shaking period for 3 hours, the mixtures were filtered and the filtrates were analyzed for cobalt(II) and lead(II) by atomic absorption spectrophotometer. The results are shown in Table 11.

### **10. Using P-TAC for the separation of cobalt(II) and lead(II) mixture solution**

The mixture solution of cobalt(II) and lead(II) was prepared by mixing 10.0 ml of 20.0 ppm cobalt(II) solution and 10.0 ml of 40.0 ppm of lead(II) solution and adjusted to pH 5.5 by 0.1 M sodium hydroxide. After that, the mixture was passed through the column which contained 300 mg of P-TAC, with the flow rate of  $0.33 \text{ ml min}^{-1}$ .

In the first column, the loaded resin was desorbed by 12 ml of 0.5 M thiourea and followed by 10 ml of 3 M HClO<sub>4</sub> with the flow rate of 0.33 ml min<sup>-1</sup>. Fractions (2.0 ml) of the effluent were determined for cobalt(II) and lead(II) by atomic absorption spectrophotometer. The results are shown in Figures 60 and 61.

In the second column, the effect of the concentration of thiourea on the separation of cobalt(II) and lead(II) mixture solution was studied by using 20 ml of 0.1 M thiourea with the flow rate 0.33 ml min<sup>-1</sup> instead of 0.5 M thiourea. Fractions (2.0 ml) of the effluent were determined for cobalt(II) and lead(II) by atomic absorption spectrophotometer. The results are shown in Figure 62.

## **11. Efficiency of P-TAC on the sorption of cobalt(II) and lead(II) by column experiment**

### 11.1 Efficiency of P-TAC on the sorption of cobalt(II)

Three hundreds milligrams of P-TAC was filled in a glass column with 1.0 cm diameter and then buffer solution at pH 7.0 was passed through this column to activated the P-TAC. Ten ppm of cobalt(II) solution at pH 7.0 was passed through the column at the flow rate of 0.25 ml min<sup>-1</sup> until the concentration of cobalt(II) in the effluent was the same as in the feed solution. The retained cobalt(II) was eluted with 3 M perchloric acid by batch method with the shaking time of 3 hours. After the filtration of these mixtures, the filtrates were determined for cobalt(II) by atomic absorption spectrophotometer. The efficiency of the used-P-TAC for the sorption of cobalt(II) was studied by repeating the previous procedure for 4 times. The results are shown in Figure 63.

### 11.2 Efficiency of P-TAC on the sorption of lead(II)

Three hundreds milligrams of P-TAC was filled in a glass column with 1.0 cm diameter and then buffer solution at pH 5.5 was passed through this column to activated the P-TAC. Twenty ppm of lead(II) solution at pH 5.5 was passed through

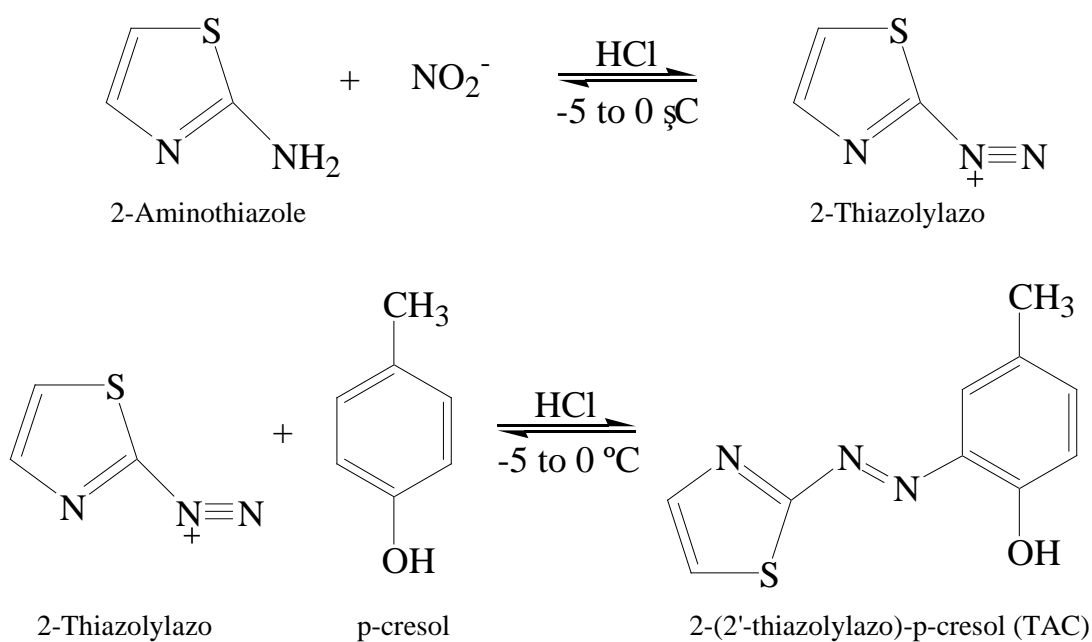
the column at the flow rate of  $0.33 \text{ ml min}^{-1}$  until the concentration of lead(II) in the effluent was the same as in the feed solution. The retained lead(II) was eluted with 0.3 M thiourea solution by batch method with the shaking time of 3 hours. After the filtration of these mixtures, the filtrates were determined for lead(II) by atomic absorption spectrophotometer. The efficiency of the used-P-TAC for the sorption of lead(II) was studied by repeating the previous procedure for 4 times. The results are shown in Figure 64.

## RESULTS AND DISCUSSIONS

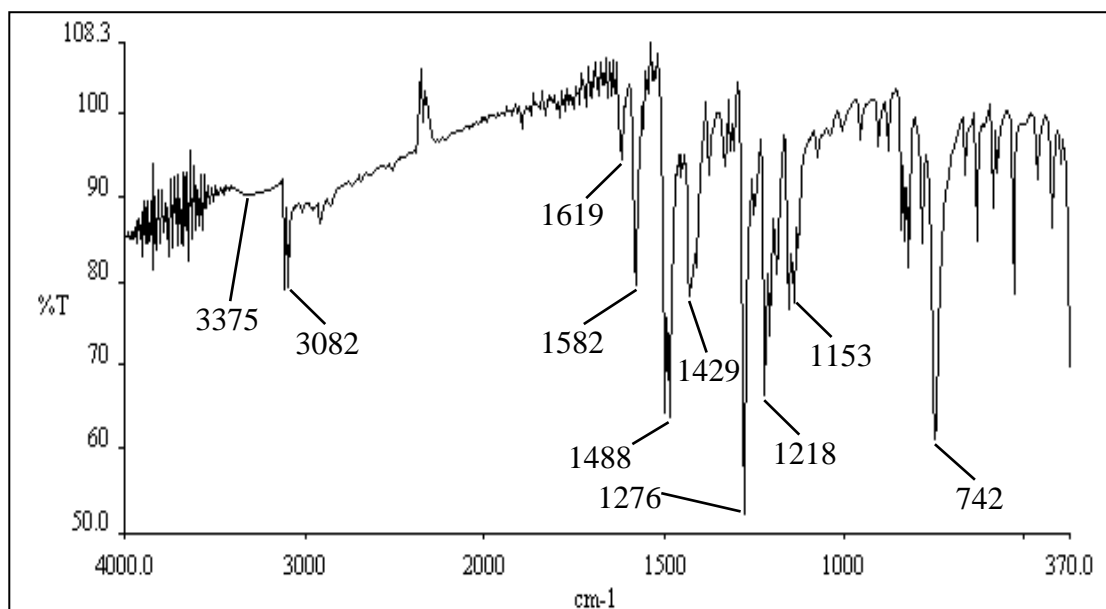
### 1. Synthesis of 2-(2'-thiazolylazo)-p-cresol (TAC)

Figure 2 shows the pathway of synthesis of 2-(2'-thiazolylazo)-p-cresol (TAC) which was synthesized by diazotisation of 2-aminothiazole in hydrochloric acid at  $-5$  to  $0$  °C, then coupling with p-cresol in hydrochloric acid at the same temperature. Finally, the crude product of TAC was precipitated with 40% v/v sodium acetate solution. The crude product was purified by recrystallization from ethanol-water (1:1) solution, which gave TAC as brown needle crystal with the melting point of  $131$ - $132$  °C and 74.52% yield.

The brown needle shaped crystalline of TAC was characterized by FTIR spectrophotometry,  $^1\text{H}$  NMR, mass spectrometry and elemental analysis, the results are shown in Figures 3, 4, 5, 6, 7 and Table 4. The solution of TAC in acidic and neutral solution gave yellow color with the maximum absorption at 372 nm while the alkaline solution gave red violet color with the maximum absorption at 532 nm.

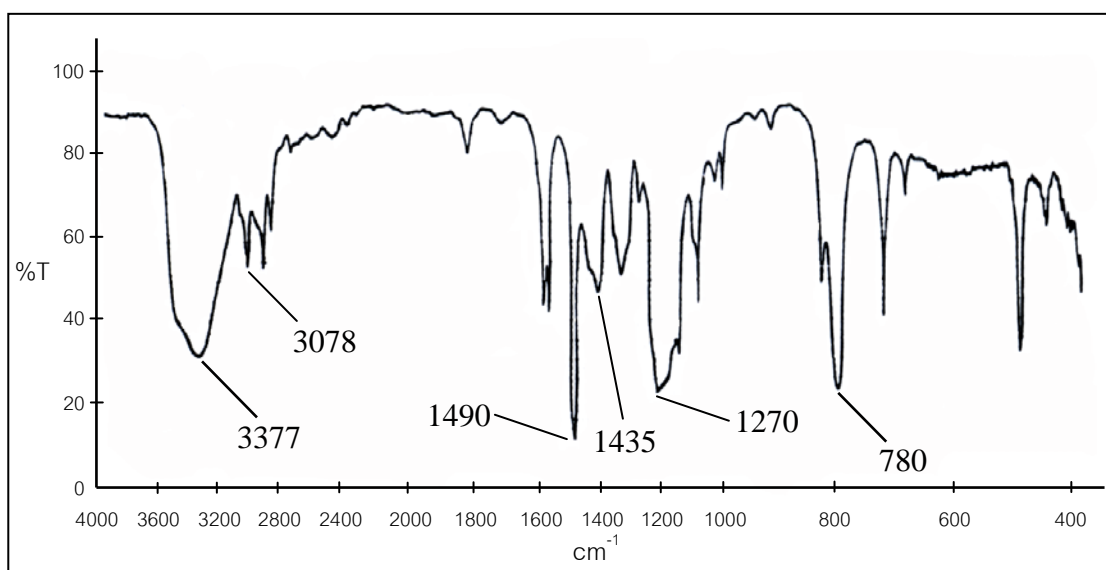


**Figure 2** Pathway of synthesis of 2-(2'-thiazolylazo)-p-cresol (TAC).



**Figure 3** IR spectrum of 2-(2'-thiazolylazo)-p-cresol (TAC).

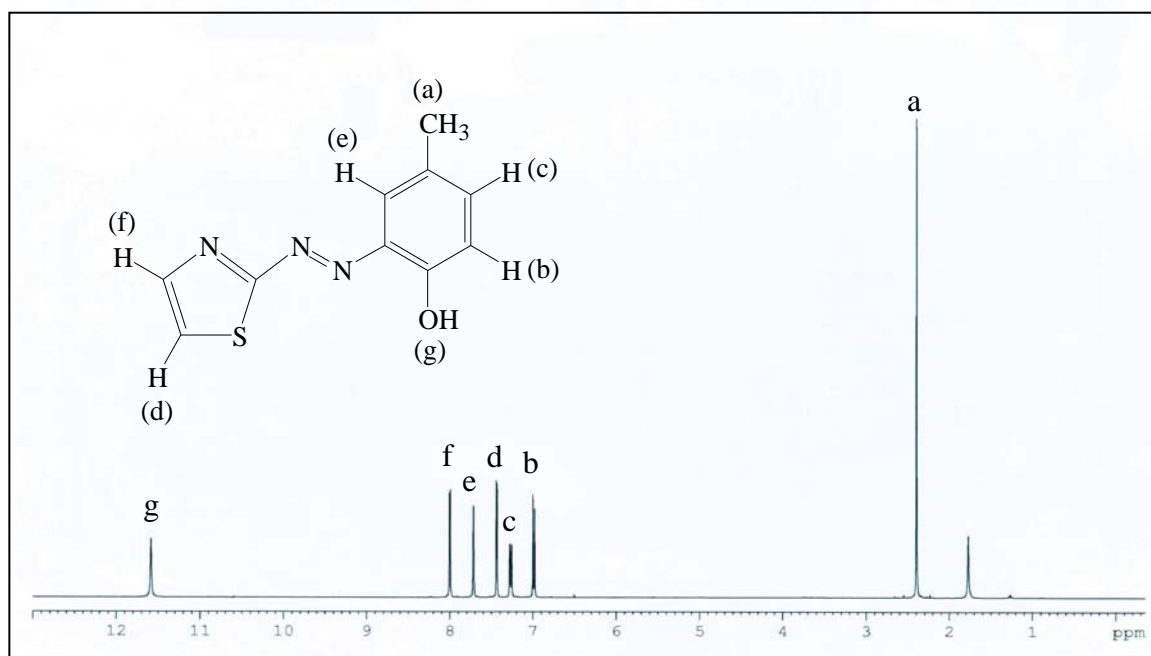
The infrared spectrum (KBr : cm<sup>-1</sup>) was as followed : 3375 (w, O-H stretch), 3082 (m, C-H stretch aromatic), 1619 (w, N=N stretch), 1582 (m, C=N stretch), 1488 and 1429 (s, C=C stretch), 1276 (vs, C-O stretch), 1218 (m, C-N stretch), 1153 (m, C-S stretch) and 742 (m, C-H bend aromatic, para substituent).



**Figure 4** IR spectrum of p-cresol.

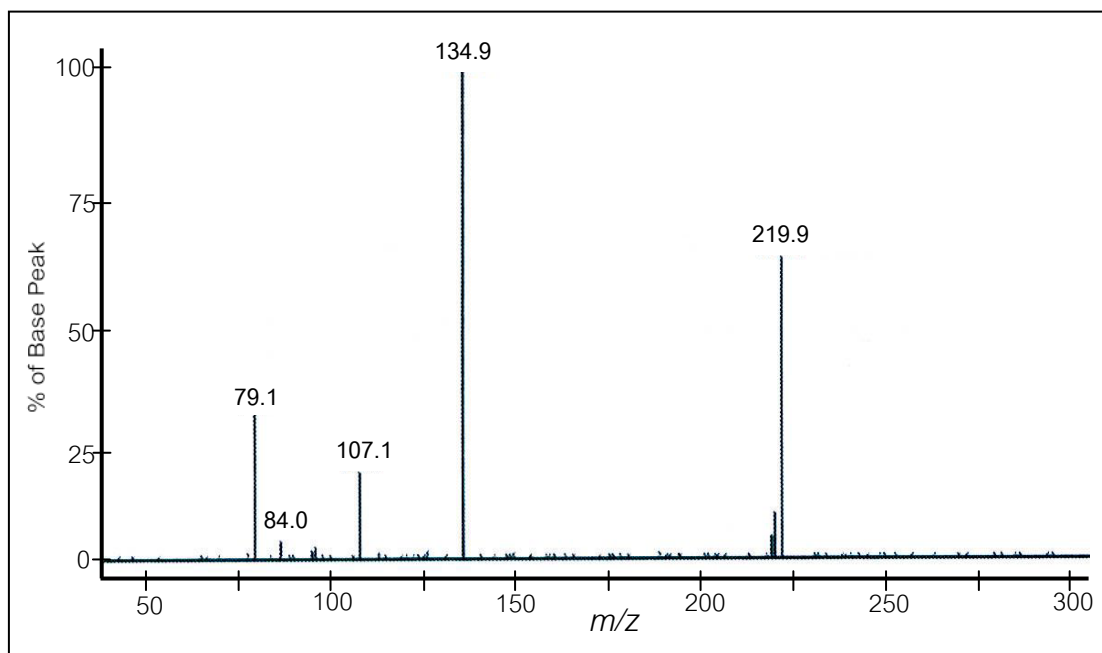
Source: Pavia (1996)

From IR spectra of TAC and p-cresol, the peaks of O-H stretch at  $3375\text{ cm}^{-1}$ , C-H stretch aromatic at  $3082\text{ cm}^{-1}$ , C=C stretch at  $1488$  and  $1429\text{ cm}^{-1}$ , C-O stretch at  $1276\text{ cm}^{-1}$  and C-H bend aromatic (para substituent) at  $742\text{ cm}^{-1}$  of TAC were determined at the closely wavenumber with p-cresol. Because of the peak of O-H stretch of TAC was very weak, so the  $^1\text{H}$  NMR spectrum of TAC was used to confirm the O-H group in TAC. The result is shown in Figure 5.



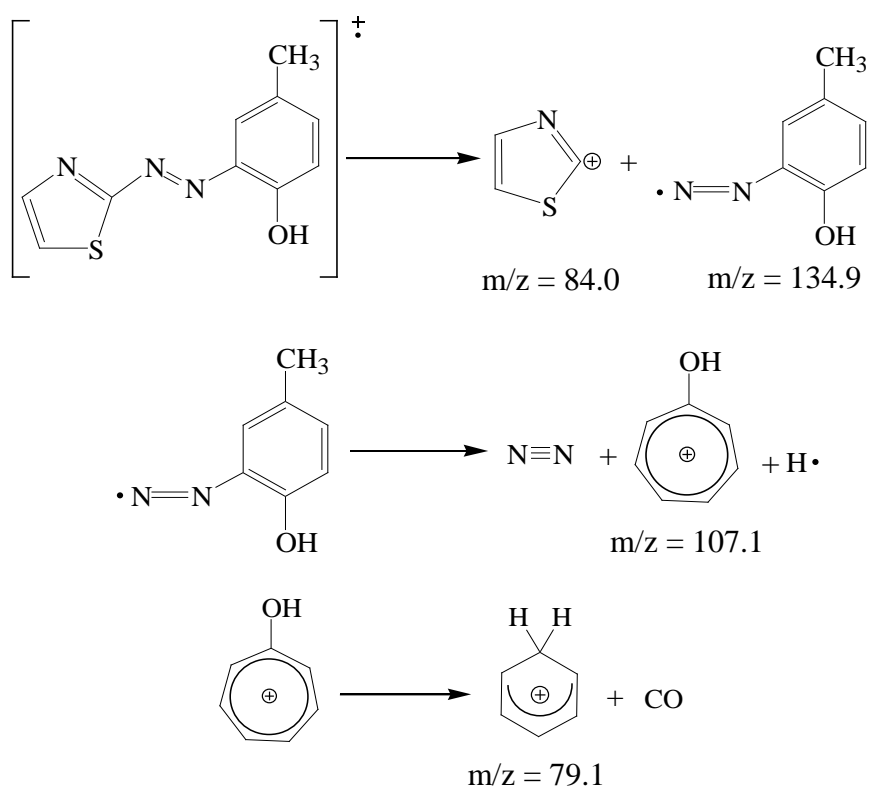
**Figure 5**  $^1\text{H}$  NMR spectrum of 2-(2'-thiazolylazo)-p-cresol (TAC).

The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) was as follow:  $\delta$  2.394 (3H, s,  $\text{H}_a$ ), 6.990 (1H, d,  $\text{H}_b$ ), 7.270 (1H, d,  $\text{H}_c$ ), 7.439 (1H, d,  $\text{H}_d$ ), 7.719 (1H, s,  $\text{H}_e$ ), 8.003 (1H, d,  $\text{H}_f$ ) and 11.585 (1H, s,  $\text{H}_g$ ).



**Figure 6** Mass spectrum of 2-(2'-thiazolylazo)-p-cresol (TAC).

$m/z$  (relative intensity) : 219.9 (61.67), 134.9 (100.00), 107.1 (17.78) , 84.0 (3.05) and 79.1 (29.44).



**Figure 7** Pathway of the fragmentation of 2-(2'-thiazolylazo)-p-cresol (TAC).



From Figures 6 and 7, TAC could fragment to cation ( $m/z = 84.0$ ) and free radical ( $m/z = 134.9$ ). The high relative intensity at  $m/z = 134.9$  indicated the stability of the free radical. For the  $m/z = 84.0$ , the low relative intensity indicated the instability of the cation.

**Table 4** The elemental analysis of 2-(2'-thiazolylazo)-p-cresol (TAC)

% Element	Theoretical value*	Experimental value	% Error
%C	54.78%	53.84%	1.716%
%H	4.137%	4.149%	0.290%
%N	19.16%	19.21%	0.261%
%S	14.62%	15.30%	4.651%
%O	7.297%	7.501%	2.796%

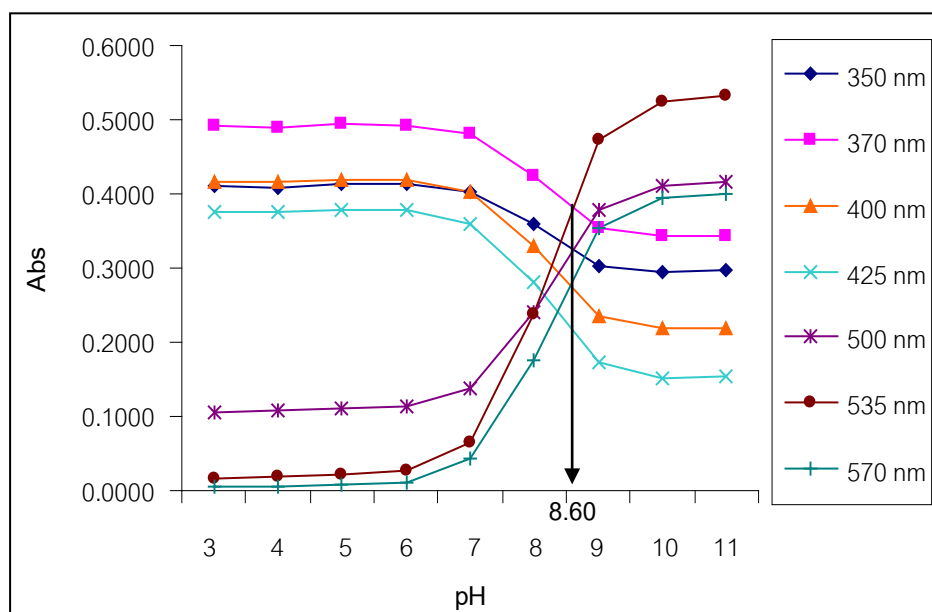
\* The calculation for the theoretical value is shown in Appendix A.

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

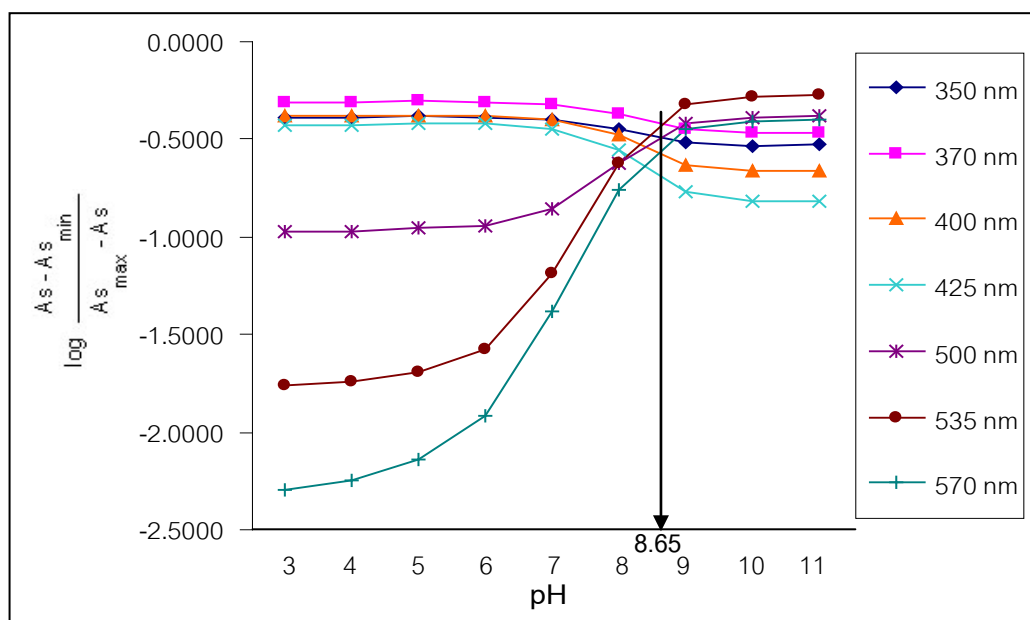
## 2. Determination of the acid dissociation constant ( $\text{pK}_a$ ) of 2-(2'-thiazolylazo)-p-cresol (TAC)

From the chemical structure of TAC, oxygen atom has an important role for the complexation between TAC and metal ions. The proton of the hydroxyl group could be deprotonated. So it is necessary to determine the  $\text{pK}_a$  of TAC. The chemical structures of TAC in acid and basic form are shown in Figure 8.





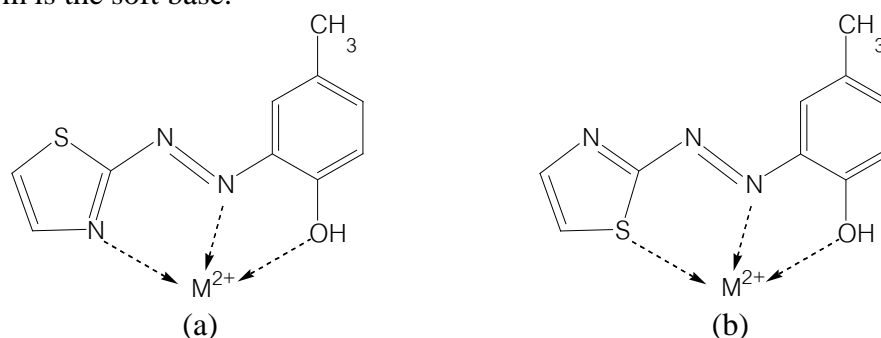
**Figure 10** Absorbance-pH curve of TAC (Half height method).



**Figure 11**  $\log \frac{A_s - A_{s_{\min}}}{A_{s_{\max}} - A_s}$  -pH curve of TAC (Limiting Absorbance method).

### 3. Structural determination of complex between 2-(2'-thiazolylazo)-p-cresol (TAC) and cobalt(II) and between TAC and lead(II)

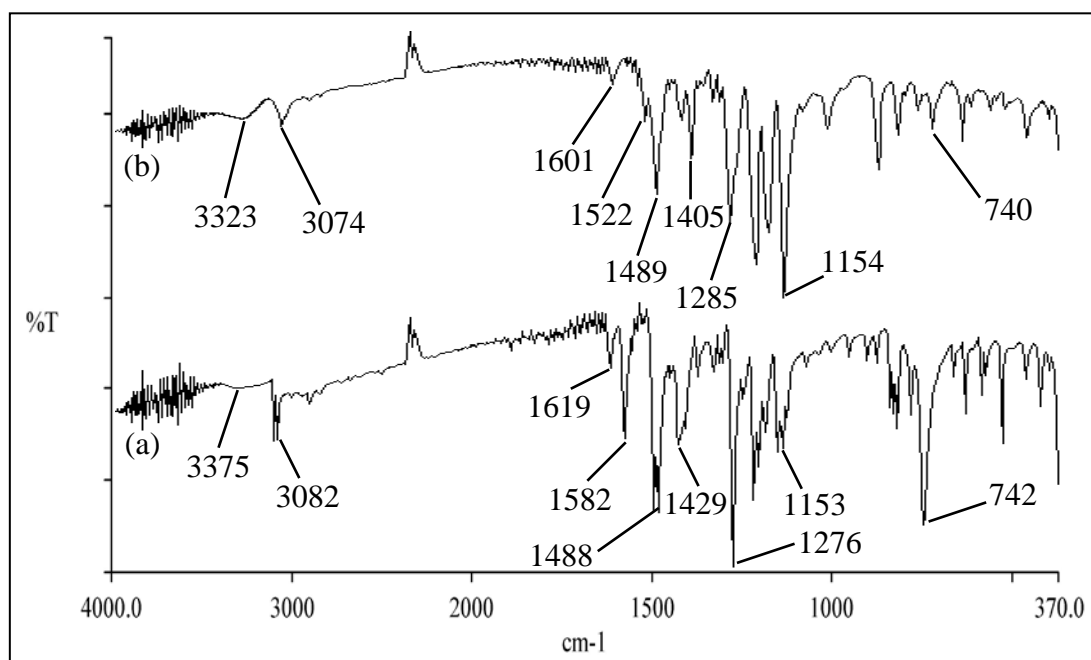
TAC is a polydentate ligand which can form complex with metal ions by using nitrogen, sulfur and oxygen as donor atom. Cobalt(II) and lead(II) are transition metals which are the characteristic of the borderline acid (Shriver, 1999). TAC might act as chelating ligand with two probable formulas of complex formed as shown in Figure 12. However, the structure in Figure 12 (a) is likely to be the correct structure due to the softness parameter because of nitrogen atom is the borderline base while sulfur atom is the soft base.



**Figure 12** Postulated structures of complex between metal ions and TAC.

- a) Oxygen atom and two atoms of nitrogen are donor atoms
- b) Oxygen, nitrogen and sulfur atoms are donor atoms

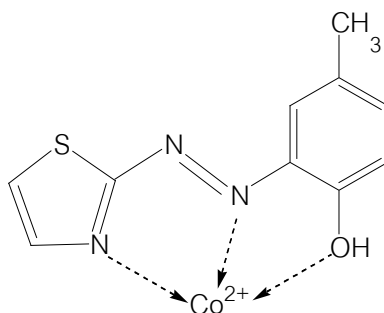
IR spectrum could indicated the donor atoms for bonding with metal ions by the decreasing of wavenumber due to the decreasing of the bond order of the donor atom. The results from the infrared spectra of TAC and cobalt(II)-TAC complex are shown in Figure 13 and Table 5. For the complex, the peak assigned for N=N bond was shifted from  $1619\text{ cm}^{-1}$  to  $1601\text{ cm}^{-1}$ , the peak assigned for C=N bond was shifted from  $1582\text{ cm}^{-1}$  to  $1522\text{ cm}^{-1}$  and the peak assigned for O-H bond was shifted from  $3375\text{ cm}^{-1}$  to  $3323\text{ cm}^{-1}$ . Therefore, the cobalt(II) could form complex with might acted as a tridentate ligand. The intensity of the peak at  $742\text{ cm}^{-1}$ , assigned for C-H bend aromatic (para substituent), was decreased may be because the oxygen atom of TAC formed coordinate covalent bond with cobalt(II) so that the aromaticity of p-cresol was decreased. The postulated structure of the complex is shown in Figure 14.



**Figure 13** IR spectra of (a) 2-(2'-thiazolylazo)-p-cresol (TAC) and (b) cobalt(II)-TAC complex.

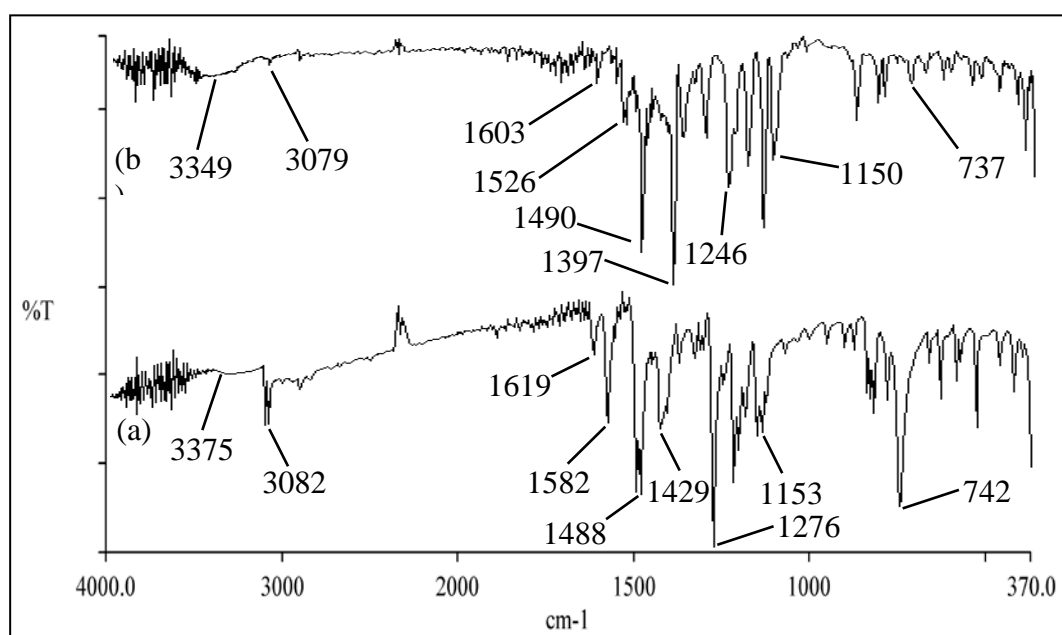
**Table 5** Data from the IR spectra of TAC and cobalt(II)-TAC complex

2-(2'-thiazolylazo)-p-cresol (TAC)		Cobalt(II)-TAC complex	
Wavenumber ( $\text{cm}^{-1}$ )	Functional group	Wavenumber ( $\text{cm}^{-1}$ )	Functional group
3375	O-H stretch	3323	O-H stretch
3082	C-H stretch (aromatic)	3074	C-H stretch (aromatic)
1619	N=N stretch	1601	N=N stretch
1582	C=N stretch	1522	C=N stretch
1488 and 1429	C=C stretch	1489 and 1405	C=C stretch
1276	C-O stretch	1285	C-O stretch
1153	C-S stretch	1154	C-S stretch



**Figure 14** Postulated structure of cobalt(II)-TAC complex.

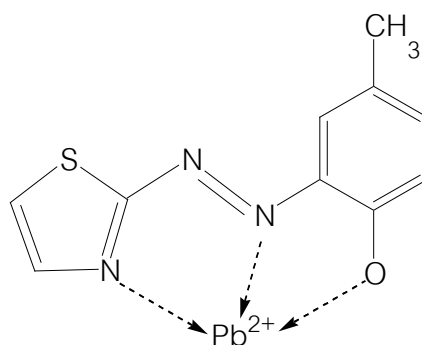
From the results of infrared spectra of TAC and the lead(II)-TAC complex (Figure 15 and Table 6), the peak assigned for O-H bond at  $3375\text{ cm}^{-1}$  was shifted to  $3349\text{ cm}^{-1}$ , the peak assigned for N=N bond at  $1619\text{ cm}^{-1}$  was shifted to  $1603\text{ cm}^{-1}$  and the peak assigned for C=N bond at  $1582\text{ cm}^{-1}$  was shifted to  $1526\text{ cm}^{-1}$ . The using of nitrogen and oxygen atom for the bonding with lead(II) could caused the O-H, N=N and C=N bond in the complex weaker than in TAC. The intensity of the peak at  $742\text{ cm}^{-1}$ , assigned for C-H bend aromatic (para substituent), was decreased may be because the oxygen atom of TAC formed coordinate covalent bond with lead(II) so that the aromaticity of p-cresol was decreased. The postulated structure of the lead(II)-TAC complex is shown in Figure 16.



**Figure 15** IR spectra of (a) 2-(2'-thiazolylazo)-p-cresol (TAC) and (b) lead(II)-TAC complex.

**Table 6** Data from the IR spectra of TAC and lead(II)-TAC complex

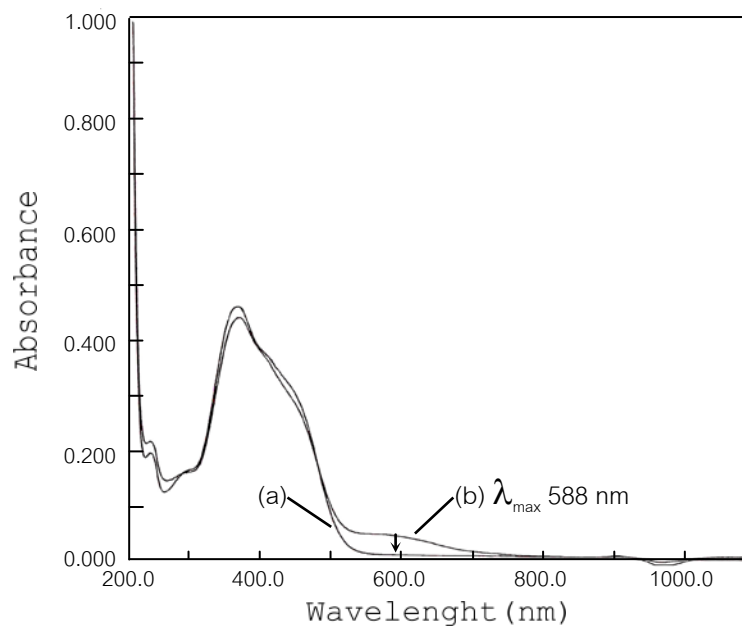
2-(2'-thiazolylazo)-p-cresol (TAC)		Lead(II)-TAC complex	
Wavenumber (cm <sup>-1</sup> )	Functional group	Wavenumber (cm <sup>-1</sup> )	Functional group
3375	O-H stretch	3349	O-H stretch
3082	C-H stretch (aromatic)	3079	C-H stretch (aromatic)
1619	N=N stretch	1603	N=N stretch
1582	C=N stretch	1526	C=N stretch
1488 and 1429	C=C stretch	1490 and 1397	C=C stretch
1276	C-O stretch	1246	C-O stretch
1153	C-S stretch	1150	C-S stretch

**Figure 16** Postulated structure of lead(II)-TAC complex.

#### **4. Complex formation between 2-(2'-thiazolylazo)-p-cresol (TAC) and cobalt(II) and between TAC and lead(II)**

The absorption of TAC was studied in aqueous buffer solution in the visible region. The azo compound displays mainly a broad band in the visible region which was assigned as  $n \rightarrow \pi^*$  transition within the azo linkage influenced by intramolecular charge transfer. The formation of complex between TAC and cobalt(II) at various pH showed that TAC could form complexes with cobalt(II) at pH 5, 6, 7, 8, 9 and 10. The cobalt(II) complex gave a yellow brown color at pH 5 and 6, violet color at pH 7 and

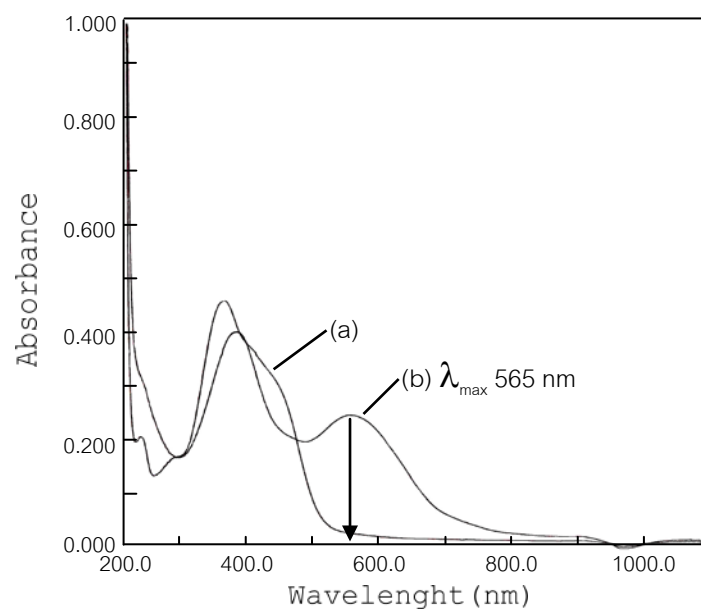
8 and green color at pH 9 and 10. The results are shown in Figures 17 to 22 and Table 7.



**Figure 17** Absorption spectra of TAC and cobalt(II)-TAC complex at pH 5.

(a) TAC  $4 \times 10^{-5}$  M

(b) Complex of cobalt(II)-TAC (cobalt(II)  $4 \times 10^{-5}$  M and TAC  $4 \times 10^{-5}$  M)

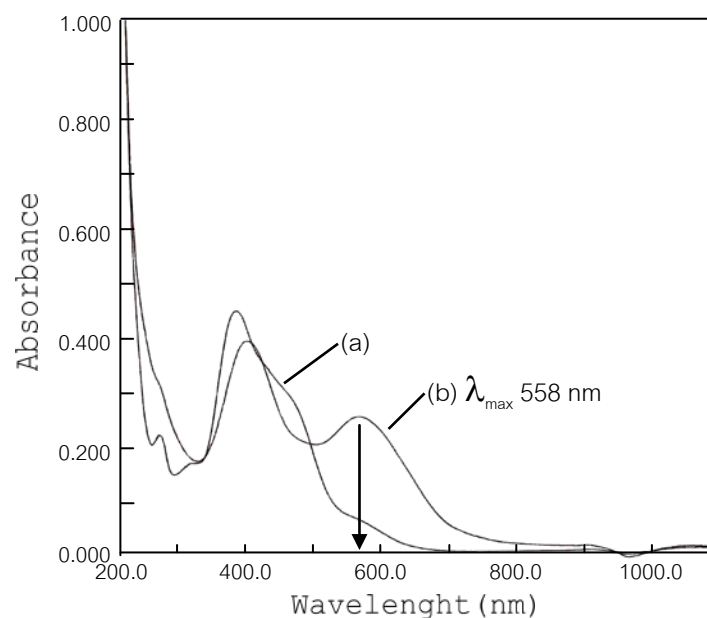


**Figure 18** Absorption spectra of TAC and cobalt(II)-TAC complex at pH 6.

(a) TAC  $4 \times 10^{-5}$  M

(b) Complex of cobalt(II)-TAC (cobalt(II)  $4 \times 10^{-5}$  M and TAC  $4 \times 10^{-5}$  M)

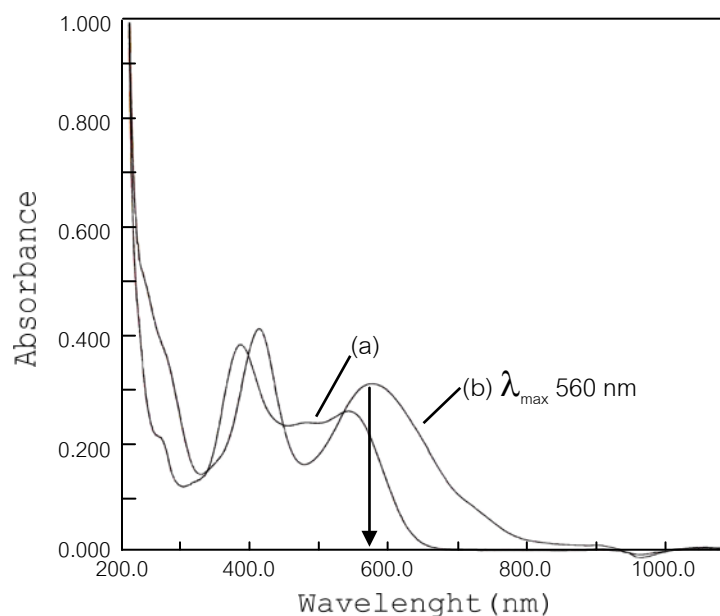




**Figure 19** Absorption spectra of TAC and cobalt(II)-TAC complex at pH 7.

(a) TAC  $4 \times 10^{-5}$  M

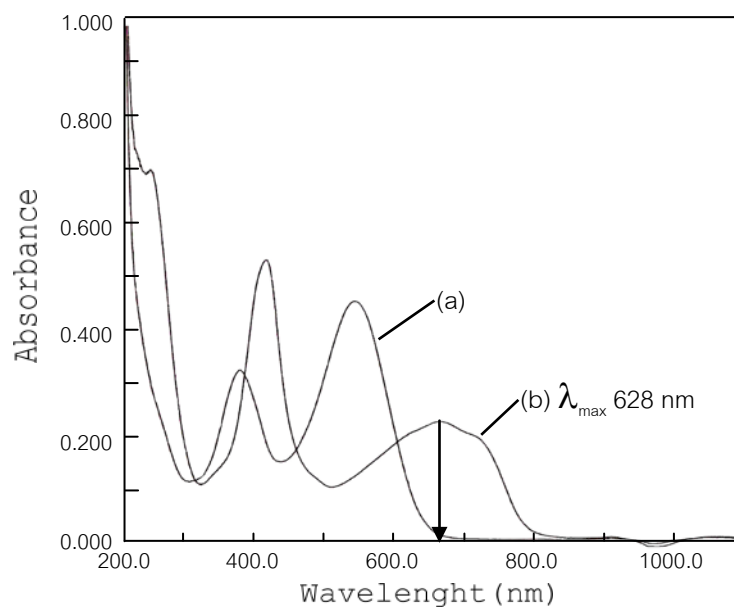
(b) Complex of cobalt(II)-TAC (cobalt(II)  $4 \times 10^{-5}$  M and TAC  $4 \times 10^{-5}$  M)



**Figure 20** Absorption spectra of TAC and cobalt(II)-TAC complex at pH 8.

(a) TAC  $4 \times 10^{-5}$  M

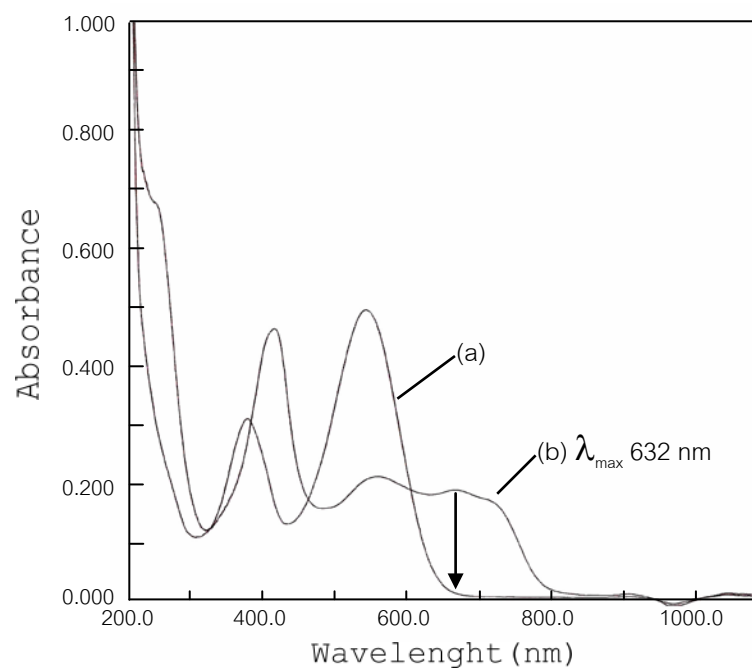
(b) Complex of cobalt(II)-TAC (cobalt(II)  $4 \times 10^{-5}$  M and TAC  $4 \times 10^{-5}$  M)



**Figure 21** Absorption spectra of TAC and cobalt(II)-TAC complex at pH 9.

(a) TAC  $4 \times 10^{-5}$  M

(b) Complex of cobalt(II)-TAC (cobalt(II)  $4 \times 10^{-5}$  M and TAC  $4 \times 10^{-5}$  M)



**Figure 22** Absorption spectra of TAC and cobalt(II)-TAC complex at pH 10.

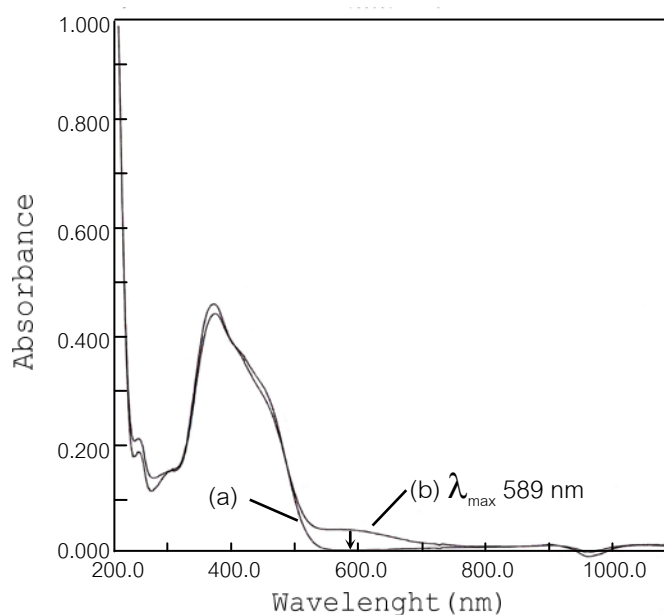
(a) TAC  $4 \times 10^{-5}$  M

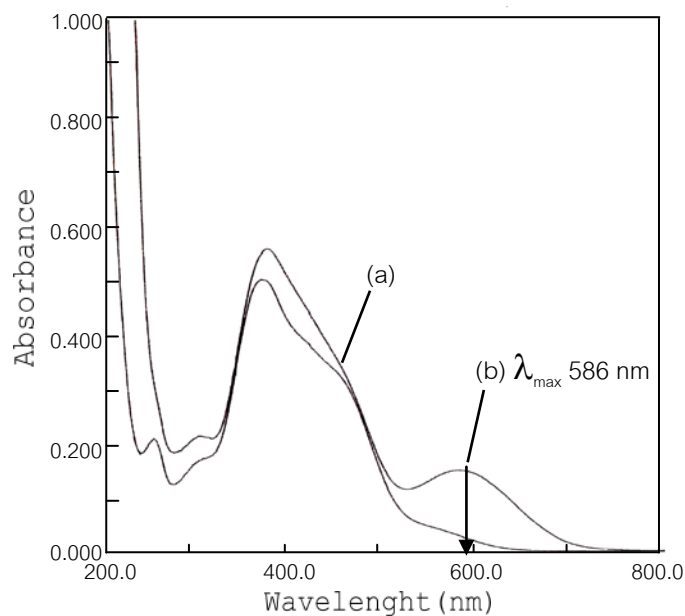
(b) Complex of cobalt(II)-TAC (cobalt(II)  $4 \times 10^{-5}$  M and TAC  $4 \times 10^{-5}$  M)

**Table 7** Complex formation between cobalt(II) and TAC at pH 5-10

pH	Color of TAC solution	Color of Co(II)-TAC complex solution	$\lambda_{\max}$
5	light yellow	yellow brown	588
6	light yellow	yellow brown	565
7	yellow	violet	558
8	red	violet	560
9	red	green	628
10	red	green	632

The absorption spectra of TAC and lead(II) complex at pH 6 and 7 are shown in Figures 23, 24 and Table 8. From the results, lead(II) formed yellow brown complexes with TAC at pH 6 and 7. At pH 9 and 10, TAC formed violet complexes with lead(II) but these complexes precipitated immediately.

**Figure 23** Absorption spectra of TAC and lead(II)-TAC complex at pH 6.(a) TAC  $4 \times 10^{-5}$  M(b) Complex of lead(II)-TAC (lead(II)  $4 \times 10^{-5}$  M and TAC  $4 \times 10^{-5}$  M)



**Figure 24** Absorption spectra of TAC and lead(II)-TAC complex at pH 7.

(a) TAC  $4 \times 10^{-5}$  M

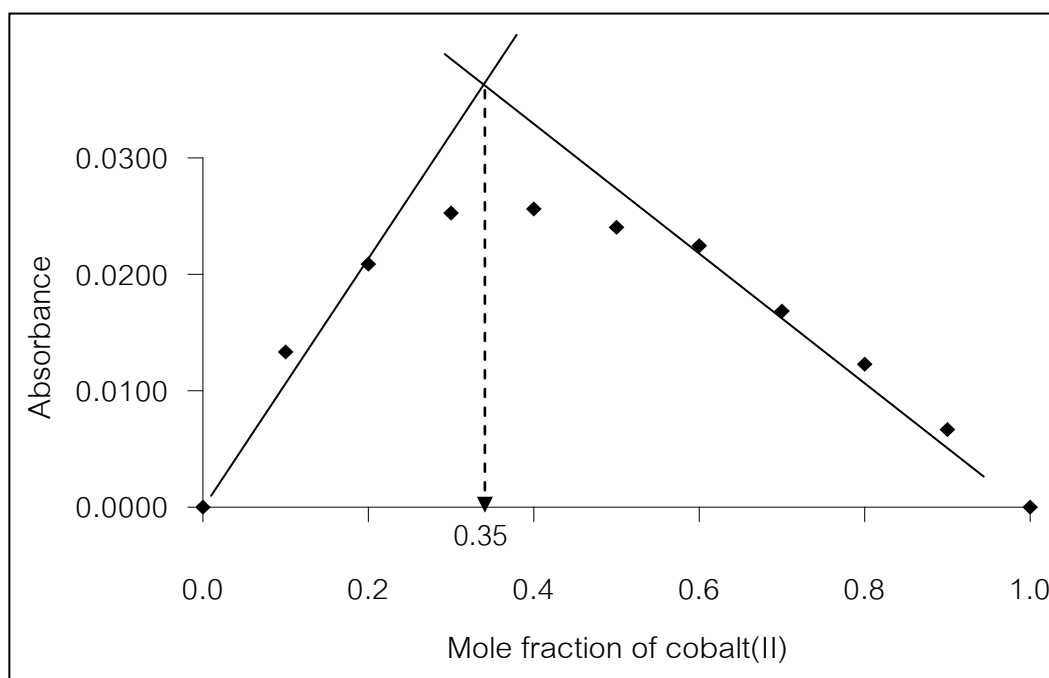
(b) Complex of lead(II)-TAC (lead(II)  $4 \times 10^{-5}$  M and TAC  $4 \times 10^{-5}$  M)

**Table 8** Complex formation between lead(II) and TAC at pH 6-10

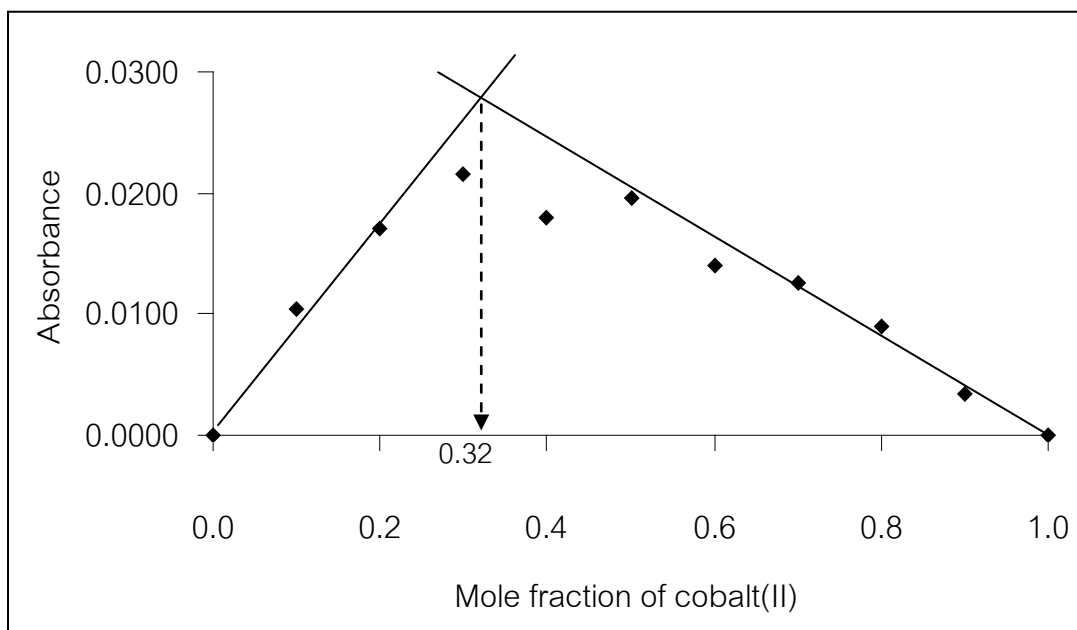
pH	Color of TAC solution	Color of Co(II)-TAC complex solution	$\lambda_{\max}$
6	light yellow	yellow brown solution	589
7	yellow	yellow brown solution	586
8	red	violet precipitate	-
9	red	violet precipitate	-
10	red	violet precipitate	-

**5. Stoichiometric determination of complex between 2-(2'-thiazolylazo)-p-cresol (TAC) and cobalt(II) and between TAC and lead(II) by continuous variation method**

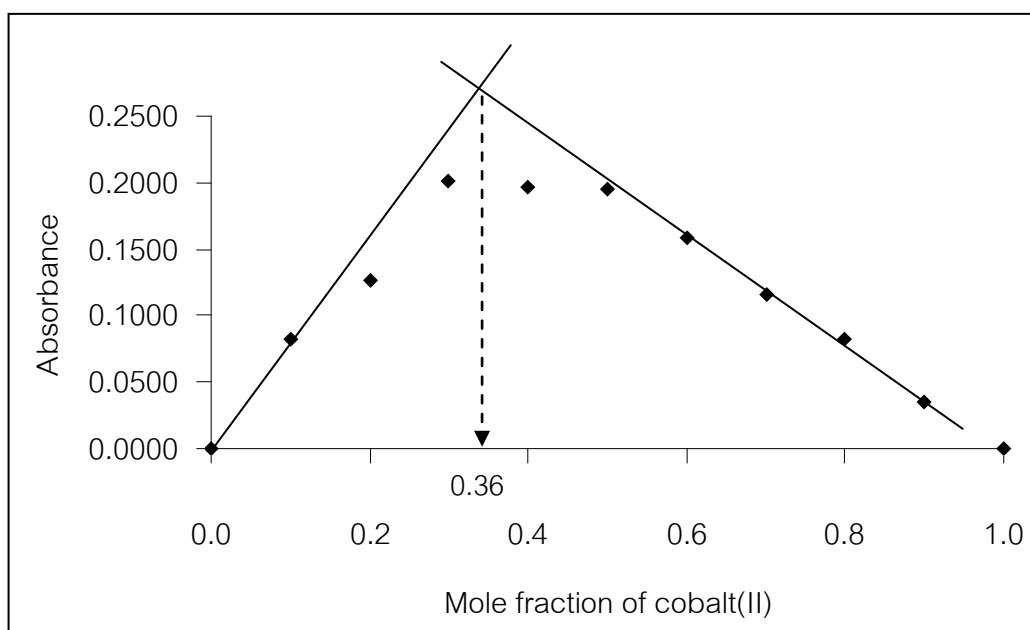
The stoichiometry of complex between cobalt(II) and 2-(2'-thiazolylazo)-p-cresol (TAC) was determined by continuous variation method at pH 5, 6, 7, 8, 9 and 10. The results are shown in Figures 25 to 40 and Table 9. The maximum absorption from spectra (shown in Figure 17, 18, 19, 20, 21 and 22) of cobalt(II) complex at pH 5, 6, 7, 8, 9 and 10 were 588, 565, 558, 560, 628 and 632 nm, respectively. Therefore, these wavelengths were chosen as reasonable wavelength for studying on the formation of cobalt(II) complex at the corresponding pH.



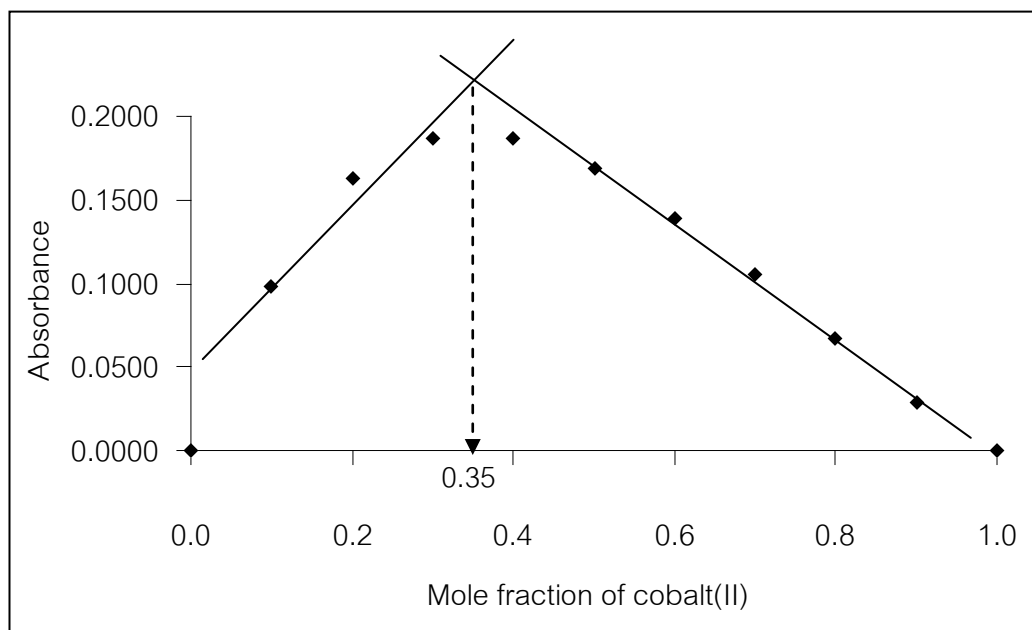
**Figure 25** Stoichiometric determination of complex between cobalt(II) and TAC in acetic acid and sodium acetate buffer solution at pH 5.



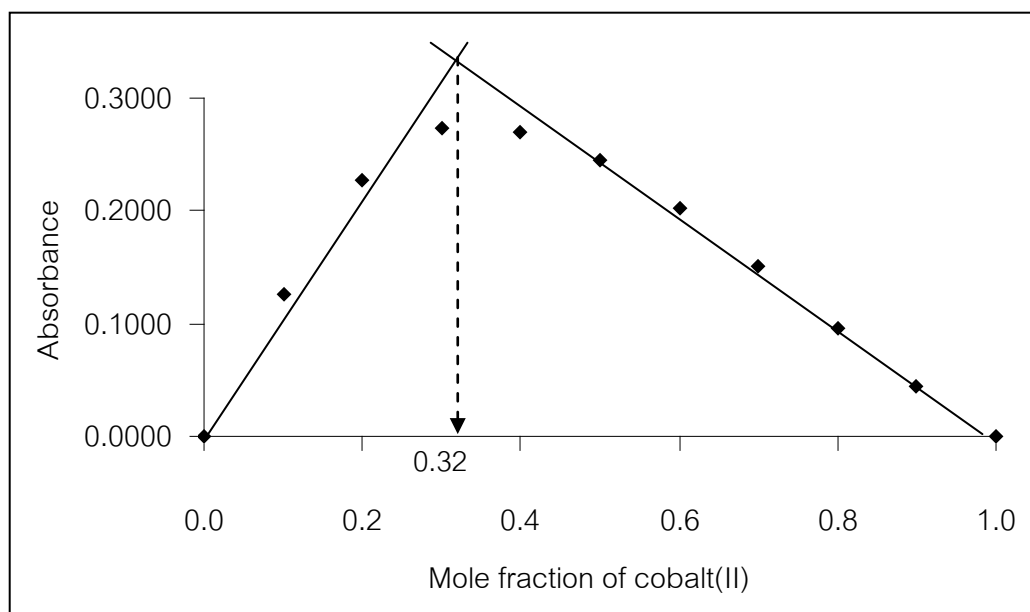
**Figure 26** Stoichiometric determination of complex between cobalt(II) and TAC in potassium hydrogen phthalate and sodium hydroxide buffer solution at pH 5.



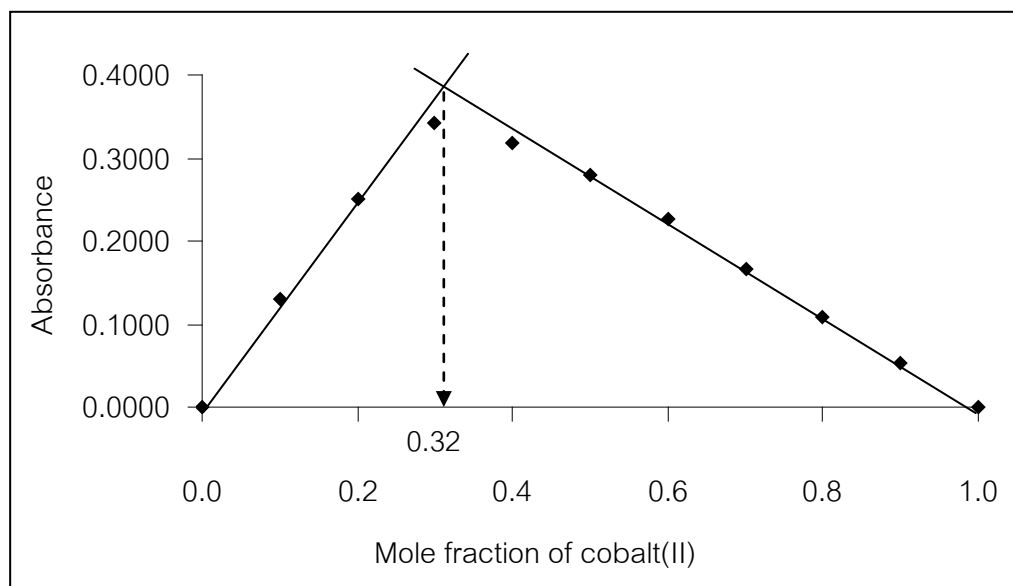
**Figure 27** Stoichiometric determination of complex between cobalt(II) and TAC in acetic acid and sodium acetate buffer solution at pH 6.



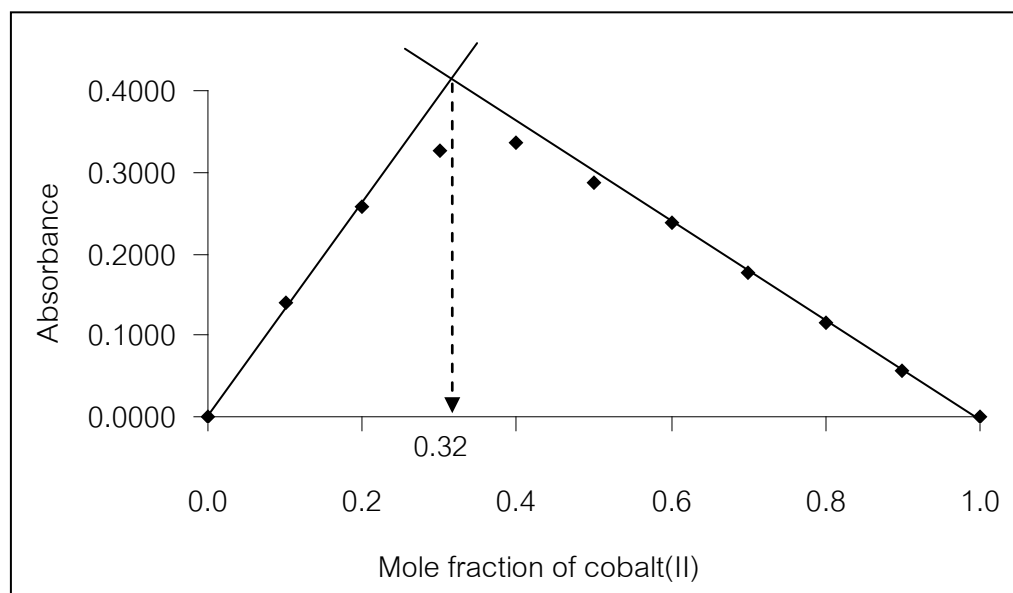
**Figure 28** Stoichiometric determination of complex between cobalt(II) and TAC in potassium dihydrogen phosphate and sodium hydroxide buffer solution at pH 6.



**Figure 29** Stoichiometric determination of complex between cobalt(II) and TAC in sodium dihydrogen phosphate and disodium hydrogen phosphate buffer solution at pH 7.

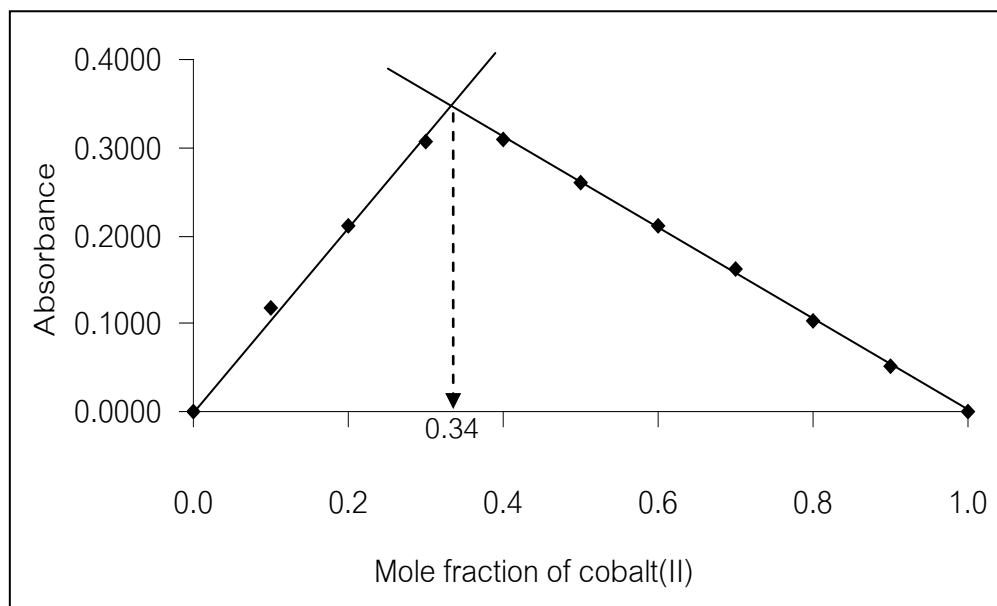


**Figure 30** Stoichiometric determination of complex between cobalt(II) and TAC in potassium dihydrogen phosphate and sodium hydroxide buffer solution at pH 7.

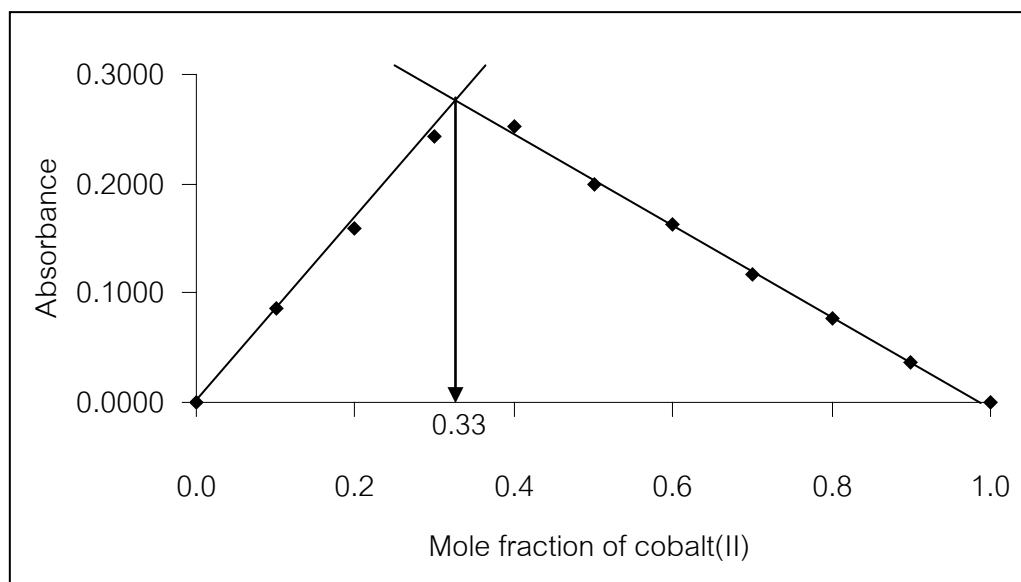


**Figure 31** Stoichiometric determination of complex between cobalt(II) and TAC in tris-(hydroxymethyl)aminomethane and hydrochloric acid buffer solution at pH 7.

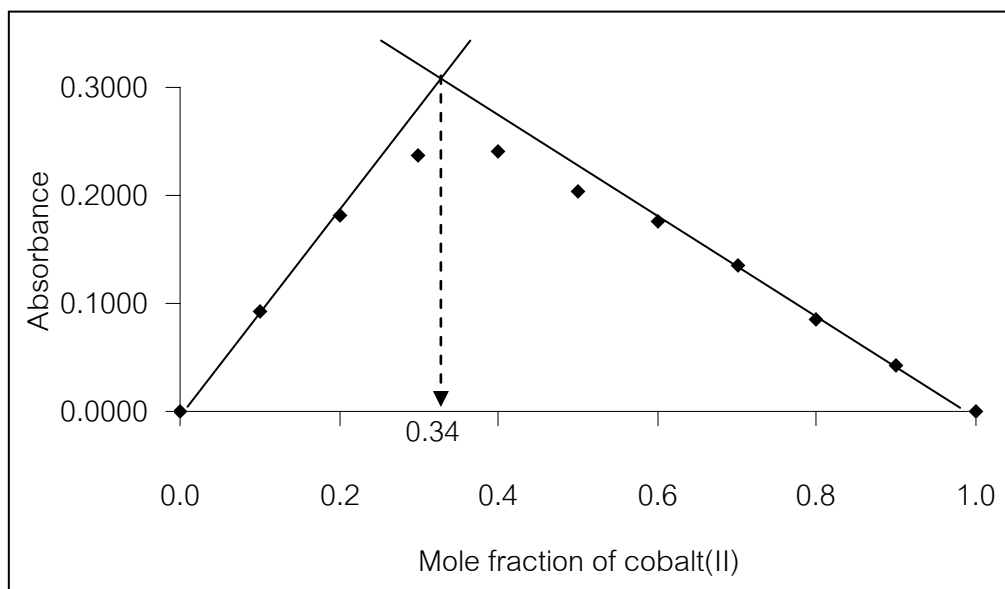




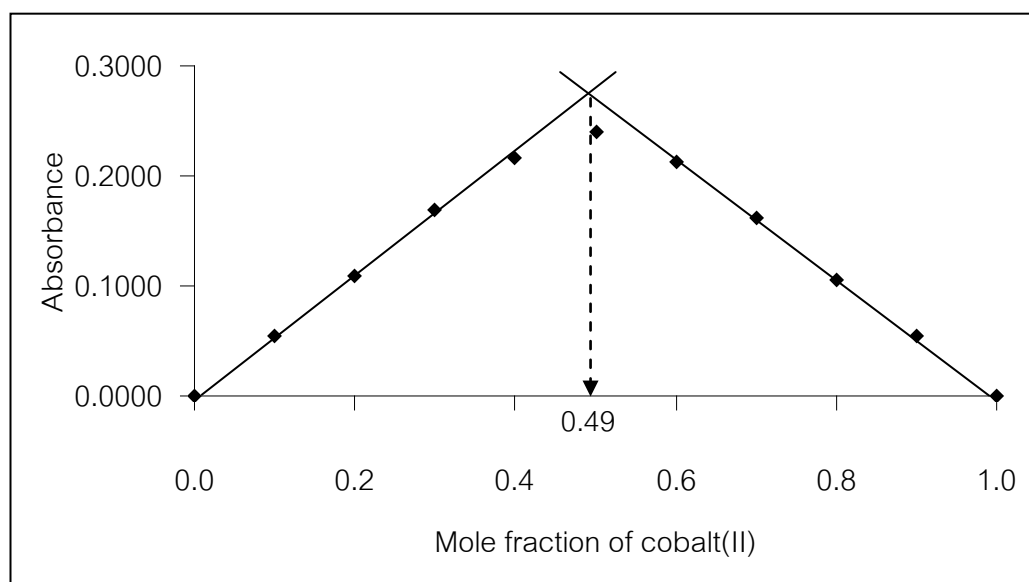
**Figure 32** Stoichiometric determination of complex between cobalt(II) and TAC in ammonium hydroxide and ammonium chloride buffer solution at pH 8.



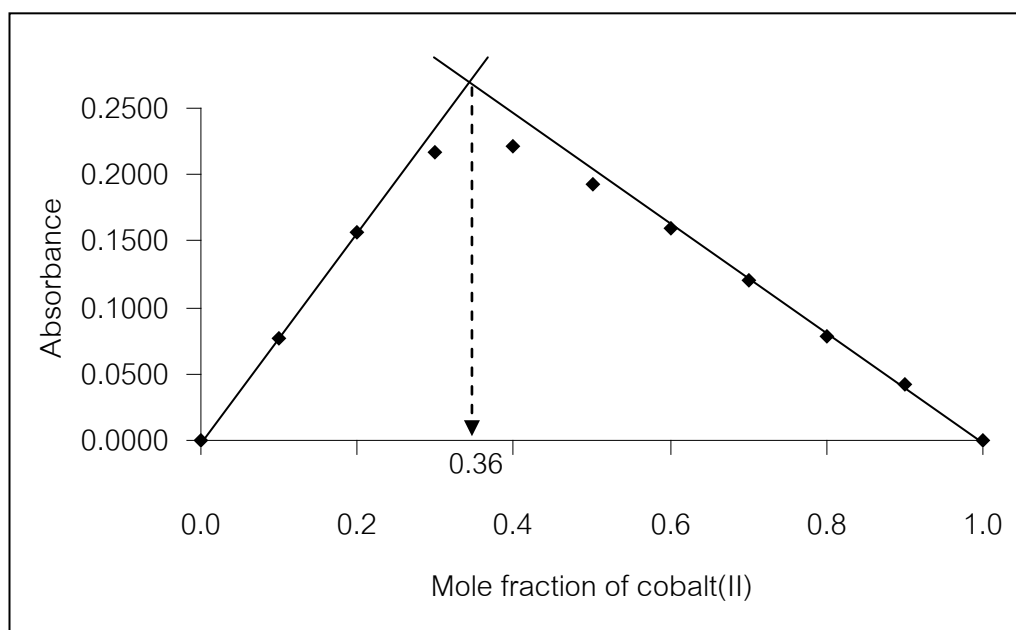
**Figure 33** Stoichiometric determination of complex between cobalt(II) and TAC in potassium dihydrogen phosphate and sodium hydroxide buffer solution at pH 8.



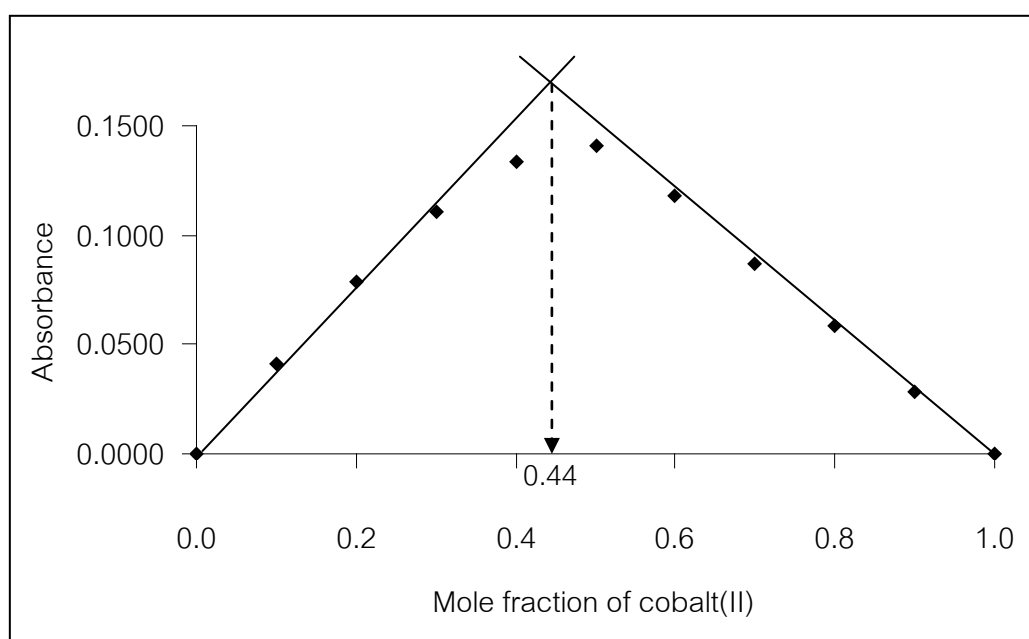
**Figure 34** Stoichiometric determination of complex between cobalt(II) and TAC in tris-(hydroxymethyl)aminomethane and hydrochloric acid buffer solution at pH 8.



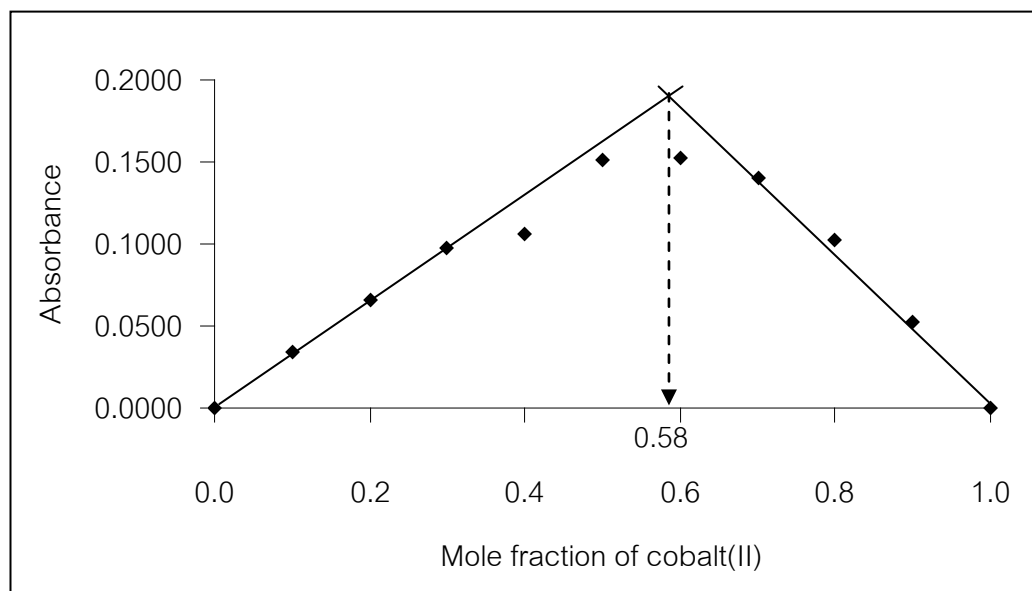
**Figure 35** Stoichiometric determination of complex between cobalt(II) and TAC in ammonium hydroxide and ammonium chloride buffer solution at pH 9.



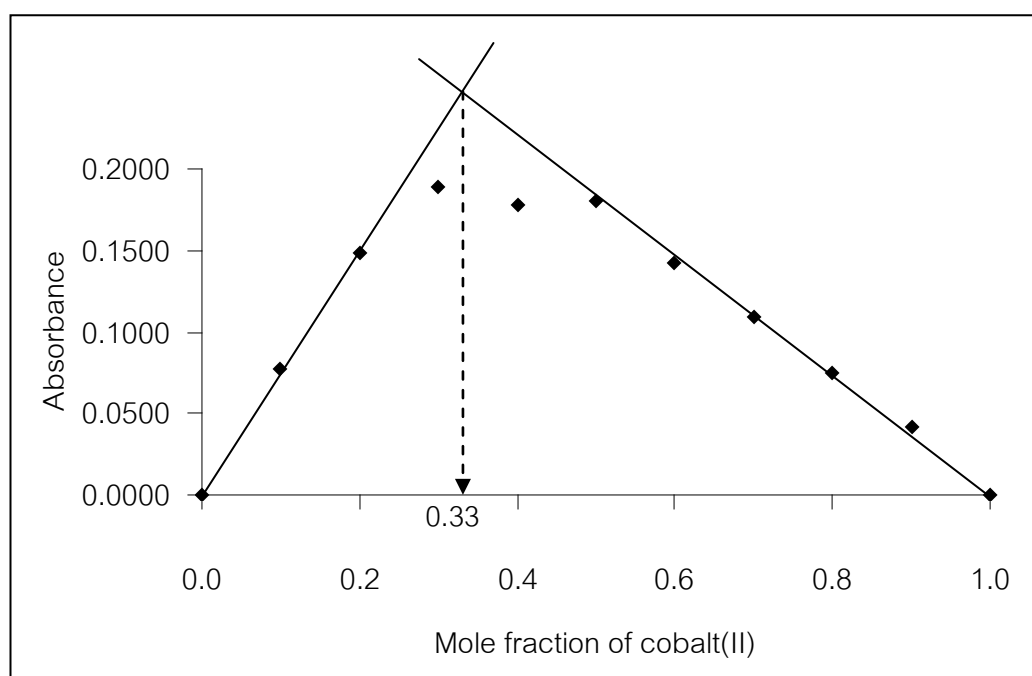
**Figure 36** Stoichiometric determination of complex between cobalt(II) and TAC in sodium hydrogen carbonate and sodium carbonate buffer solution at pH 9.



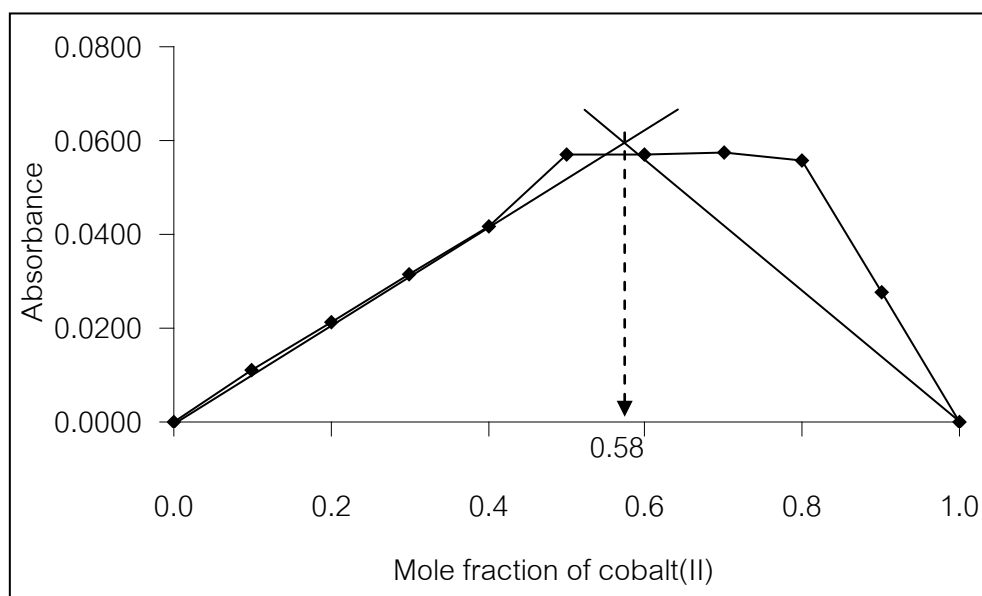
**Figure 37** Stoichiometric determination of complex between cobalt(II) and TAC in tris-(hydroxymethyl)aminomethane and hydrochloric acid buffer solution at pH 9.



**Figure 38** Stoichiometric determination of complex between cobalt(II) and TAC in ammonium hydroxide and ammonium chloride buffer solution at pH 10.



**Figure 39** Stoichiometric determination of complex between cobalt(II) and TAC in sodium hydrogen carbonate and sodium carbonate buffer solution at pH 10.



**Figure 40** Stoichiometric determination of complex between cobalt(II) and TAC in tris-(hydroxymethyl)aminomethane and hydrochloric acid buffer solution at pH 10.

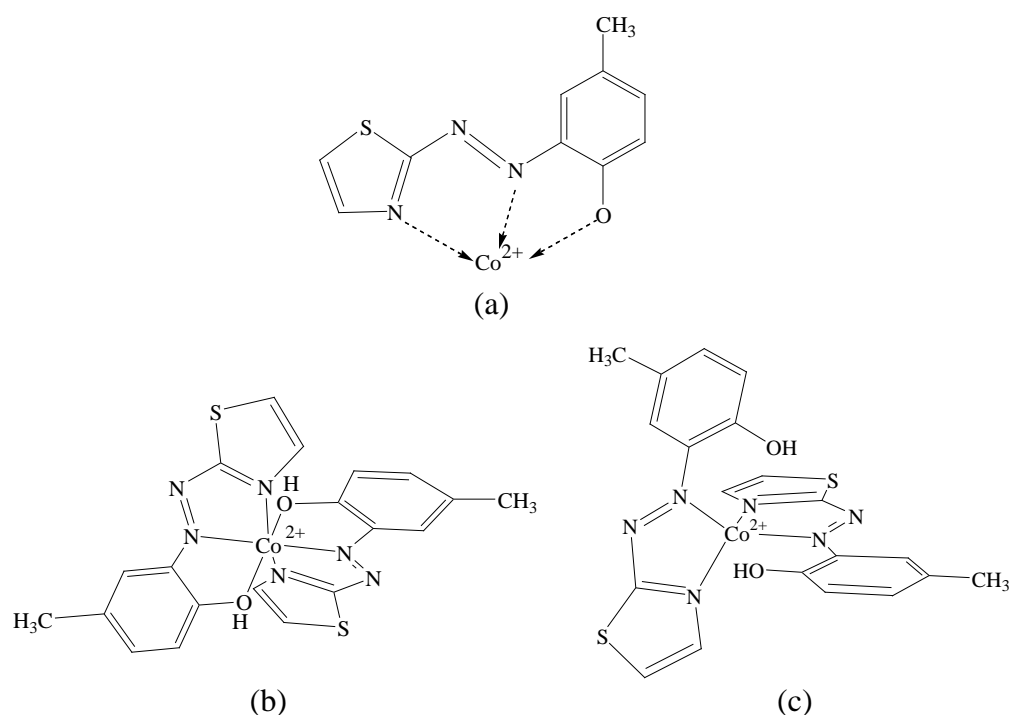
**Table 9** The ratio of cobalt(II) : TAC in the complex at pH 5, 6, 7, 8, 9 and 10 by continuous variation method

pH of cobalt(II) complex solution	Buffer solution	The ratio of cobalt(II) : TAC
5.0	CH <sub>3</sub> COOH/CH <sub>3</sub> COONa	1 : 2
5.0	KHP/NaOH	1 : 2
6.0	CH <sub>3</sub> COOH/CH <sub>3</sub> COONa	1 : 2
6.0	KH <sub>2</sub> PO <sub>4</sub> /NaOH	1 : 2
7.0	NaH <sub>2</sub> PO <sub>4</sub> /Na <sub>2</sub> HPO <sub>4</sub>	1 : 2
7.0	KH <sub>2</sub> PO <sub>4</sub> /NaOH	1 : 2
7.0	C <sub>4</sub> H <sub>11</sub> NO <sub>3</sub> /HCl	1 : 2
8.0	NH <sub>4</sub> OH/NH <sub>4</sub> Cl	1 : 2
8.0	KH <sub>2</sub> PO <sub>4</sub> /NaOH	1 : 2
8.0	C <sub>4</sub> H <sub>11</sub> NO <sub>3</sub> /HCl	1 : 2
9.0	NH <sub>4</sub> OH/NH <sub>4</sub> Cl	1 : 1
9.0	NaHCO <sub>3</sub> /Na <sub>2</sub> CO <sub>3</sub>	1 : 2
9.0	C <sub>4</sub> H <sub>11</sub> NO <sub>3</sub> /HCl	1 : 1
10.0	NH <sub>4</sub> OH/NH <sub>4</sub> Cl	1 : 1
10.0	NaHCO <sub>3</sub> /Na <sub>2</sub> CO <sub>3</sub>	1 : 2
10.0	C <sub>4</sub> H <sub>11</sub> NO <sub>3</sub> /HCl	1 : 1

At pH higher than pK<sub>a</sub> (pH 9 and 10), TAC is in basic form, which hydroxyl group was deprotonated and the oxygen atom could form strong coordinate covalent bond with metal ions. So TAC might acted as tridentate ligand in the complex formation. On the other hand, at pH lower than pK<sub>a</sub> (pH 5-8), TAC is in acid form, therefore hydroxyl group could form weaker bond with metal ions. In this case, TAC might acted as bidentate ligand which the ratio of cobalt(II) : TAC was 1 : 2. However, TAC in acid form as the tridentate ligand could not rule out.

At pH lower than the  $pK_a$  (pH 5-8), type of buffer did not have effect on the complexation between cobalt(II) and TAC. The ratio of cobalt(II) : TAC was 1 : 2. At pH 9 and 10, the ratio of cobalt(II) : TAC were 1 : 2 for  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  buffer and 1 : 1 for  $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$  and  $\text{C}_4\text{H}_{11}\text{NO}_3/\text{HCl}$  buffer. When the  $\text{C}_4\text{H}_{11}\text{NO}_3/\text{HCl}$  buffer was used in the preparation of complex between cobalt(II) and TAC, at pH 8 which lower than the  $pK_a$  the ratio was 1 : 2 but at pH 9 and 10 which higher than the  $pK_a$  the ratio was 1 : 1. This may be because nitrogen atom of the buffer molecules could be the donor atom for the complexation with cobalt(II). While the molecule of  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  buffer could not coordinate with cobalt(II) because the oxygen atom in this buffer was the hard base comparing with the nitrogen atom of TAC.

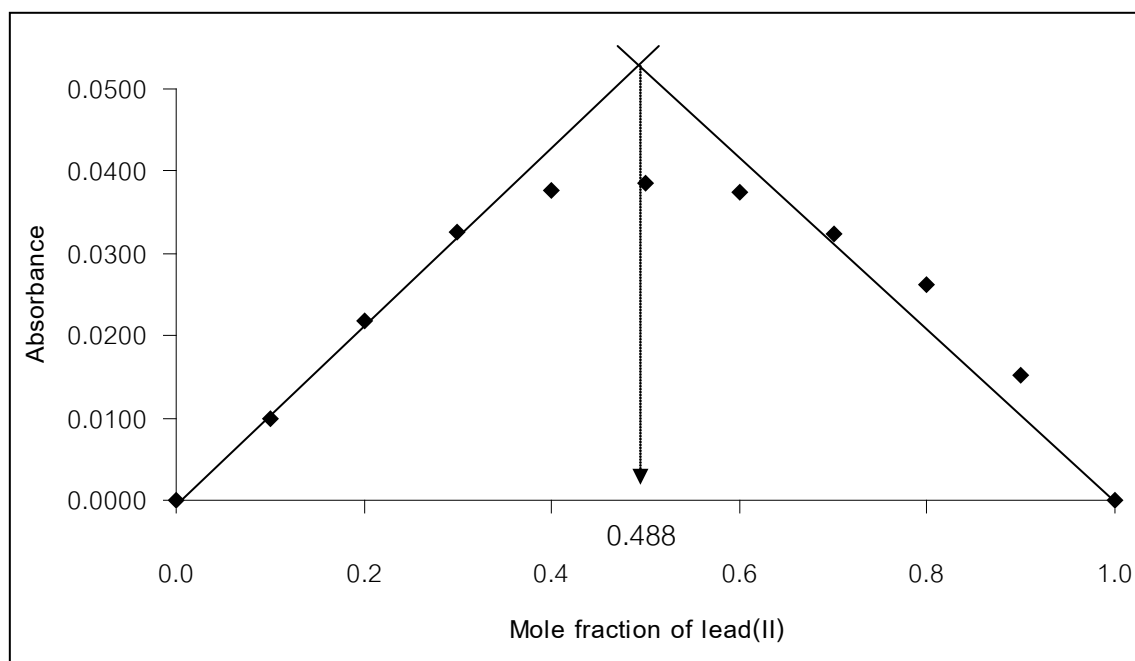
The postulated structures from continuous variation method of ratio 1 : 1 and 1 : 2 of cobalt(II)-TAC complex are shown in Figure 41.



**Figure 41** Postulated structures of cobalt(II)-TAC complex.

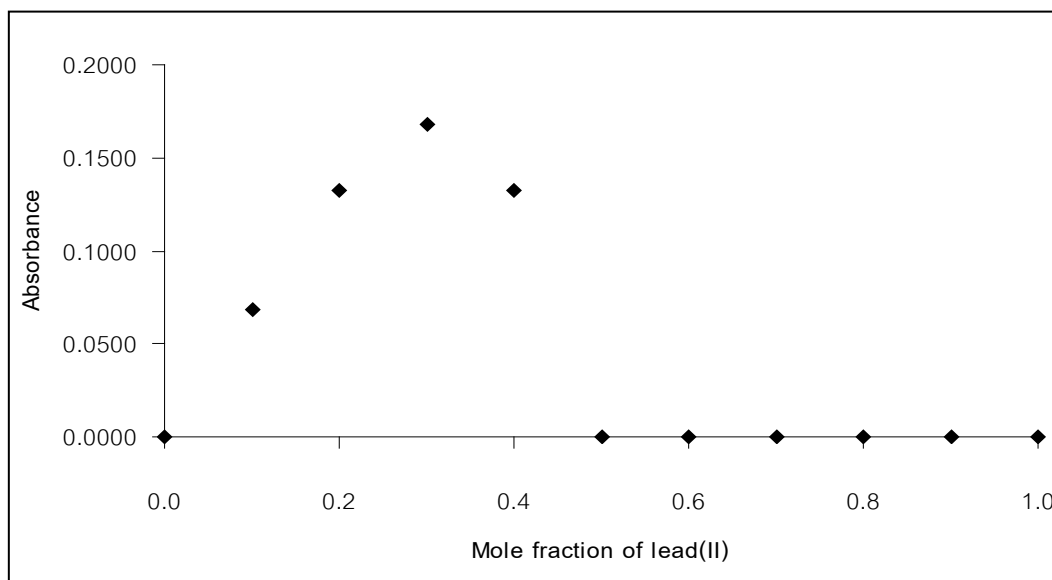
- (a) 1 : 1 complex
- (b) 1 : 2 complex (TAC as tridentate ligand)
- (c) 1 : 2 complex (TAC as bidentate ligand)

Figures 42 and 43 show stoichiometric determination of complexes between lead(II) and TAC by continuous variation method at pH 6 and 7. The maximum absorption from spectra (shown in Figures 23 and 24) of lead(II) complex at pH 6 and 7 were 589 and 586 nm, respectively. Therefore, these wavelength were chosen as reasonable wavelength for studying on the formation of lead(II) complex at corresponding pH. From Figure 42, the complexation ratio between lead(II) and TAC was 1 : 1. From Figure 43, at pH 7, it is difficult to make the conclusion on the complexation ratio. This may be due to the type of buffer system. The postulated structures from continuous variation method for the ratio of 1 : 1, lead(II)-TAC complex was already shown in Figure 16.



**Figure 42** Stoichiometric determination of complex between lead(II) and TAC in acetic acid and sodium acetate buffer solution at pH 6.

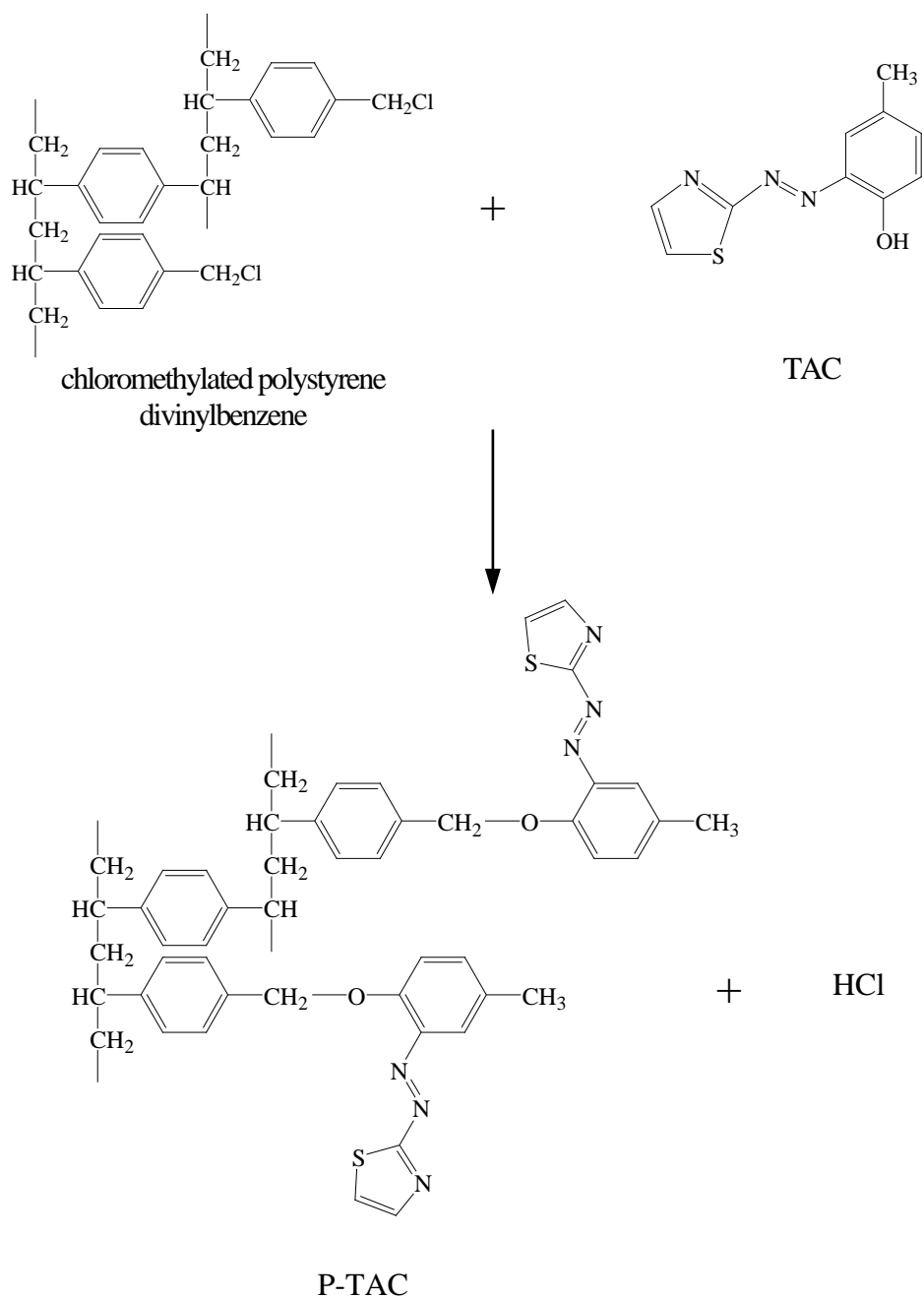




**Figure 43** Stoichiometric determination of complex between lead(II) and TAC in sodium dihydrogen phosphate and disodium hydrogen phosphate buffer solution at pH 7.

## 6. Preparation of and 2-(2'-thiazolylazo)-p-cresol resin (P-TAC)

P-TAC was prepared by the immobilization of TAC on chloromethylated polystyrene divinylbenzene. The preparation pathway of P-TAC is shown in Figure 44. The data from the infrared spectrum of P-TAC (Rerkpalin, 2003) was found that chloromethylated polystyrene divinylbenzene was chemically modified by TAC. The chemical modification was achieved through O-alkylation leading to the formation of polymer-supported.



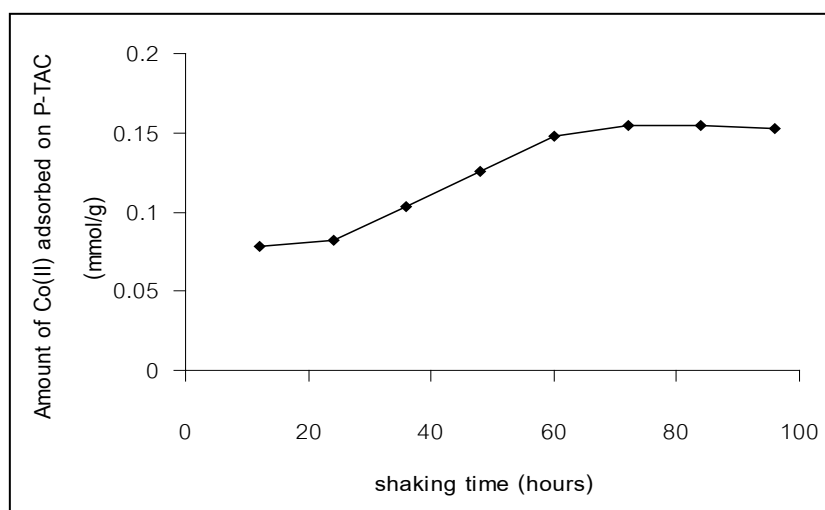
**Figure 44** O-alkylation of chloromethylated polystyrene divinylbenzene copolymer with TAC.

The P-TAC was prepared in various organic solvents. The influence of the type of organic solvent was examined as shown in Table 10. It shows that the adsorption capacity of P-TAC prepared in the mixture solvent of dimethylformamide and triethylamine (1:1) was better than other solvents.

**Table 10** Effect of solvent on the preparation of P-TAC

Solvent	Capacity of cobalt(II) (mmol g <sup>-1</sup> )
Dimethylformamide	$6.25 \times 10^{-2}$
Dimethylamine	$6.03 \times 10^{-2}$
Diethylamine	$6.34 \times 10^{-2}$
Triethylamine	$6.71 \times 10^{-2}$
Dimethylformamide : Triethylamine (1:1)	$7.51 \times 10^{-2}$

The effect of shaking time on the preparation of P-TAC is shown in Figure 45. It was found that the adsorption capacity of P-TAC increased with increasing shaking time up to 72 hours or above, the adsorption of cobalt(II) on the P-TAC was almost constant. Therefore, the chelating resin (P-TAC) was synthesized from the reaction of TAC in a mixture of 1:1 triethylamine and dimethylformamide on chloromethylated polystyrene divinylbenzene. The mixture was shaken at room temperature for 72 hours.

**Figure 45** The effect of shaking time on the preparation of P-TAC.

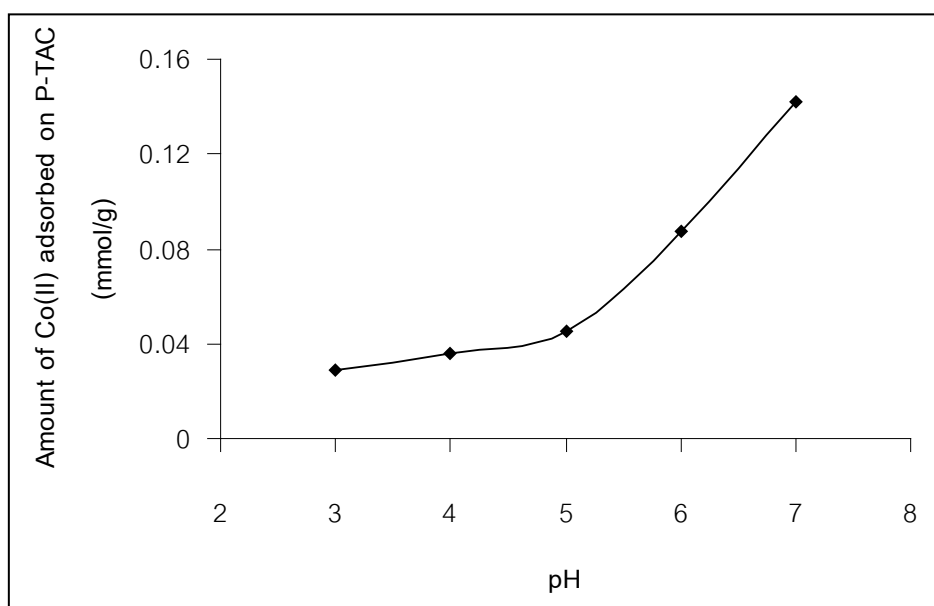
The result from the elemental analysis indicated that, the incorporation of TAC on chloromethylated polystyrene divinylbenzene was 0.178 mmol of TAC per 1 g of chloromethylated polystyrene divinylbenzene. The calculation is shown in Appendix B.

## 7. Determination of capacity for the adsorption of cobalt(II) by P-TAC

### 7.1 Optimization of parameters for the maximum adsorption of cobalt(II) on P-TAC by batch equilibrium experiment

#### 7.1.1 Effect of pH

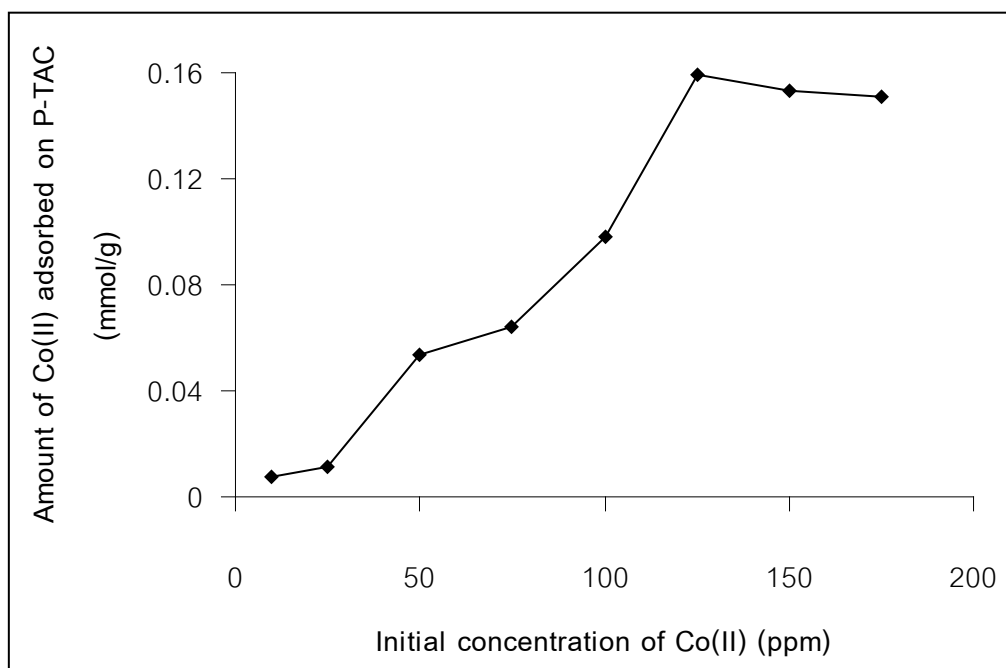
The capacity of P-TAC at pH 3, 4, 5, 6 and 7 were 0.0292, 0.0357, 0.0456, 0.0878 and 0.1420 mmol/g, respectively. The results are shown in Figure 46. It was found that the adsorption efficiency of P-TAC increased when the pH was increased and the highest capacity for cobalt(II) on P-TAC was obtained at pH 7. Due to the hydrolysis of cobalt(II) over pH 7 (observed white precipitate of  $\text{Co}(\text{OH})_2$ ), therefore the experiment could not be performed at the pH higher than 7.



**Figure 46** Effect of pH on the adsorption of cobalt(II) by P-TAC (P-TAC 50 mg, initial concentration of cobalt(II) 125 ppm and shaking time 3 hours).

### 7.1.2 Effect of initial concentration of cobalt(II)

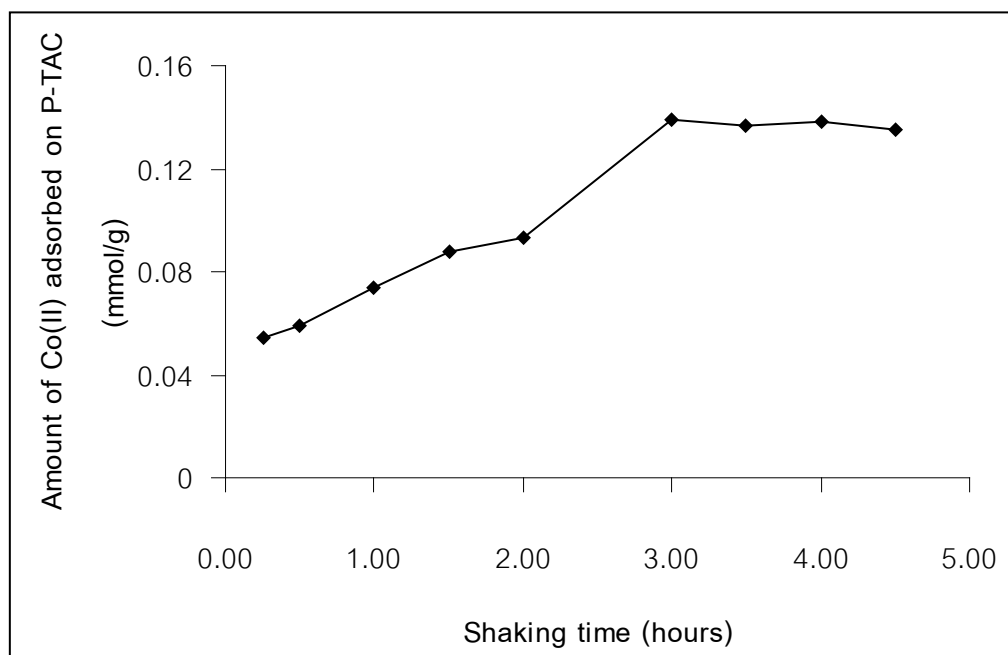
Figure 47 indicated that the initial concentration had affect on the adsorption of cobalt(II) by P-TAC. The capacity of P-TAC for cobalt(II) reached maximum when the concentration of cobalt(II) was 125 ppm.



**Figure 47** Effect of initial concentration of cobalt(II) on the adsorption of cobalt(II) by P-TAC (P-TAC 50 mg, pH 7 and shaking time 3 hours).

### 7.1.3 Effect of shaking time

The capacity of P-TAC for the adsorption of cobalt(II) as a function of shaking time is shown in Figure 48. It was found that the adsorption of cobalt(II) on P-TAC increased with increasing shaking time up to 3 hours, which the capacity of P-TAC was almost constant.



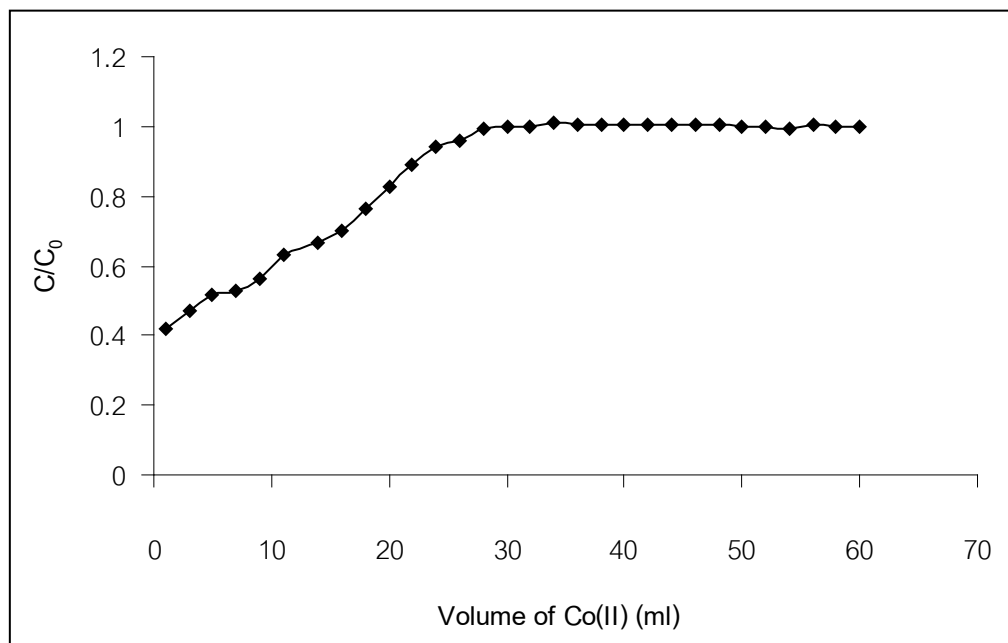
**Figure 48** Effect of shaking time on the adsorption of cobalt(II) by P-TAC (P-TAC 50 mg, initial concentration of cobalt(II) 125 ppm and pH 7).

From the results, the capacity of P-TAC of cobalt(II) at the optimum condition (pH 7, shaking time 3 hours and initial concentration of cobalt(II) 125 ppm) was 0.159 mmol/g.

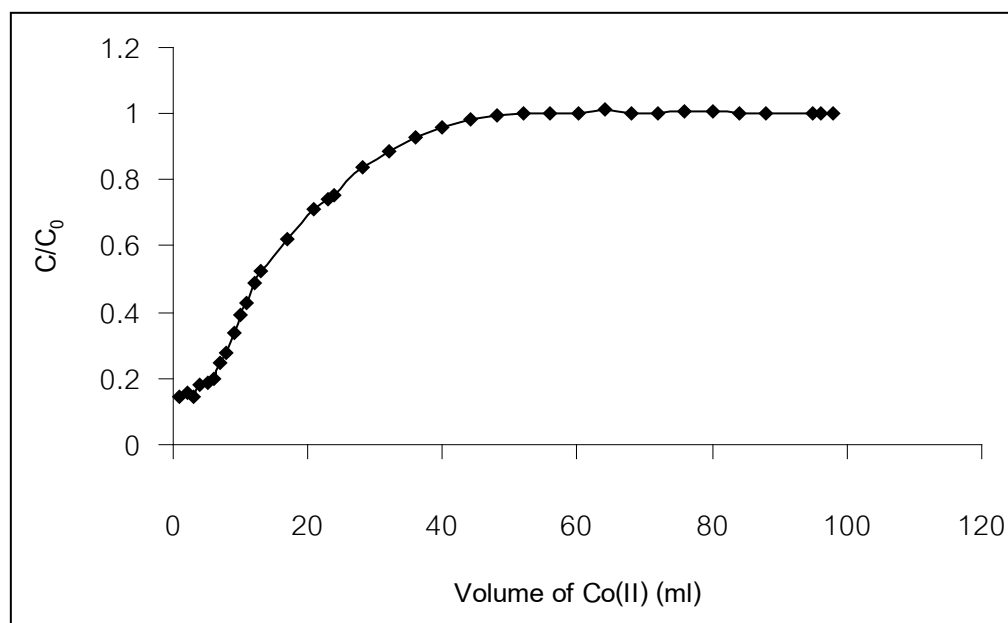
## 7.2 Optimization of parameters for the maximum adsorption of cobalt(II) on P-TAC by column equilibrium experiment

After all the parameters were optimized, the optimum condition was used to determine the capacity of P-TAC for cobalt(II) by column equilibrium experiment. The effect of flow rate on the adsorption of cobalt(II) on P-TAC had been studied. The flow rates used in this study were 0.50, 0.33 and 0.25 ml/min. The results are shown in Figures 49, 50 and 51 (where  $C_0$  is initial concentration of cobalt(II) and  $C$  is concentration of cobalt(II) at each fraction). It was found that the flow rate of 0.25 ml/min was more suitable than the flow rate of 0.50 and 0.33 ml/min because the first 30 ml of cobalt(II) was adsorbed completely. The capacity of cobalt(II) on P-TAC at flow rate 0.25 ml/min determined by breakthrough column experiment was

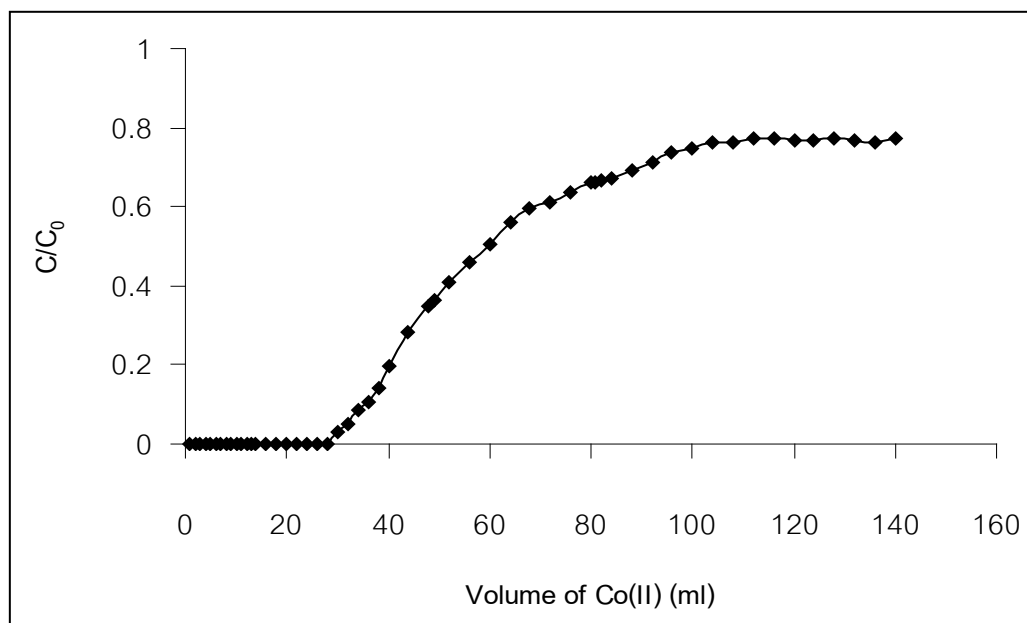
$9.989 \times 10^{-3}$  mmol/g, which was lower than the capacity obtained from batch equilibrium experiment.



**Figure 49** Breakthrough curve of cobalt(II) on P-TAC (P-TAC 0.300 g, initial concentration of cobalt(II) 10 ppm, pH 7 and flow rate 0.50 ml/min).



**Figure 50** Breakthrough curve of cobalt(II) on P-TAC (P-TAC 0.301 g, initial concentration of cobalt(II) 10 ppm, pH 7 and flow rate 0.33 ml/min).



**Figure 51** Breakthrough curve of cobalt(II) on P-TAC (P-TAC 0.298 g, initial concentration of cobalt(II) 10 ppm, pH 7 and flow rate 0.25 ml/min).

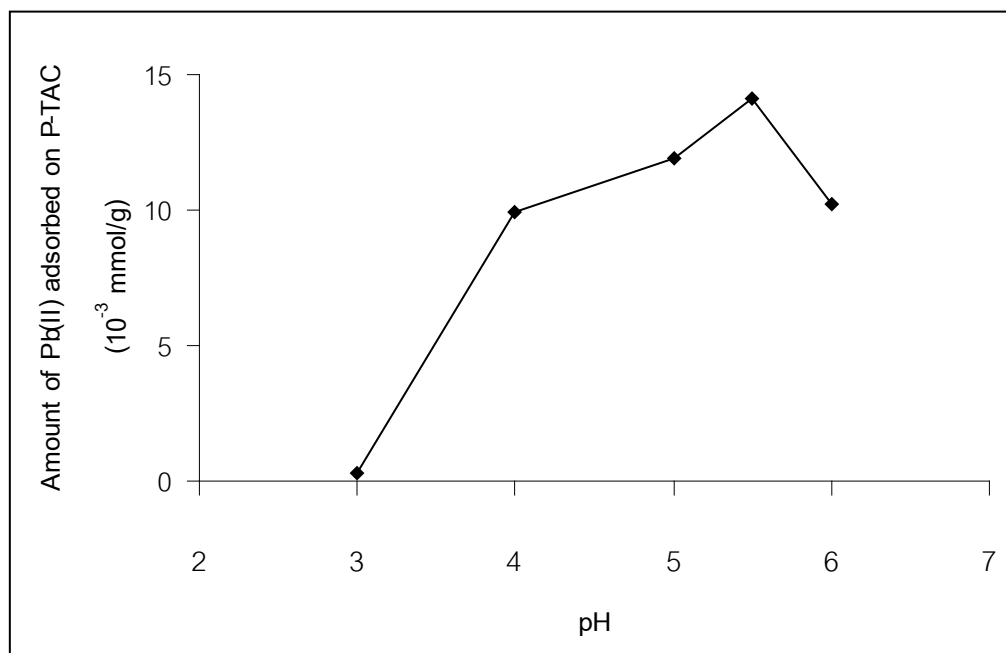
## 8. Determination of capacity for the adsorption of lead(II) by P-TAC

### 8.1 Optimization of parameters for the maximum adsorption of lead(II) on P-TAC by batch equilibrium experiment

#### 8.1.1 Effect of pH

The effect of pH on the adsorption of lead(II) was studied on pH range from 3-6. The capacity of P-TAC at pH 3, 4, 5, 5.5 and 6 were  $0.29 \times 10^{-3}$ ,  $9.95 \times 10^{-3}$ ,  $11.90 \times 10^{-3}$ ,  $14.10 \times 10^{-3}$  and  $10.20 \times 10^{-3}$  mmol/g, respectively. The results are shown in Figure 52. It was found that the highest capacity for lead(II) on P-TAC was obtained at pH 5.5. The lead(II) was hydrolyzed at pH higher than 6. Therefore, pH 5.5 was chosen as the appropriate pH for the adsorption of lead(II) on P-TAC.

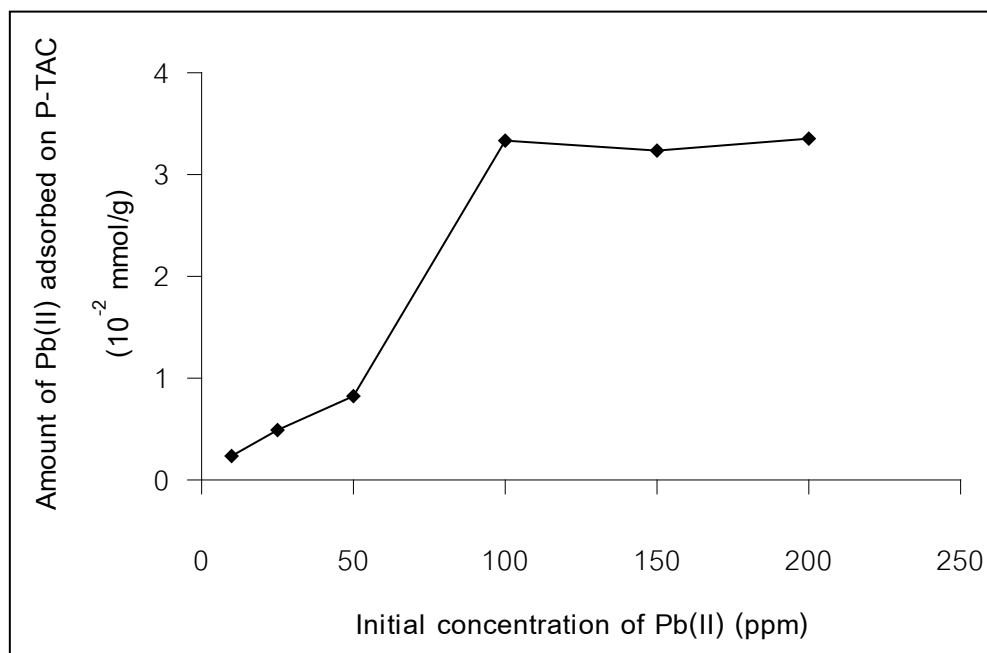




**Figure 52** Effect of pH on the adsorption of lead(II) by P-TAC (P-TAC 50 mg, initial concentration of lead(II) 100 ppm and shaking time 24 hours).

#### 8.1.2 Effect of initial concentration of lead(II)

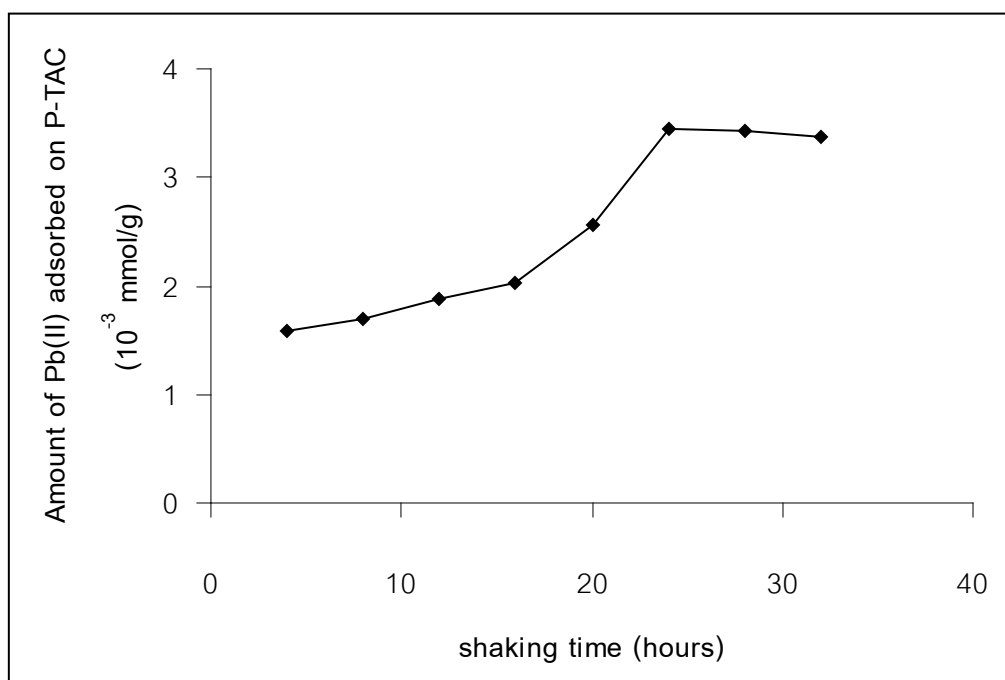
The effect of initial concentration of lead(II) on the adsorption of lead(II) on P-TAC was studied at pH 5.5. Figure 53 indicated the initial concentration had affect on the adsorption of lead(II) by P-TAC. The capacity of P-TAC for lead(II) reached maximum when the concentration of lead(II) was 100 ppm.



**Figure 53** Effect of initial concentration of lead(II) on the adsorption of lead(II) by P-TAC (P-TAC 50 mg, pH 5.5 and shaking time 24 hours).

### 8.1.3 Effect of shaking time

The capacity of P-TAC for the adsorption of lead(II) as a function of shaking time is shown in Figure 54. It was found that the adsorption of lead(II) on P-TAC increased with increasing shaking time up to 24 hours, which the capacity of P-TAC was almost constant.



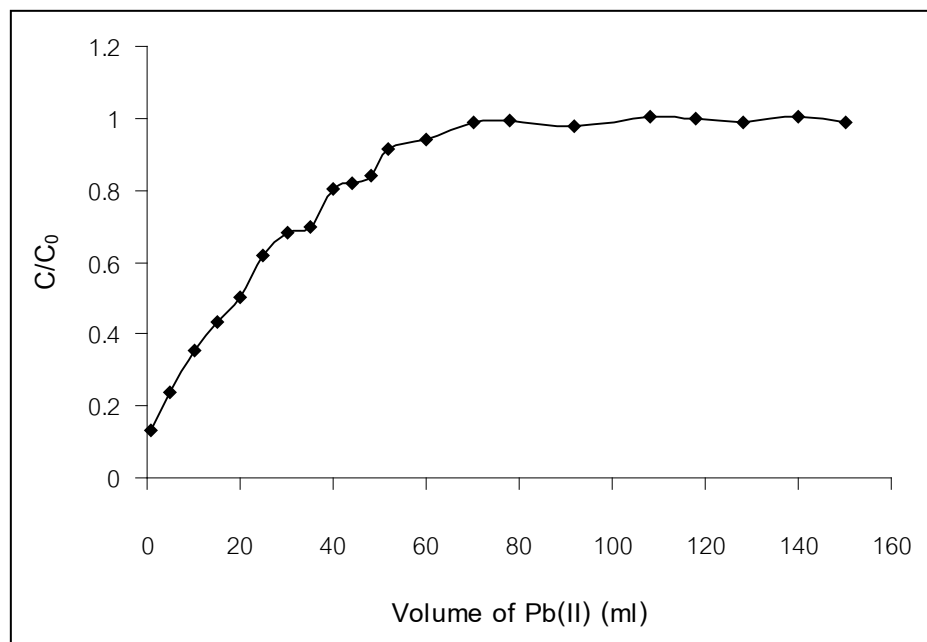
**Figure 54** Effect of shaking time on the adsorption of lead(II) by P-TAC (P-TAC 50 mg, initial concentration of lead(II) 100 ppm and pH 5.5).

From the results, the capacity of P-TAC of lead(II) at the optimum condition (pH 5.5, shaking time 24 hours and initial concentration of cobalt(II) 100 ppm) was  $3.45 \times 10^{-2}$  mmol/g.

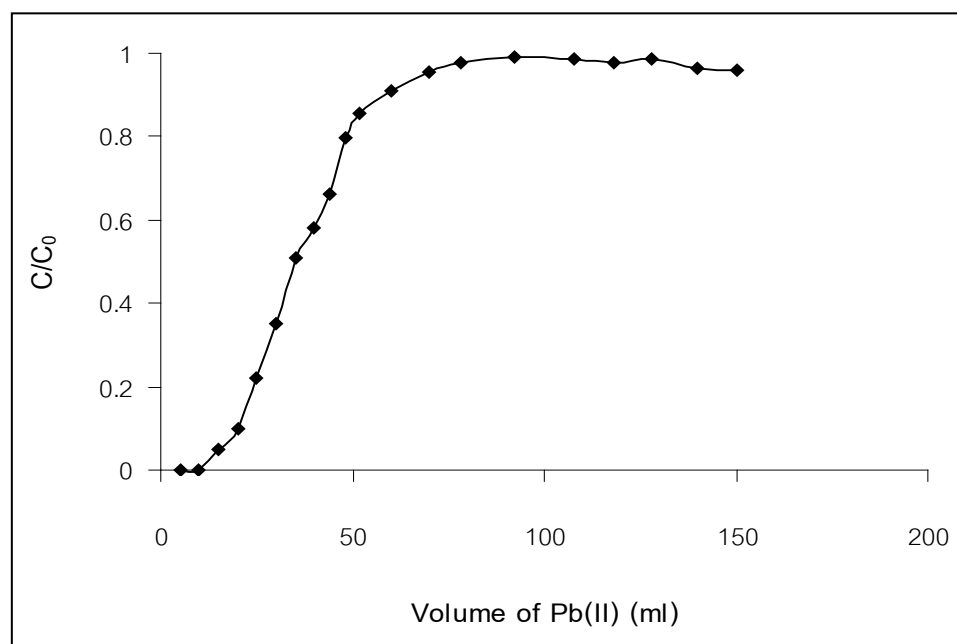
## 8.2 Optimization of parameters for the maximum adsorption of lead(II) on P-TAC by column equilibrium experiment

After all of the parameters were optimized, the optimum condition was used to determine the capacity of P-TAC for lead(II) by column equilibrium experiment. The effect of flow rate on the adsorption of lead(II) on P-TAC had been studied. The flow rates used in this study were 0.50, 0.33 and 0.25 ml/min. The results are shown in Figures 55, 56 and 57 (where  $C_0$  is initial concentration of lead(II) and  $C$  is concentration of lead(II) at each fractions). It was found that the flow rate of 0.25 ml/min was more suitable than the flow rate of 0.50 and 0.33 ml/min because the first 40 ml of lead(II) was adsorbed completely. The capacity of lead(II) on P-TAC at flow rate 0.25 ml/min determined by breakthrough column experiment was  $2.267 \times 10^{-2}$

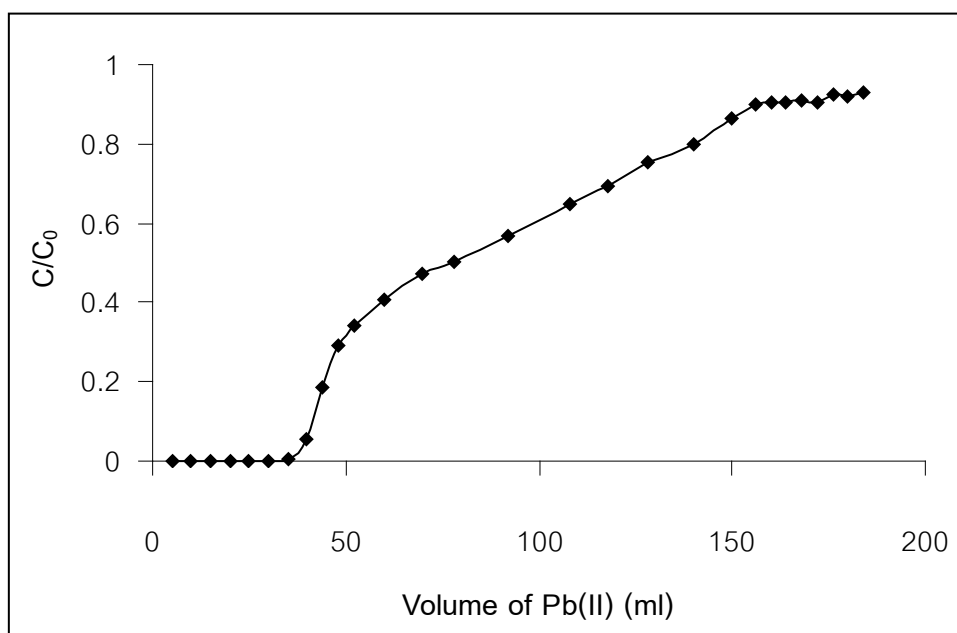
mmol/g, which was lower than the capacity obtained from batch equilibrium experiment.



**Figure 55** Breakthrough curve of lead(II) on P-TAC (P-TAC 0.299 g, initial concentration of lead(II) 16 ppm, pH 5.5 and flow rate 0.50 ml/min).



**Figure 56** Breakthrough curve of lead(II) on P-TAC (P-TAC 0.296 g, initial concentration of lead(II) 16 ppm, pH 5.5 and flow rate 0.33 ml/min).



**Figure 57** Breakthrough curve of lead(II) on P-TAC (P-TAC 0.298 g, initial concentration of lead(II) 16 ppm, pH 5.5 and flow rate 0.25 ml/min).

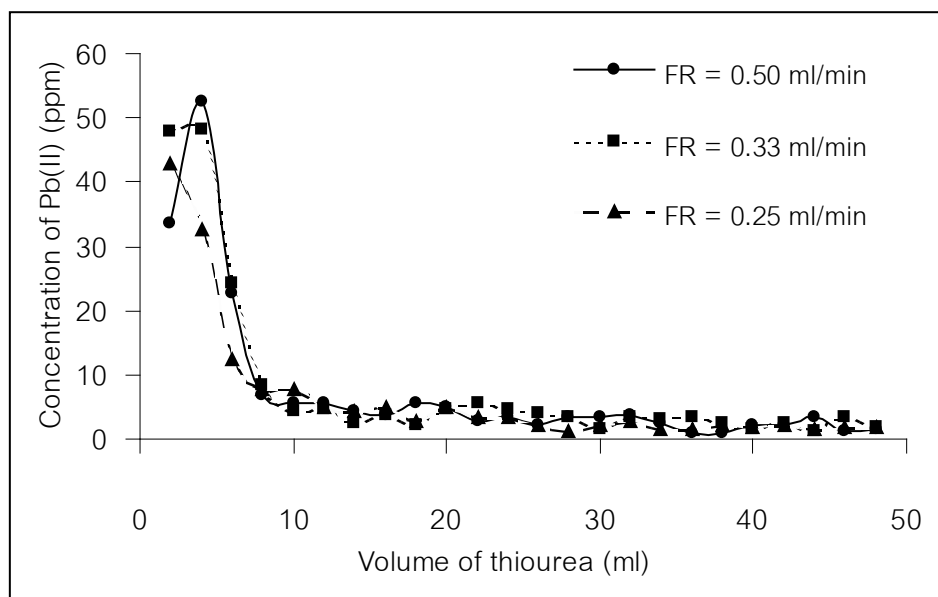
### 9. Desorption of cobalt(II) and lead(II) on P-TAC

In batch equilibrium experiment, the desorption of cobalt(II) and lead(II) from P-TAC by various eluents were examined. The results are shown in Table 11. It was suggested that 0.5 M thiourea and 3 M perchloric acid can be used as eluent for the desorption of lead(II) and cobalt(II) from P-TAC, respectively. Thiourea has sulfur as a donor atom which could elute metal ions because it could form complex with metal ions better than TAC. For the desorption of lead(II) and cobalt(II), lead(II) could eluted by thiourea better than cobalt(II) because lead(II) was the characteristic of the soft acid than cobalt(II) so that it could form complex with sulfur atom of thiourea better than cobalt(II). Lead(II) and cobalt(II) were eluted from P-TAC successively because perchloric acid was a very strong acid which could protonate at the nitrogen atom of TAC. Then, the metal ions which were adsorbed on the P-TAC could exchanged by the proton of perchloric acid. In the application, the mixture of cobalt(II) and lead(II) could be separated by using 0.5 M thiourea for the desorption of lead(II) and followed by 3 M perchloric acid for the desorption of cobalt(II).

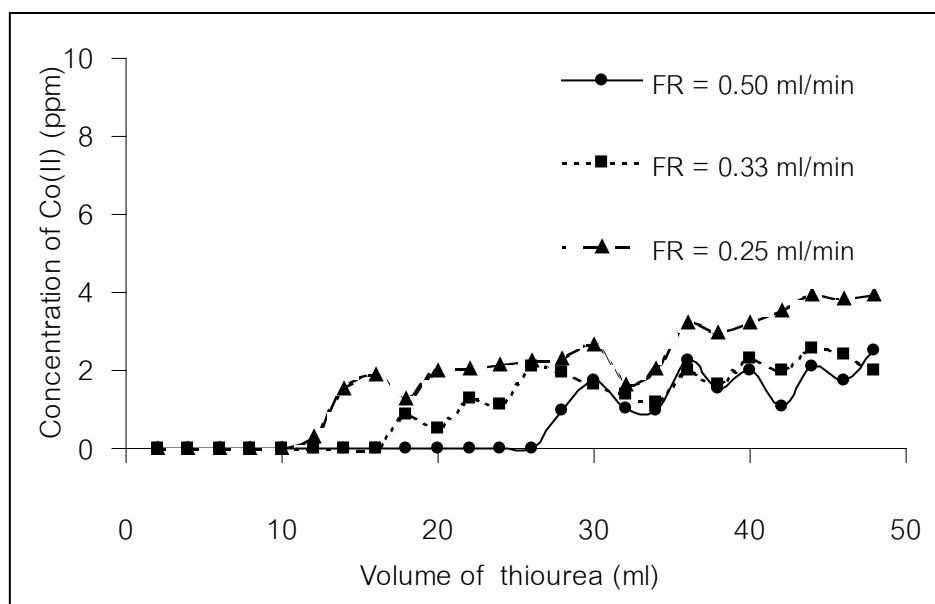
**Table 11** The percentage of the desorption of cobalt(II) and lead(II) from P-TAC by various eluents (loaded P-TAC 50 mg and shaking time 3 hours)

Eluent	% Desorption of cobalt(II)	% Desorption of lead(II)
1.0 M hydrochloric acid	21.15	69.28
2.0 M hydrochloric acid	25.21	72.61
3.0 M hydrochloric acid	28.72	75.26
4.0 M hydrochloric acid	20.16	55.36
5.0 M hydrochloric acid	17.42	54.82
6.0 M hydrochloric acid	20.57	50.20
0.1 M thiourea	20.07	63.05
0.25 M thiourea	19.79	92.65
0.5 M thiourea	23.25	99.27
0.75 M thiourea	22.47	86.02
1.0 M thiourea	20.61	85.54
1.0 M perchloric acid	57.20	42.30
2.0 M perchloric acid	92.66	75.75
3.0 M perchloric acid	93.41	90.83
4.0 M perchloric acid	90.50	56.76
5.0 M perchloric acid	71.74	59.38
6.0 M perchloric acid	73.57	62.16
0.1 M EDTA	38.92	58.90
0.2 M EDTA	61.51	70.69

The desorption of cobalt(II) and lead(II) by 0.5 M thiourea were obtained from column equilibrium experiment, the results are shown in Figures 58 and 59. It was found that the flow rate of 0.5 ml/min gave a better separation result of cobalt(II) and lead(II) than others flow rates. At this flow rate, lead(II) was well eluted from column but cobalt(II) was adsorbed in column at the first 26 ml.



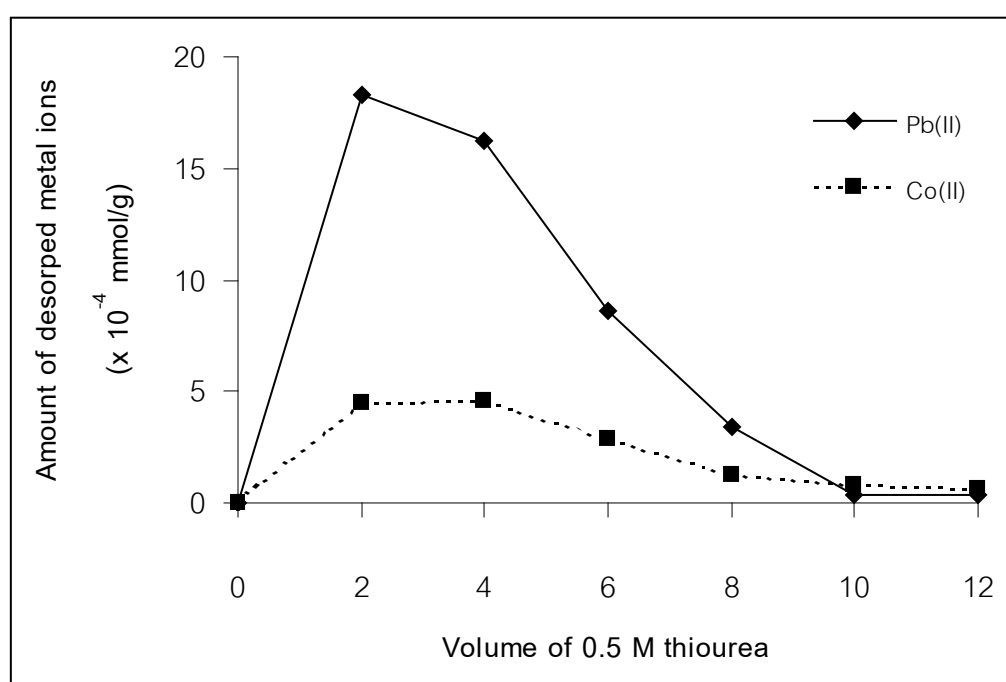
**Figure 58** Efficiency of the desorption of lead(II) from P-TAC by 0.5 M thiourea (column equilibrium experiment).



**Figure 59** Efficiency of the desorption of cobalt(II) from P-TAC by 0.5 M thiourea (column equilibrium experiment).

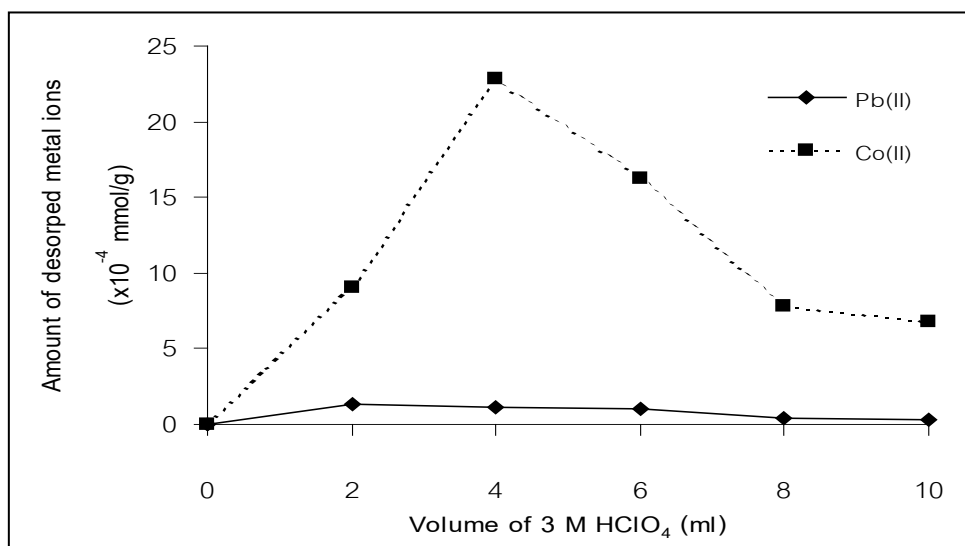
### 10. Using P-TAC for the separation of cobalt(II) and lead(II)

From the previous study, the separation of cobalt(II) and lead(II) were obtained by using two eluents, 0.5 M thiourea and 3 M perchloric acid. Firstly, the Co-Pb-P-TAC column was eluted by 12 ml of 0.5 M thiourea at flow rate 0.5 ml/min and followed by 10 ml of 3 M perchloric acid at the same flow rate. The results are shown in Figures 60 and 61.



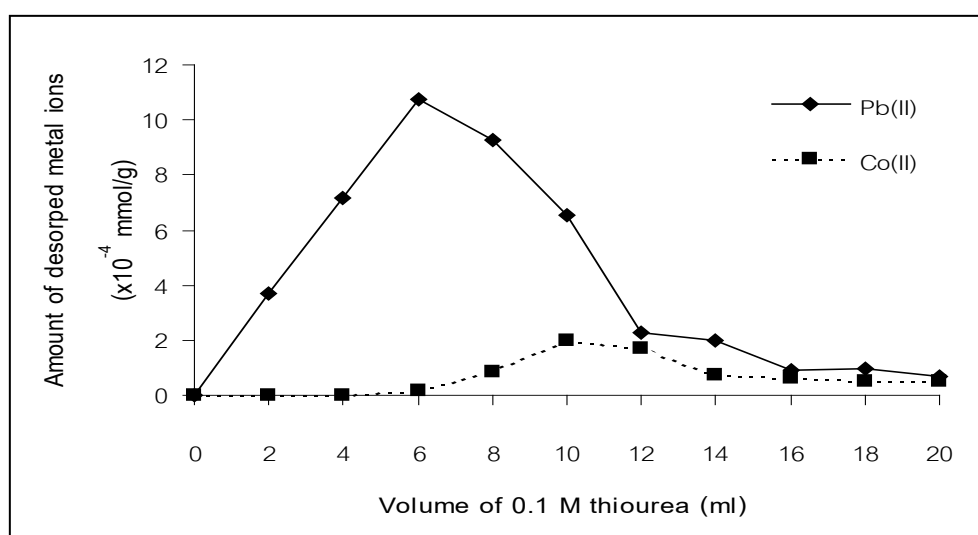
**Figure 60** Efficiency of the desorption of cobalt(II) and lead(II) from P-TAC by 0.5 M thiourea (flow rate 0.5 ml/min).





**Figure 61** Efficiency of the desorption of cobalt(II) and lead(II) from P-TAC by 3 M HClO<sub>4</sub> (flow rate 0.5 ml/min).

From the results showed in Figure 60, It was found that 0.5 M thiourea could eluted both cobalt(II) and lead(II) at the same time. In order to separate the two metal ions from each other, 0.1 M thiourea was chosen as the eluent instead of 0.5 M thiourea. The result show in Figure 62 indicated that 0.1 M thiourea could partially separate lead(II) from the mixture of lead(II) and cobalt(II).

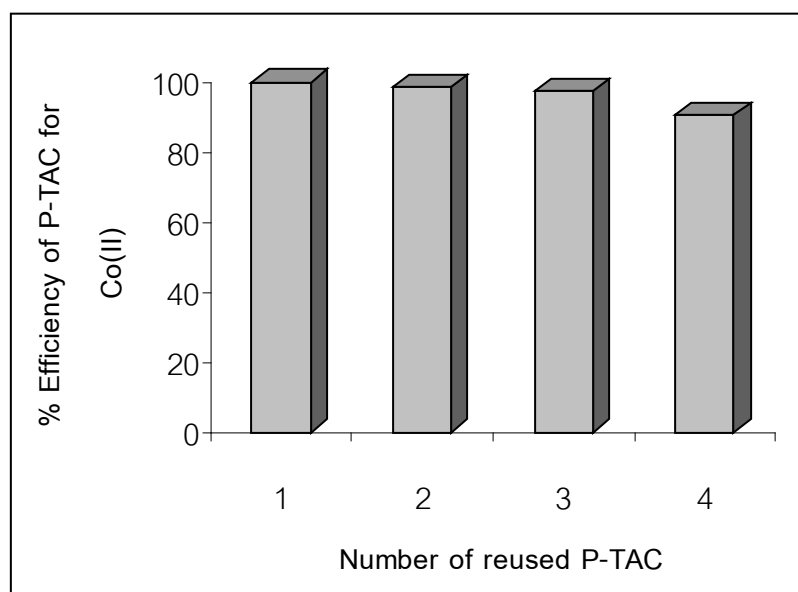


**Figure 62** Efficiency of the desorption of cobalt(II) and lead(II) from P-TAC by 0.1 M thiourea (flow rate 0.5 ml/min).

## **11. Efficiency of P-TAC on the adsorption of cobalt(II) and lead(II) by column equilibrium experiment**

### 11.1 Efficiency of P-TAC on the adsorption of cobalt(II)

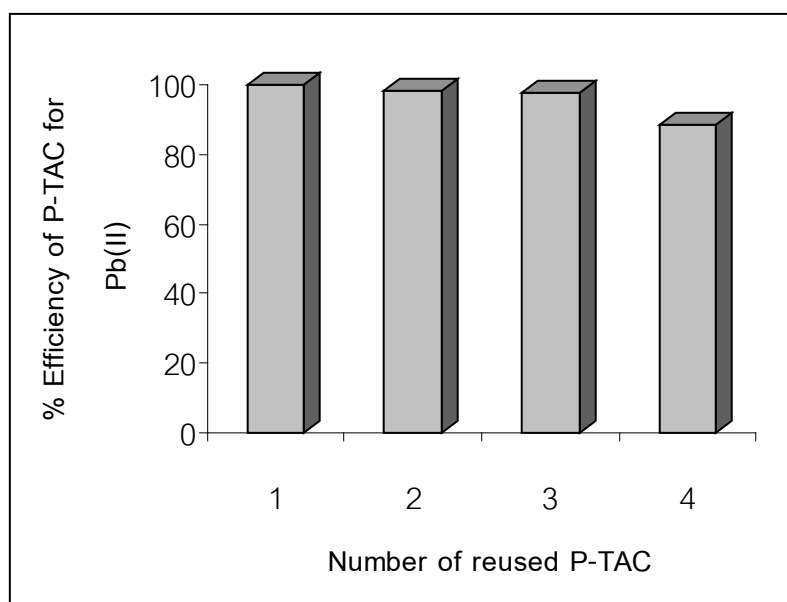
The efficiency of used-P-TAC for adsorption of cobalt(II) was determined by column equilibrium experiment. The results are shown in Figure 63. It showed that the P-TAC can be reused as adsorbent for cobalt(II), which could be eluted from P-TAC by 3 M perchloric acid, three times for adsorption capacity higher than 95%.



**Figure 63** The percentage of efficiency of P-TAC for the adsorption of cobalt(II) by column equilibrium experiment (P-TAC 50 mg, pH 7, initial concentration of cobalt(II) 125 ppm and shaking time 3 hours).

### 11.2 Efficiency of P-TAC on the adsorption of lead(II)

The efficiency of used-P-TAC for adsorption of lead(II) was determined by column equilibrium experiment. The results are shown in Figure 64. It showed that the P-TAC can be reused as adsorbent for lead(II), which could be eluted from P-TAC by 0.5 M thiourea, three times for adsorption capacity higher than 95%.



**Figure 64** The percentage of efficiency of P-TAC for the adsorption of lead(II) by column equilibrium experiment (P-TAC 50 mg, pH 5.5, initial concentration of lead(II) 100 ppm and shaking time 24 hours).

## CONCLUSION

2-(2'-thiazolylazo)-p-cresol (TAC) has been synthesized and characterized. The dissociation constant value ( $pK_a$ ) of TAC had been determined by the half height method and the limiting absorbance method which the calculated  $pK_a$  of TAC from both methods were approximately 8.6.

The complex formation of TAC with cobalt(II) and lead(II) were studied. TAC could form complex with cobalt(II) at pH 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0. At pH 5-8, the ratio of cobalt(II) : TAC was 1 : 2. At pH 9-10, the ratios of cobalt(II) : TAC were 1 : 1 in  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  buffer solution and 1 : 2 in  $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$  and  $\text{C}_4\text{H}_{11}\text{NO}_3/\text{HCl}$  buffer solutions. TAC could form complex with lead(II) at pH 6.0. The ratios of lead(II) : TAC was 1 : 1.

The structure of complexes between TAC and cobalt(II) and between TAC and lead(II) were determined. TAC might acted as tridentate ligand which had nitrogen atoms of 2-aminothiazole and azo group and oxygen atom of p-cresol as donor atoms.

A selective polystyrene-divinylbenzene sorbent containing substituted 2-(2'-thiazolylazo)-p-cresol (P-TAC) has been developed for selective sorption of cobalt(II) and lead(II) from aqueous solution. The optimum conditions of P-TAC for the adsorption of cobalt(II) and lead(II) were pH 7 and 5.5, initial concentration 125 and 100 ppm and shaking time 3 and 24 hours, respectively. The loaded P-TAC has been eluted by 3 M perchloric acid and 0.5 M thiourea for cobalt(II) and lead(II), respectively. The efficiency of P-TAC is good, the exchange capacity of the resin remain constant after three times of working cycles.

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**APPENDICES**

## APPENDIX A

### The theoretical value of element in TAC

Molecular formula of TAC is C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>SO. From molecular weight of TAC (219.267 g/mol), the percentage of elements of TAC can be determined as follow:

$$\begin{aligned} \text{Percentage of carbon} &= \frac{\text{number of carbon} \times \text{atomic weight of carbon}}{\text{Molecular weight of TAC}} \times 100 \\ &= \frac{10 \times 12.011}{219.267} \times 100 \\ &= 54.78\% \end{aligned}$$

$$\begin{aligned} \text{Percentage of hydrogen} &= \frac{\text{number of hydrogen} \times \text{atomic weight of hydrogen}}{\text{Molecular weight of TAC}} \times 100 \\ &= \frac{9 \times 1.008}{219.267} \times 100 \\ &= 4.137\% \end{aligned}$$

$$\begin{aligned} \text{Percentage of nitrogen} &= \frac{\text{number of nitrogen} \times \text{atomic weight of nitrogen}}{\text{Molecular weight of TAC}} \times 100 \\ &= \frac{3 \times 14.007}{219.267} \times 100 \\ &= 19.16\% \end{aligned}$$

$$\begin{aligned} \text{Percentage of sulfur} &= \frac{\text{number of sulfur} \times \text{atomic weight of sulfur}}{\text{Molecular weight of TAC}} \times 100 \\ &= \frac{1 \times 32.066}{219.267} \times 100 \\ &= 14.62\% \end{aligned}$$

$$\begin{aligned}\text{Percentage of oxygen} &= \frac{\text{number of oxygen} \times \text{atomic weight of oxygen}}{\text{Molecular weight of TAC}} \times 100 \\ &= \frac{1 \times 15.999}{219.267} \times 100 \\ &= 7.297\%\end{aligned}$$

## APPENDIX B

### **Determination of amount of TAC immobilized on of chloromethylated polystyrene divinylbenzene**

Elemental analysis of P-TAC was found that, there are 83.95% carbon, 8.195% hydrogen, 4.463% nitrogen and 0.549% sulfur. Molecular formula and molecular weight of TAC are  $C_{10}H_9N_3SO$  and 219.268, respectively. Chloromethylated polystyrene divinylbenzene was composed of carbon, hydrogen and chlorine elements. From %sulfur, the weight of TAC coated on chloromethylated polystyrene divinylbenzene can be calculated as follow:

$$\text{The amount of TAC in the P-TAC} = \frac{219.268 \times 0.549}{32.066} = 3.754 \text{ g or } 17.12 \text{ mmol}$$

The weight of chloromethylated polystyrene divinylbenzene is  $100 - 3.754 = 96.246$  g. Therefore, the amount of TAC per 1 g of chloromethylated polystyrene divinylbenzene is 0.178 mmol/g.

## APPENDIX C

### Methods applied to determine the dissociation constant (pK<sub>a</sub>) of TAC

#### 1. Half Height Method (Masoud, 2003)

At a constant wavelength, the pK value of the compound can be evaluated (where half of the compound exists in the ionized form and the other half in the non-ionized). It is known that:

$$\text{pH} = \text{pK} + \log \gamma + \log \frac{A_s}{A_{s_{\max}} - A_s}$$

( $\gamma$  = activity coefficient term and controlled by ionic strength of a supporting electrolyte)

Where  $A_s$  is the absorbance of the solution at given pH ;  $A_{s_{\max}}$  the absorbance of the solution when the total amount of reagent is in the form  $H_nA$ .

An example, Appendix Figure 1 shows Absorption spectra of  $4 \times 10^{-5}$  M of p-Cl-phenylazo-R-acid in aqueous solution of varying pH values. Changes in the absorption spectra at various pH values were followed.  $\log \frac{A_s}{A_{s_{\max}} - A_s}$  has approximate value by absorbance, so that the relationship of absorbance and pH can plotted at various wavelength. The pK<sub>a</sub> was obtained form the interception of lines. The results are shown in Appendix Figure 2 (a).

#### 2. Limiting Absorbance Methods (Masoud, 2003)

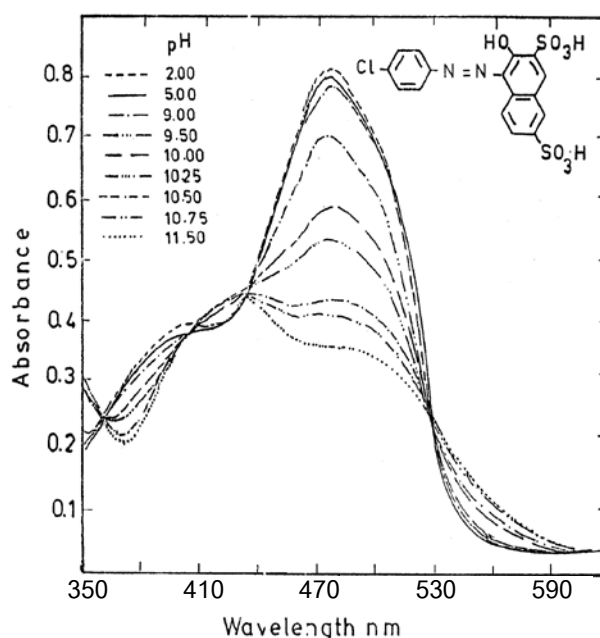
For an organic compound of formula  $H_nA$ , the first ionization for the ligand takes place as follows:



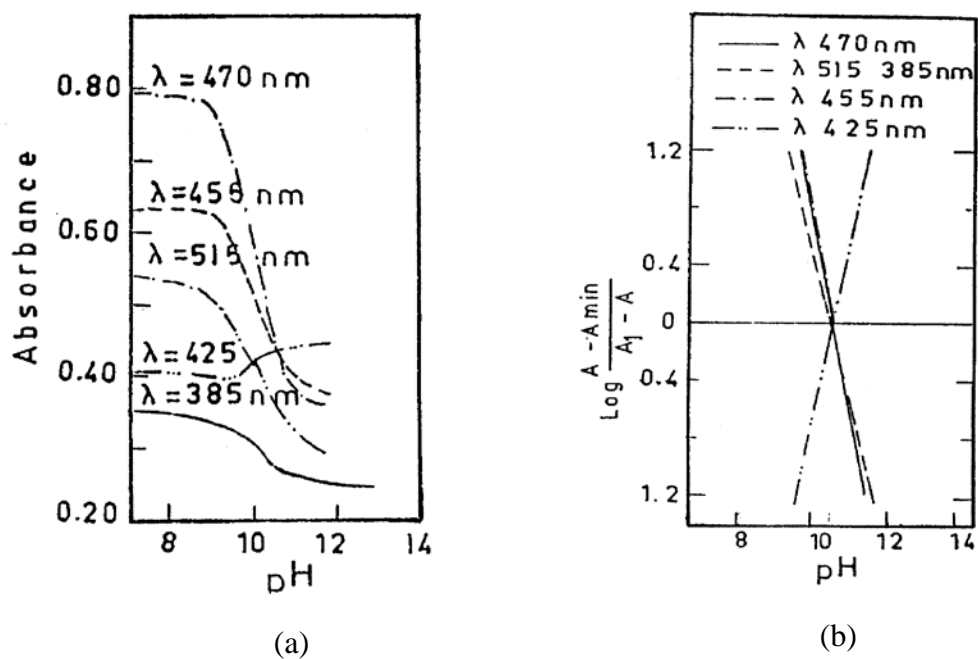
$$\text{pH} = \text{pK}_1 + \log \gamma + \log \frac{A_s - A_{s_{\min}}}{A_{s_{\max}} - A_s}$$

Where  $A_s$  is the absorbance of the solution at given pH ;  $A_{s_{\min}}$  the absorbance of the solution when the total amount of reagent is in the ionized form  $H_{n-1}A^-$  ;  $A_{s_{\max}}$  the absorbance of the solution when the total amount of reagent is in the form  $H_nA$ .

Changes in the absorption spectra at various pH values were followed . The absorbance at more characteristic wavelengths was measured as a function of the pH value. The relationship of  $\log(\text{absorbance})$  and pH can be plotted. The  $\text{pK}_a$  was obtained from the interception of lines. The results are shown in Appendix Figure 2 (b).



**Appendix Figure C1** Absorption spectra of  $4 \times 10^{-5}$  M of p-Cl-phenylazo-R-acid in aqueous solution of varying pH values.



**Appendix Figure C2** (a) Absorbance-pH curves (half height method)  
 (b)  $\text{Log}(A - A_{\text{min}})$ -pH curves (limiting absorbance method)