

A Mini Anion Exchange Column for the Separation of Cobalt and Nickel

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Tygon tubings with internal diameters of 1.00 and 1.25 mm respectively were packed with anion-exchange resins, Dowex-1X8 (200 mesh), at resin lengths of 15-, 20-, 25- and 30-cm. Each packed tygon tubing served as mini anion exchange columns to separate a mixture of nickel and cobalt using 9 M and 4 M HCl as eluents. Flow rates were optimized to achieve efficient separation of the two metals which were detected as $\text{Ni}(\text{DMG})_2$ and $[\text{Co}(\text{SCN})_4]^{2-}$ at 435 and 625 nm, respectively.

An optimized column was found to have an internal diameter of 1.25 mm, column resin length of 25 cm, flow rates of 0.376 mL/min (9 M HCl) and 0.448 mL/min (4 M HCl), and a volume capacity of 1.00 mL. This column was tested in the separation of nickel and cobalt in two sets of synthetic samples (SS-I and SS-II) and a wastewater laboratory sample giving acceptable percentage recoveries except for the low concentration level of cobalt (< 10 ppm). The study shows that the tygon mini column shows potential for the separation and analysis of the two metals.

Keywords: anion-exchange, cobalt, nickel, ion-exchange column

INTRODUCTION

Cobalt and nickel, belonging to the late transition metals, are said to be inseparable in nature due to their similarity in characteristics and properties. Evidence of their association is found in their minerals such as skutterudite, smaltite, chloanthite and ferro-arsenite. The inseparability of cobalt and nickel is also evident in the manufacture of various metal alloys. It is known that compared with nickel only, alloys of nickel and cobalt are harder and stronger. Electroplating solutions used in the manufacture of fashion accessories are also

known to contain varied proportions of the two metals.

The analytical determination of cobalt and nickel presupposes that a separation is accomplished prior to any spectrophotometric detection. Since they are oftentimes associated with each other, a separation technique is ideal in order to facilitate its measurement in varying sample matrices. A number of separation mechanisms have been proposed for the two metals, one of which is anion-exchange chromatography. In 9 M HCl, cobalt exists as an anionic chlorocomplex, CoCl_4^{2-}

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while nickel exists as a cation, Ni^{2+} (or NiCl^+). Elution of the two metals can be achieved by 9 M HCl for nickel and 4 M HCl for cobalt, 70% acetone-30% 2 M HCl, 90% acetone-10% 6 M HCl as solvent medium for the two metals [1] and 2 M NH_4Cl in dilute ammonia solution using malonic acid solution with sodium nitrite as the solvent medium [2].

Conventional anion exchange separation of nickel(II) and cobalt (II) utilizing wide bore glass columns (burette) and gravity elution is time consuming. This is due to two major reasons; first, optimum flow rate is difficult to attain and secondly, the elution is very slow. Moreover, the conventional method of detection is carried out by volumetric methods that make use of toxic chemicals such as pyridine, a reagent known to cause urinary ailments.

Bahowick and Synovec implied that the use of short columns (3.2 mm i.d. x 3, 7.5, 15, 20 and 50-cm length) in chromatography increase the precision of qualitative analysis [3]. Columns with dimensions of (1.0 cm i.d. x 8 cm) and (2 mm i.d. x 3 cm) have also been utilized for the analyses of anions and metals [4-5], preconcentration [6] and removal of interferences [7-9]. Column packings vary from Dionex ion exchange resins, Sephadex, and Dowex-1 anion exchange resins [3-7]. Amberlite IRC 748 ion exchanger with imidoacetic acid group was used for the selective removal of Ni and Co from a high pressure acid leach solution of a Brazilian laterite nickel ore [10].

This study intends to develop a mini-anion exchange column with the following starting features; tygon tubings with internal diameters of 1.00 and 1.25 mm packed with anion-exchange resins as separation columns, a laboratory-reconditioned peristaltic pump to semi-automate the elution and separation process, varied resin length of the column to obtain optimum elution, varied flow rates of the acid eluents to obtain optimum separation of cobalt and nickel. Measures of separation efficiency were carried out by detection of nickel as the dimethylglyoxime complex and cobalt as the thiocyanate complex in the effluent by visible spectrophotometry.

EXPERIMENTAL

Materials and Equipment

Working Standards of Ni(II) and Co(II)

Solutions. Separate solutions of Ni(II) and Co(II) with a concentration of 100 ppm each was made. This was prepared by dissolving 0.0495 g of $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$ (APS, AR) in 9 M HCl (APS, AR) in a 100-mL volumetric flask and diluted to the mark with 9 M HCl. The same procedure was carried out for the preparation of the Co(II) solution using 0.0494 g of $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (APS, LR). These solutions were used in generating calibration curves.

Synthetic Sample I (SS-I). A Ni(II) and Co(II) mixed solution, which is 500 ppm in each metal, was prepared by dissolving 0.1239 g of $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.1235 g of $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in a small amount of 9 M HCl. This was transferred into a 50-mL volumetric flask and diluted to the mark using 9 M HCl.

Synthetic Samples II (SS-II). Ni(II) and Co(II) mixed solutions of about 400, 100, and 10 ppm in each metal, were prepared from SS-I.

Dimethylglyoxime (DMG) Solution. The dimethylglyoxime solution was prepared by dissolving 0.10 g of A.R. grade DMG (Ajax) in 100 mL of 95 % ethyl alcohol.

Ammonium Thiocyanate Solution. This was prepared by dissolving ammonium thiocyanate in distilled water with a ratio of 4 g NH_4SCN (Merck, AR) in 7 mL distilled water.

Bromine Water. This was done by saturating the desired amount of distilled water with bromine (Merck, AR).

Other Materials. Other chemicals used were 9 M and 4 M HCl solutions, 15 M NH_4OH , 95 % ethyl alcohol (technical grade), and acetone (Merck, AR). Tygon tubings (1.00 mm i.d. and 1.25 mm i.d.), Dowex 1 X8, 200 mesh (Sigma), and glass wool were also used. Equipment included a UV-Vis 1601 double beam spectrophotometer (Shimadzu) and a peristaltic pump (reconditioned from an old flow injection analyzer).

Preparation of the Mini Anion-Exchange Columns

Two sets of tygon tubings with internal diameters of 1.00 and 1.25 mm were prepared. With the use of a long thin wire, an ample amount of glass wool was inserted into the mini columns, until it reaches about 1-cm away from one end of the column. The amount of glass wool used was just enough to support the anion exchange resins and should not cause clogging of the columns. These columns were then installed and positioned vertically in the cartridge of the peristaltic pump. The screw supporting the cartridge of the pump was tightened lightly, applying just enough pressure to allow water to be propelled through the columns.

An appropriate amount of Dowex 1X8 (200-mesh) was placed in a 100-mL beaker and distilled water of about ten times the amount of the resin was poured in carefully with continuous stirring. The resin mixture was stirred for about a minute, allowed to stand for 30 minutes with occasional stirring until the resin swelled completely. The slurry was pumped into the columns until the desired column length was obtained. Columns were packed initially using 15, 30 and 45-cm resin lengths for both sets of tubings. A total of six mini anion exchange columns were prepared.

With the use of the peristaltic pump, 10 mL of 9 M HCl was introduced into the column to allow the resin to attain its chloride exchange complex. This was followed by washing with 10 mL of distilled water. Air was not allowed to get into the column since it would cause an error in the exchange of the metal chlorocomplex with that of the resin.

Preliminary Characterization of the Mini Columns

Qualitative Tests. One of the mini columns (1.00 mm x 30 cm) was used for this test. A 1.00 mL mixed metal solution was propelled into the column, followed by 5 mL of the 9 M HCl. The acid effluent was collected and a spot test for nickel and cobalt was conducted. About 5.0 mL of the 4 M HCl was propelled through the mini column and the effluent was collected. Spot tests for the two metals were again conducted on the 4 M effluent.

For the spot test of nickel, a drop of 9 M effluent was added to 1.0 mL water containing 5 drops of 5 M NH_4Cl . This was then followed by 3 drops of 6 M NH_4OH and 2 drops of 1% DMG. The formation of a red precipitate is a positive result for the presence of nickel. The spot test for cobalt was carried out by adding 1 mL of water, 5 drops of 5M NH_4Cl and 2 drops of 15M NH_4OH to 5 drops of the acid effluent. The resulting solution was then added with 10 drops of 1% DMG. The formation of a brown precipitate is a positive result for the presence of cobalt.

Volume Capacity of the Columns. The same column used for the qualitative tests was used in determining the typical volume capacity of the mini columns. The column was washed with distilled water until the effluent was neutral to methyl orange. A known amount of the acid influent (9 M HCl), measured out in a graduated cylinder was propelled into the column and collected into a vial containing methyl red indicator. The first drop of effluent which causes a color change from yellow to red indicates that the acid has already filled the column. When this was achieved, the pumped was turned off and the remaining amount of acid was measured.

Flow Rates of the Acid Eluents. All mini columns were washed with distilled water, followed by 5 mL of the acid. With a known initial volume of acid in the receiver (10-mL graduated cylinder), the acid influent was pumped into the column for one minute. The pump was turned off and the resulting amount of effluent was then recorded. The final volume of effluent was subtracted from the initial reading and divided with time. The resulting flow rate was expressed in mL/min. This procedure was done 10 times for each acid and the average flow rate obtained was used in succeeding analyses.

Separation of Binary Mixtures of Nickel(II) and Cobalt(II)

About 5.0 mL of 9 M HCl was first pumped into the column followed by an appropriate volume of a known concentration of a mixture of the two metals. This was done by placing the inlet of the tubing into the 10-mL graduated cylinder with a known amount of the 500 ppm mixed solution of

Ni(II) and Co(II). The pump was turned on, the solution was propelled through the column and the volume of the solution was monitored. When the metal solution was siphoned out, the pump was turned off.

After the sample was propelled through the column, a 25.0 mL volumetric flask was placed at the outlet of the tubing to serve as the receiver for the nickel effluent. About 5.0 mL of 9 M HCl was introduced into the column using the same procedure when the sample was pumped into the columns. After 5.0 mL was completely propelled through the column, the pump was turned off. The influent was replaced with 4 M HCl and the receiver was replaced with another 25.0 mL volumetric flask. The acid was propelled through the column and collected. The two flasks were diluted to the mark with distilled water and set aside for the analysis of nickel and cobalt.

Analyses of Metals in the Acid Effluents

Analysis of Nickel (II) in the 9 M HCl effluent.

A 2.0-mL aliquot of the nickel effluent was placed in a 25-mL volumetric flask. This was added with 6.25 mL of 1M HCl, 1.25 mL bromine water, 2.50 mL of concentrated NH_4OH , 5 mL of the DMG reagent, and 5.0 mL 95% ethanol. It was then diluted to the mark with distilled water. It must be noted that after the addition of concentrated NH_4OH , the DMG reagent must be immediately added in order to detect a color change from colorless to red. After 10 minutes, its absorbance was measured at 445 nm using a reagent blank as its reference.

Analysis of Cobalt(II) in the 4 M HCl effluent.

A 5.0-mL aliquot of the cobalt effluent was used in the determination of its concentration. The 5-mL aliquot was placed in a 25-mL volumetric flask. About 12.5 mL of neat (100%) acetone and 2 mL NH_4SCN solution were added and shaken vigorously to ensure mixing and diluting to the mark with distilled water. Its absorbance was measured at 625 nm, using a reagent blank as its reference.

Preparation of an External Calibration

Curve. Standards of 0.50, 1.00, 1.50, 2.00, and 2.50 ppm of Ni(II) was used in generating the calibration curve. On the other hand, 0.50, 1.00,

1.50, 2.00, 3.00 ppm of Co(II) was used in making its calibration curve. The range of calibration standards were based on the expected concentration of both metals.

Optimization of Flow Rates of the 9 M and 4 M HCl

The mini columns with the highest percentage recovery were subjected to further optimization with respect to flow rates within the range of ± 0.10 mL/min of the values obtained in the preliminary work. The flow rates were varied by manually adjusting the pressure applied to the tubing in the set-up.

Separation of Metals in Synthetic Samples (SS-II) and Laboratory Wastewater Sample using the Optimized Mini Column

The optimized mini column was used for the separation of the two metals in the prepared synthetic samples to verify the accuracy and reproducibility of the method. The volume of the optimized column was also determined as described earlier to increase the size of the sample, hence, increasing the sensitivity and detection limit for both Ni(II) and Co(II) in the synthetic and real sample. The same procedure was followed in separating the two metals, as well as their detection.

The waste water that was generated during the optimization was determined for the amounts of Ni(II) and Co(II) present. This was considered as the real wastewater sample. A 2.0-mL aliquot was dissolved in a 25.0-mL volumetric flask with 9 M HCl. The same procedure for the separation of the two metals was followed as well as the determination of the concentrations of nickel and cobalt.

Regeneration of the Column

The column was regenerated by allowing 20.0 mL of 0.5M HCl to pass the column, followed by washing with distilled water until the effluent was neutral to methyl red. The glass wool at the outlet of the tubing was removed and the resin was allowed to flow until all of it has been pumped out. The resin was collected in a 50-mL beaker and the slurry was filtered. The resin was air-dried and the resin was kept for further use.

RESULTS AND DISCUSSION

Three parameters affect the results of the anion-exchange separation of cobalt(II) and nickel(II) in aqueous solutions. These are the internal diameter of the tygon pump tubing, the column resin length, and the flow rate of the acid eluent. In this study, two sets of tygon pump tubings with internal diameters of 1.00 mm and 1.25 mm were utilized. The length of each tygon tubing available for column packing was 50-cm which allows the study of column resin lengths of 15-, 30- and 45-cm [3]. A variable revolutions-per-minute (rpm)-peristaltic pump was used, allowing variable flow rates of the acid eluents.

Preliminary Characterization of the Mini Columns

The qualitative analysis showed that nickel was detected only in the 9 M HCl effluent using the (1.00 mm x 30-cm) column and a 1.0 mL mixed metal solution. Cobalt, on the other hand, which is expected to be detected only in the 4 M HCl, was also detected in the 9 M HCl. This suggests that the separation process was not good and implies that the amount of sample introduced into the column may have exceeded the column capacity. Indeed, the volume capacity of the same mini column was determined to be only 0.93 mL of the sample (rsd = 0.70%, $n = 3$). The sample size of 1.00 mL used in the qualitative tests exceeded the column's volume capacity and therefore could account for the Co (II) detected in the 9 M HCl. In succeeding experiments, the sample size was thus reduced to 0.50 mL.

The average flow rate of the acid eluents in the qualitative tests using the (1.00 mm x 30-cm) mini column was measured to be 0.301 mL/min ($n = 10$). On the other hand, the 15-cm and 45-cm mini columns showed average flow rates of 0.561 mL/min and 0.154 mL/min ($n = 10$), respectively. The latter was too slow for the intended analysis. A total of eight columns were available for succeeding tests as described in Table 1. Figure 2 shows the effect of inner diameter, flow rate, resin length and acid concentration for all mini columns. As expected, the flow rates increased as the inner diameter increased and the column resin length decreased.

Also, the flow of the acid through the mini column was reduced by the interaction of chloride ions with the resin. Thus, the flow rate for the 9 M HCl is slower than that for the 4 M HCl which contains less concentration of chloride ions [11].

Table 1. Physical Characteristics of the Tygon Tubings used as Mini Columns

Code	Color	Internal Diameter (mm)	Column Resin Length (cm)
A	red/red	1.00	15
B	red/red	1.00	20
C	red/red	1.00	25
D	red/red	1.00	30
E	grey/grey	1.25	15
F	grey/grey	1.25	20
G	grey/grey	1.25	25
H	grey/grey	1.25	30

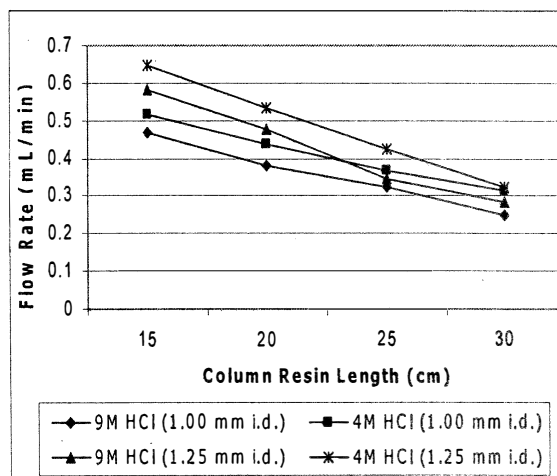


Fig. 2. Flow Rates of 9 M and 4 M HCl in 1.00 and 1.25 mm i.d. mini anion exchange columns at varying column resin lengths

Choosing the Optimum Mini Column

The optimum column was chosen based on the percentage recovery of the two metals from the synthetic samples and the results from the optimization of flow rates.

A 0.50 mL binary mixture of 500 ppm each of cobalt and nickel was passed through all eight

mini columns using the flow rates shown in Figure 2. The effluents were analyzed for cobalt as the thiocyanate complex and nickel as the dimethylglyoxime complex. Figure 3 shows that all mini columns gave acceptable % recoveries of the metals in the appropriate acids, ranging from 86.9 % to 108.3%. However, cobalt was also detected in the 9 M HCl effluent for most of the mini columns except for Column G (Figure 4). This indicates that the separation was still not very efficient and remained unsuitable for the intended analysis. Two columns which showed relatively high % recovery for both metals and at the same time exhibited low % cobalt in its 9 M HCl effluent (Columns B and G in Figures 3 and 4) were subjected to further optimization with respect to the flow rates of both acid eluents.

The flow rates of the 9 M and 4 M HCl in Column B were 0.382 and 0.436 mL/min, respectively and for Column G, 0.346 and 0.426 mL/min, respectively. It will be recalled that these values were used as starting flow rates in the analysis of synthetic sample I (SS-I). In order to improve column efficiency, these flow rates were adjusted at increments of ± 0.10 mL/min (Table 2). Generally, for Column B, as the flow rate was increased, the % recovery of the metals decreased as shown in Table 2. For Column G, the % recoveries for both metals peaked at a flow rate of 0.376 mL/min with recoveries of 103.31 % for Ni (II) and 100.02 % for Co (II). Column G has a longer column packing than Column B and therefore offers better column efficiency. The excess percentage nickel after optimization of flow rates is attributed to traces of cobalt in the 9 M HCl effluent which may have been detected as the dimethylglyoxime (DMG) complex [12].

Early on, it was suggested that the exact volume capacity of the column should be determined so as to discount the fact that any Co (II) detected in the 9 M HCl arise from overloading of the column. Thus, Column G was analyzed for its volume capacity. The result showed an average volume capacity of 1.43 mL with % rsd of 0.70 ($n = 3$). In succeeding experiments however, it was decided that 1.00 mL sample size would be used for the separation of the two metals. This was a compromise between a sample size which could lead to overloading of the mini column and a

sample size which would be just enough when used for dilute samples.

In summary, the optimized mini column G is thus described as having an internal diameter of 1.25 mm, column resin length of 25 cm, flow rates of 0.376 and 0.448 mL/min for the 9 M and 4 M HCl, respectively, and a volume capacity of 1.00 mL.

The results of this study show that column lengths ranging from 15-25 cm using very narrow tubings (1.00 and 1.25 mm) are feasible for the separation of metals as demonstrated in the synthetic samples. In the literature, others have used columns with inner diameters ranging from 2 mm to 10 mm and column lengths of 3 cm to 50 cm [3-9].

Table 2. Percentage Recovery of Ni (II) and Co (II) at Varying Flow Rates for Mini Columns B and G Using SS-I

Column	Flow Rates (mL/min)	% Recovery Ni (9M HCl)	Flow Rates (mL/min)	% Recovery Ni (9M HCl)
B (1.00 mm x 20-cm)	0.306	103.82	0.331	94.42
	0.412	95.03	0.453	86.71
	0.516	95.55	0.538	91.43
G (1.25 mm x 25-cm)	0.221	91.41	0.247	88.29
	0.376	103.31	0.448	100.02
	0.429	90.89	0.529	75.70

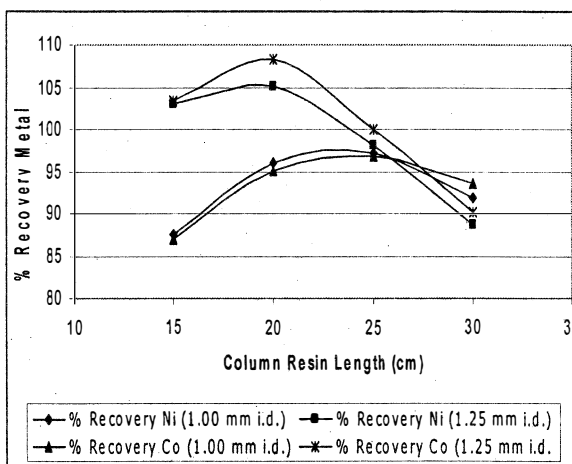


Fig. 3. Percentage Recovery of Metals Using Synthetic Samples I

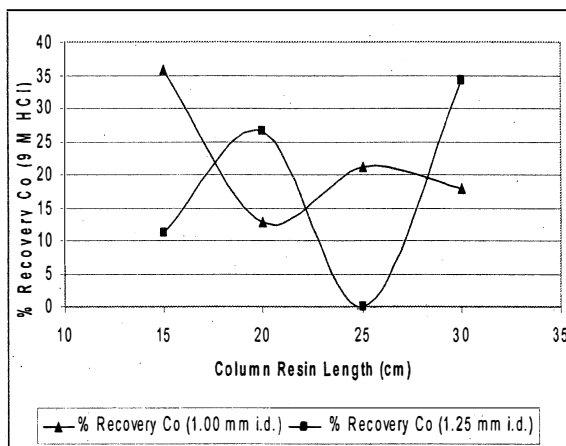


Fig. 4. Percentage Recovery of Co (II) in the 9 M HCl using SS I

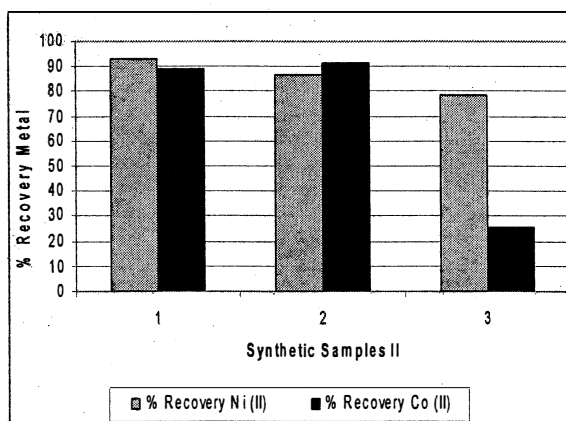


Fig. 5. Percentage Recovery of Ni (II) and Co (II) in the 9 M and 4 M HCl using SS II

Use of the Optimum Mini Column on SS II and a Real Wastewater Sample

Further tests were done using the optimum column for the analysis of Ni(II) and Co(II) in three different synthetic samples and a real wastewater sample.

Three synthetic samples (SS-II) of metal concentrations (ca. 400, 100 and 10 ppm) less than that for SS-I (500 ppm) were prepared. The percentage recoveries of the samples are shown in Figure 5. The calibration curves used in the analysis are shown in Figure 6 with calibration sensitivities of 0.228 and 0.0304 for nickel and cobalt, respectively. The percentage recoveries ranged from 78.63 % to 93.07 % (rsd of 0.79 to

10.41% , $n = 3$) for nickel and 25.43 % to 94.52% (rsd of 0.45 to 13.4 % , $n = 3$) for cobalt. The recoveries for nickel from all the synthetic samples were acceptable. However, SS-II-3 which contained 10 ppm cobalt had a % recovery of only 25.43 %. The absorbance reading for the cobalt complex from SS-II-3 (0.005, $n = 2$) was 2.8 times lower compared with the Ni(DMG)₂ absorbance of 0.014 ($n = 2$). This suggests that at low concentrations, there is a need for better detection chemistry for cobalt, which may be as the dimethylglyoxime complex like Ni [12] or as thiocyanate complex.

The mini column was used to separate the two metals from the wastewater generated during the development of the mini column. The results yielded 13.04 g/L Ni and 11.84 g/L cobalt. The high concentrations of nickel in the analysis of the real sample were already anticipated since the wastewater analyzed was a pooled wastewater generated during the method development. These observed metal chloride loadings on anion exchange columns are consistent with the findings of Wassink et al. [13].

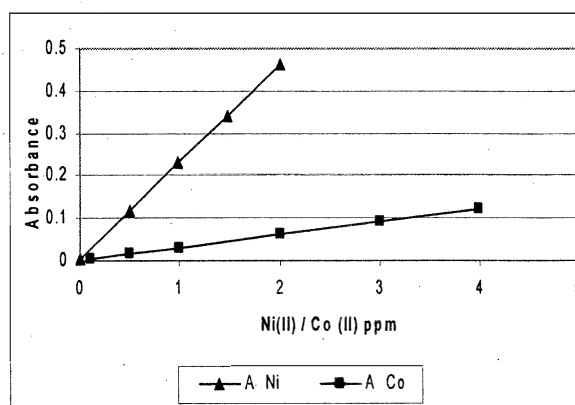


Fig. 6. Calibration Curves for the Analysis of Ni (II) and Co(II), characterized as follows:

$$A = 0.2282 [\text{Ni (II)}] + 0.00512; R^2 = 1.0000$$

$$A = 0.03044, [\text{Co (II)}] + 0.00065; R^2 = 0.9998$$

CONCLUSIONS

A tygon tubing mini anion-exchange column for the separation of Ni(II) and Co(II) was shown to have potential for the separation of nickel and cobalt at concentration levels greater than 10 ppm. The detection method needs to be further

modified in order to improve the percentage recovery of cobalt at lower concentrations.

Tygon tubings as mini columns provide better options as anion exchange columns especially when used in flow analysis. The use of tygon tubing as ion chromatographic column is scarce although it has several advantages over conventional glass chromatographic columns. The tubings are flexible and inert to organic solvents, concentrated acids, and bases. They are easy to store, easy to pack with resins and can be cleaned rather quickly. Moreover, the time to accomplish separation of two metals may be decreased and the results are obtained with high precision unlike the conventional gravity-elution method wherein good precision is very difficult to achieve and may take days, during which the flow rates may also have varied. The tygon tubing ion chromatographic column used in conjunction with a peristaltic pump delivers liquid reproducibly since the pump can be adjusted to maintain constant flow rates which may be optimized for a variable rpm-pump. The tygon tubings are robust and can be easily installed in any analytical systems especially for flow analysis [6-9, 14-15].

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