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New TLC System for Simultaneous Separation of Iron, Cobalt, and Nickel Ions from Acidic and Ammoniacal Solutions

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ABSTRACT

A new layer material consisting of stannic arsenate gel mixed with silica gel G was developed and utilized for normal-phase and reversed-phase thin-layer chromatography (TLC) of metal ions. The analytical potential of tri-n-butylphosphate (TBP) as impregnant as well as eluent has been exploited. Separation of coexisting nickel, cobalt, and iron ions from acidic and ammoniacal solutions on stannic arsenate silica gel G (10:1 w/w) mixed sorbent layers impregnated with 0.2-M tri-n-butylphosphate in acetone and 1.0 M KSCN–5.0 M HCl–1.0 M NaCl (8:1:1) mobile phase is obtained. Effect of pH of sample, loading amount of analyte, and the presence of amines, phenols, and anions on the separation of Ni^{2+} from Co^{2+} was carried out to optimize the experimental conditions.

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The identification and separation of Ni^{2+}, Co^{2+}, and Fe^{3+} from distilled water, seawater, industrial wastewater, high-speed steel sample, and geological samples was achieved.

INTRODUCTION

Of the procedures used for the separation of inorganic ions, thin layer chromatography (TLC) is probably the most simple, low cost, and highly effective separation technique. Several workers have used TLC, in the recent past for the separation of inorganics and organometallics.[1–5] Soljic and Hrestak[6] reported the systematic qualitative analysis of cations on the basis of R_F values, spot colors, spot shapes, and number of spots detected on microcrystalline cellulose layers with particular chromogenic reagents. Some studies have focused on the separation of inorganic ions on sorbent layers impregnated with liquid ion-exchanger by elution with HCl–ammonium thiocyanate,[7,8] acidified LiCl, and mineral acids.[9–11]

T. Shimizu et al exploited an hydrochloric acid–ammonium thiocyanate medium for the separation of numerous inorganic ions from multicomponent systems on thin layers of cellulose derivatives.[12–14] An interesting study on the formation and chromatographic properties of thiocyanate complexes on alumina layers developed with HCl–thiocyanate–$SnCl_2$ mixture was reported.[15] Thin layers of silica gel impregnated with ammonium thiocyanate were used to study the chromatographic behavior of inorganic pollutants in formic acid–sodium formate media.[16] None of these studies refers to the separation of nickel from iron and cobalt or the separation of Fe (II) from Fe (III).

Several methods for the separation of Ni (II) from Co (II) and of Fe (II) from Fe (III) dealing with paper chromatography,[17,18] electrophoresis,[19,20] solvent extraction,[21,22] high-performance liquid chromatography,[23,24] voltammetry,[18,25] and ion-exchange chromatography,[26,27] have been reported, but little is known about the separation of these ions by TLC.

Separation of Ni (II) from Co (II) and of Fe (II) from Fe (III) performed by TLC so far was not as good as desired. The separation distances, average ΔR_F values (difference in R_F values of Ni and Co) achieved by Canic and Perisic-Janjic[28] on a maize starch layer with butanol–pyridine–diethylaniline–5-N HCl; by Soljic and Grba[29] on a cellulose layer with acetone–concentrated HCl–water (86:8:70); by Brinkman et al.[9] with phenylpyrazole–HCl systems; and by Mohammad[30] on silica gel layer with formic acid containing solvent systems were 0.17, 0.24, 0.35, and 0.47 respectively. The present method gives a ΔR_F value of 0.60, showing the formation of better resolved spots. In regard to Fe (II)–Fe (III) separation by TLC, only two reports are available.[31,32] It is, therefore, worthwhile to develop new TLC methods for the separation of these metal ions from natural and synthetic water and wastewater samples.

The present report is an attempt to develop a new TLC procedure for the separation of coexisting iron (II), iron (III), cobalt, and nickel ions on tri-n-butylphosphate (TBP) loaded layers comprising a mixture of silica gel and stannic arsenate gel using mixed inorganic solvent system containing hydrochloric acid, potassium thiocyanate, and sodium chloride as developer. The detailed study of the various factors influencing the separation of the iron–nickel–cobalt mixture was carried out. This work allows the application of reversed-phase TLC to the separation of nickel, cobalt, and iron from acidic and ammoniacal solutions. The method can be extended to the identification and separation of these ions in rock, alloy seawater, and electroplating wastewater samples.

EXPERIMENTAL

Apparatus

A TLC applicator (Toshniwal, India), glass plates (20 × 3 cm), glass jars (24 × 6 cm), and a digital pH meter CP901 (Electrode type-PC-22, ELICO, India) were used.

Chemicals and Reagents

Stannic chloride pentahydrate, sodium arsenate, silica gel ‘G’, tri-n-butylphosphate (TBP), acetone, potassium thiocyanate, sodium chloride, hydrochloric acid, ammonium sulfide, potassium ferrocyanide, 1,10-phenanthroline (CDH, India); dimethlyglyoxime, acetic acid (Qualigens, India) were used. All other reagents were also of analytical reagent grade.

Metal Ions Studied

Fe^{3+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, VO^{2+}, $UO_2{}^{2+}$, Zn^{2+}, Cd^{2+}, Ag^{+}, Pb^{2+}, Tl^{+}, Bi^{3+}, and Hg^{2+}.

Test Solutions

Chromatography was performed on 1% standard solutions (w/v%) of the chloride, nitrate, or sulfate salts of previously mentioned metal ions, except Fe (II), for which 1% ferrous ammonium sulfate salt solution with 3 mL of H_2SO_4 and diluted to 1 L was used.

Detection

Fe^{2+} was detected with 0.5% solution of 1,10-phenanthroline; Fe^{3+}, Cu^{2+}, VO^{2+}, $UO_2{}^{2+}$ were detected with 1% potassium ferrocyanide; Ni^{2+}, and Co^{2+} with 1% solution of alcoholic dimethylglyoxime; Zn^{2+} and Cd^{2+} with 0.5% dithizone in CCl_4; while Ag^+, Pb^{2+}, Tl^+, Bi^{3+}, and Hg^{2+} were detected with 1% ammonium sulfide solution.

Mobile Phases

The following solvents (EDTA, acid, and salt solutions were prepared in distilled water) were used as mobile phases:

M_1 = 1.0 M KSCN–5.0 M HCl–1.0 NaCl (8:1:1) v/v

M_2 = 0.10, 0.50, 1.0, and 2.0 M KSCN

M_3 = 1, 3, 5, 7 and 10 M HCl

M_4 = 0.10, 0.50, 1.0, and 2 M NaCl

M_5 = 0.001, 0.01, and 0.1 M EDTA

M_6 = Acetone

M_7 = Isobutyl methyl ketone (IBMK)

M_8 = Ethyl methyl ketone (EMK)

M_9 = Methanol

M_{10} = Butanol

M_{11} = Isopropanol

M_{12} = 1.0 M NH_4SCN

M_{13} = 1.0 and 2.0 M formic acid (FA)

M_{14} = DMSO–1.0 M FA and DMSO–2.0 M FA 1:1, 1:3, and 3:1 ratio v/v

M_{15} = DMSO–acetone (1:1)

M_{16} = 1 M NH_4Cl

M_{17} = 1 M LiCl

Stationary Phases

The stationary phases used for normal-phase and reversed-phase TLC are given below:

S_1 = Silica gel G

S_2 = Dried stannic arsenate ion-exchanger

S_3 = Dried stannic arsenate ion-exchanger silica gel G; 1:10, 10:1, 1:1 w/w

S_4 = Stannic arsenate gel–silica gel G in 1:10, 1:5, 1:1 ratio w/w

S_5 = Stannic arsenate gel–silica gel G 10:1 w/w

S_6 = S_5 impregnated with 0.1, 0.5, 1.0, and 2.0 M TBP in acetone

S_7 = S_5 impregnated with 0.2 M TBP in acetone

SYNTHESIS OF STANNIC ARSENATE ION EXCHANGER

Stannic arsenate ion-exchanger was prepared as reported earlier[33] by mixing 0.1-M solutions of stannic chloride and sodium arsenate in the volume ratio of 3:2 and digesting the resulting precipitate at 30°C for 24 hours. The gel so obtained is washed several times with dimineralized water. The gel is allowed to settle for 2 to 3 hours, then the excess water is drained off. This ion-exchanger gel was used after mixing with silica gel in different weight ratio as mixed sorbent phase.

To obtain a dried stannic arsenate ion-exchanger, the ion-exchanger gel is dried for 6 h at 80°C in an electrically controlled oven. Drying at higher temperature results in the reduction of ion-exchange capacity and at the lower temperature, drying requires a longer period. The completely dried gel was washed with double distilled water, which leads to cracking of the ion-exchanger into small granules of uniform size. The ion-exchanger is then kept in 1-M HNO_3 overnight to convert it into H^+ form. After decantation, the ion-exchanger in the H^+ form was washed several times with water to make it free from acid and dried at 80°C.

Preparation of Thin Layer Plates

Stannic Arsenate Gel Mixed with Silica Gel Plates

Stannic arsenate gel was mixed with silica gel G in 1:10, 1:5, 1:1, and 10:1 ratio (w/w) to make a homogeneous slurry in a glass mortar. This slurry was then spread over a clean glass plate (20 × 3 cm) by means of a TLC applicator (Toshniwal, India) to produce a 0.25-mm layer. The plates were air dried at room temperature and activated by heating at 100 ± 2°C for 1 h in an electrically controlled oven. After activation, the plates were cooled to room temperature and stored in a desiccator until use.

Plates of Pure Dried Stannic Arsenate Ion-Exchanger and Its Mixture with Silica Gel 'G'

TLC plates of pure dried stannic arsenate ion-exchanger and its mixture with silica gel G in 1:10, 10:1, and 1:1 ratio by weight were similarly prepared. For the preparation of TLC plates of pure stannic arsenate, approximately 50 g of dried stannic arsenate granules were mixed with 100 mL of distilled water. The mixture was ground vigorously in a glass mortar for half an hour to make homogeneous slurry. This step proved to be very important for proper adhesion. The resultant slurry, in the form of a fine uniform paste, was spread over the glass plates by TLC applicator to give a layer of 0.25-mm thickness. The plates were dried at room temperature and used as such. A set of such plates was activated at 100°C for 1 h but since slight cracking of coated ion-exchange material was observed, these plates were not found suitable for use.

To prepare TLC plates by coating dried stannic arsenate mixed with silica gel, silica gel G was mixed with stannic arsenate in 1:1, 1:10, and 10:1 weight ratio and the mixture was tritrated well in a mortar with double distilled water to make homogeneous slurry. The slurry so obtained was coated on glass plates to get a layer of 0.25-mm thickness. The plates were air dried at room temperature and activated at 100 ± 2°C for 1 h in an electrically controlled oven. The plates were kept in a desiccator until used.

Preparation of TBP Impregnated TLC Plates

The TLC plates prepared by coating a mixture prepared from stannic arsenate gel and silica gel G were impregnated with various concentrations (0.1 to 2 M) of TBP. The plates were impregnated by developing with a TBP solution of required concentration in acetone and dried at room temperature followed by activation at 100°C as in the previously mentioned case. A set of TLC plates was air dried and used without activation. After development, the detected spots on air-dried plates showed almost the same mobility, with slightly more diffused spots, compared to the spots on activated plates. Therefore, for obtaining more compact spots of metal ions, we used activated plates for further studies. The TLC plates of plain silica gel were prepared using the method reported earlier.[34]

Sample Preparation

Spiked Water

A 10-mL sample of distilled or drinking water was spiked with 1% solution of 5-mL Fe (III), 10 mL of Co^{2+}, and 5 mL of Ni^{2+} (i.e. 1:2:1 ratio v/v). The pH of this solution was 1.82. To 10 mL of this solution, we passed ammonia to obtain a precipitate of these metals. The precipitate was separated by centrifugation, washed several times with distilled water, dried, and dissolved in a minimum volume of concentrated HCl. To another part (10 mL) of the spiked water, we add 5 mL of glacial acetic acid.

Spiked Seawater and Industrial Wastewater

Seawater, 15 mL collected from Kovalam Beach, Kerala, India, was spiked with 9 mL of 1% $CoCl_2$ + 6 mL of 1% $NiCl_2$ + 3 mL of 1% $FeCl_3$ solutions. To 5 mL of this spiked seawater, we added 3 mL of pure acetic acid, while to another 5 mL of this sample, we added ammonia. A precipitate of metals so obtained was separated out by centrifugation, washed and dissolved in concentrated HCl.

Twenty mL of industrial wastewater (collected from electroplating unit) was spiked with 10 mL of 1% $FeCl_3$ and 20 mL of 1% $CoCl_2$ solutions. To 10 mL of this spiked sample, we added 5 mL of pure acetic acid and to another 10 mL, we added ammonia to obtain a precipitate, which was dissolved in concentrated HCl after separation from the bulk and properly washed with distilled water.

Spiked High-Speed Steel Sample

A part of the high-speed steel sample was dissolved in a mixture of concentrated HCl and concentrated HNO_3 (1:1 v/v). Ten mL of this solution was diluted to 20 mL with distilled water and spiked with 5 mL of 1% Ni^{2+} solution. To 5 mL of this spiked sample, we added 3 mL of pure acetic acid while to another 5 mL of spiked sample, we added ammonia. The precipitate of metals were separated out, washed, and dissolved in concentrated HCl.

Spiked Geologic Samples

To 10 mL each of the geological samples AgV_1 Basalt USGS (United States Geological Survey, U.S.) and GSP_1, were spiked with 2 mL of 1% $CoCl_2$ and 1 mL of 1% $NiCl_2$ solutions. To 5 mL of each spiked geological sample, we added 3 mL of pure acetic acid while to another 5 mL, we added ammonia. A precipitate of metals was obtained, which was separated out from the bulk, dissolved in concentrated HCl, digested by heating, and the residue was dissolved in 2 to 3 mL of distilled water for both the samples (AgV_1 and GSP_1).

Chromatography

Thin-layer chromatography was performed on TLC plates coated with unimpregnated and TBP-impregnated sorbent layers in 24 × 6 cm glass jars. Approximately 10 μL of standard test solutions were spotted separately on the TLC plates at 2 cm from the lower edge of the plate with the help of a micropipette. The spots were allowed to dry and then the plates were developed in the desired solvent system by the ascending technique, keeping the solvent ascent up to 10 cm from the point of application at room temperature (30°C).

After development, the plates were air dried at room temperature and the position of metal ions on the plates was identified by detecting the spots (1) as self-detected colored spots of Co^{+2} and Fe^{3+} and (2) by spraying the appropriate reagent as mentioned under the experimental section for the other metal ions. R_F values were determined for the metal ions from the values of R_L

(R_F of the leading front) and R_T (R_F of trailing front). Normal-phase TLC was performed on S_1 to S_5 stationary phases with a different solvent system, whereas reversed-phase TLC was carried out on layers of S_1, S_6, and S_7. The effect of the concentration of TBP (0.01 M to 2.0 M) as an eluent and as an impregnant was studied on S_5 stationary phase. The mobility of Ni^{2+}, Co^{2+}, Fe^{2+}, and Fe^{3+}, was investigated with varying concentrations of KSCN, HCl, and NaCl as mobile phase to select the proper solvent system for the four-component separation Ni^{2+}, $Co^{2+}-Fe^{2+}-Fe^{3+}$. The limit of detection of Ni^{2+}, Co^{2+}, and Fe^{3+} were determined by spotting 0.01 mL of cation solution of different concentrations on the chromatoplates, which were developed with 1-M KSCN, and the spots were visualized using appropriate detection reagent. This procedure was repeated with successive reductions of the concentration of the cation solution until no detection of the spot was possible. The minimum amount of metal salt just detectable in the solution was taken as the detection limit.

To study the effect of the pH of the test samples on the mobility and separation of metal ions, the pH of the standard solutions of the concerned metals or their mixture was brought to the required pH value by the addition of few drops of either dilute sodium hydroxide solution or dilute hydrochloric acid. The fixed volumes of Ni^{2+}, Co^{2+}, or Fe^{3+} solution, or their mixture in 1:1:1 ratio, was adjusted to different pH values and were applied on the TLC plates. The plates were developed with M_1 and the R_F values of the metal ions were calculated after detection.

For studying the effect of some anions, amines, and phenols on the separation of Ni^{2+} from Co^{2+}, synthetic mixtures containing Ni^{2+}, Co^{2+} and anion, amine, or phenol solution in 1:1:2 were prepared. The synthetic mixture solution was spotted on the chromatoplates and the plates were developed with 1-M KSCN. The R_F values of Ni^{2+} and Co^{2+}, were determined and compared with the standard R_F values obtained in the absence of additives.

To study the loading effect on the R_F values of Ni^{2+}, the fixed volumes of various standard solutions of the metal salts were spotted on the TLC plates with the aid of a micropipette. The plates were developed and M_1 and R_F values were calculated. To investigate the effect of mineral or carboxylic acids, 5.0-M HCl in M_1 was replaced by another mineral or carboxylic acid of the same strength. The separation of Ni^{2+}, Co^{2+}, Fe^{2+}, and Fe^{3+} was monitored on S_7. Similarly, to examine the separation possibility of $Ni^{2+}-Co^{2+}-$Fe (II)–Fe (III) separation in the presence of other salt solutions, 1.0-M NaCl in M_1 was substituted by 1.0-M solutions of NH_4Cl, $(NH_4)_2SO_4$, $NaNO_2$, $NaNO_3$, or LiCl. The four-component mixture was chromatographed on S_7. The R_F values of separated metal ions were recorded. For the identification of Ni^{2+}, Co^{2+}, and Fe (II) 0.01 mL of spiked water samples (acidic and ammoniacal) of seawater, industrial wastewater, geological sample, and high-speed steel sample solutions were spotted on TLC plates (S_7), developed with M_1, detected with the appropriate reagent, and the R_F values of separated metal ions were determined.

RESULTS AND DISCUSSION

The main features of this study are (1) the use of silica gel G mixed with stannic arsenate gel as layer material, for normal-phase and reversed-phase TLC; (2) the application of TBP as an impregnant as well as an eluent; (3) the separation of coexisting nickel, cobalt, and iron ions from acidic and ammoniacal solutions; (4) effect of pH of sample, loading amount of analyte, and the presence of amines, phenols, and anions on the separation of Ni^{2+} from Co^{2+}; and (5) the identification and separation of Co^{2+}, Ni^{2+}, and Fe^{3+} from distilled water, seawater, industrial wastewater, high-speed steel sample, and geological samples.

The normal-phase TLC with thin layers of pure stannic arsenate has been earlier used to get some interesting analytical separations.[35–37] However, in our case, the dried stannic arsenate ion-exchanger was found unsuitable for reversed-phase TLC since the plate made of pure dried stannic arsenate got deformed on impregnation with TBP. Even our efforts to utilize this dried ion-exchanger as a coating material after mixing with silica gel G failed, as the preparation of homogeneous slurry to obtain good quality plates was very difficult. Besides this, the use of inorganic ion-exchange materials as thin layers has the following main drawbacks:

1. The preparation of a dried ion-exchanger is a very slow and lengthy process.
2. The yield of ion-exchanger is low and a large quantity of ion-exchange material is required to prepare the TLC plates.
3. The time required for the development of the plate with most of solvent system is, generally, longer.
4. The inorganic ion-exchange materials are not well characterized.

Therefore we used the ion-exchanger in its gel form but since plates cannot be prepared with gel alone we added a sufficient quantity of silica gel G to obtain good quality, uniform, and stable plates. Thin layers prepared from a mixture of stannic arsenate gel and silica gel G in 10:1 ratio w/w, was found to be the most suitable stationary phase (S_5) for TLC of cations. This phase was selected for further studies using both normal-phase and reversed-phase techniques. Some useful TLC separations of inorganic ions on combined thin layers of stannic arsenate gel and silica gel using mixed organic[38] and buffer solutions[39] as mobile phases have been achieved by Husain et al. However, their studies were of a preliminary nature and suffer from the following limitations:

1. Comparative study on metal ions separation has not been examined.
2. The effect of anionic and organic impurities on metal ions separation has not been studied.
3. Separation of co-existing Ni (II), Co (II), Fe (II), and Fe (II) ions could not be achieved.
4. The method was not applied to real/synthetic environmental and geological samples.

Normal-phase TLC was performed on S_5 with several solvent systems (M_1 to M_{17}). It was observed that with the increase in length of carbon chain (C_1 to C_4) in alcohols, both development time and tailing of the spots of metal ions increased, while in case of ketones, and increase in the carbon chain length yields more compact spots, leading to the selective separation of Hg^{2+} in ethylmethylketone. In fact, several mobile phases were found suitable for normal-phase TLC but M_1 to M_4 and M_{16} yielded good results for reversed-phase TLC. Though TBP as an impregnant improves the separation efficiency of S_5, its use as an eluent results in unsatisfactory separations, needing longer development time, along with the formation of elongated spots for most of metal ions. In view of these observations, S_5 impregnated with TBP was selected for the present study as a stationary phase.

To optimize the impregnant concentration, S_5 was impregnated at different concentration levels (0.01, 0.10, 0.20, 0.50, 1.0, and 2.0 M) of TBP in actone and the R_F values of metal ions were determined after developing the plates with M_1. The R_F values of all metal ions except Ni^{2+}, Ag^+, and Pb^{2+} decreased with an increase in the concentration of impregnation (i.e., the extraction increases with concentration of TBP). Ni^{2+} moves with the solvent front giving R_F value of 0.95 at all degrees of impregnation. Conversely, Pb^{2+} remains at the point of application over the entire concentration range of TBP. Ag^+ shows maximum mobility at 0.1 M impregnation ($R_F = 0.75$), followed by a decreasing trend in R_F values with the increase in impregnant concentration. Metal ions generally yield tailed spots in the impregnant concentration range of 0.5 to 2.0 M. The development time also increases from 15 min (impregnant concentration, 0.2 M) with the increase in impregnant concentration to 15 h (impregnant concentration 2.0 M). Hg^{2+} could not be detected at any level of impregnation. Thus, the optimum concentration of impregnant was found in the range of $0.1\,M < TBP < 0.5\,M$, yielding the best results at 0.2 M impregnant concentration. Therefore, S_5 impregnated with 0.2 M TBP (S_7) was found most suitable for reversed-phase TLC.

Though Ni^{2+}–Co^{2+} separation could be achieved on S_7 with 1 M NH_4SCN, the use of 1.0-M KSCN instead of 1.0-M NH_4SCN provided better separation in terms of spot resolution and compactness. The effect of anions $Fe(CN)_6{}^{3-}$, $Fe(CN)_6{}^{4-}$, SCN, $VO_3{}^{2-}$, $WO_4{}^{2-}$, $MnO_4{}^{-}$, $CrO_4{}^{2-}$, $Cr_2O_7{}^{2-}$, $MoO_4{}^{2-}$, $Mo_7O_{24}^{6-}$, Br, $IO_3{}^{-}$, $IO_4{}^{-}$; amines (*p* and *m*-nitroaniline, *m*-phenylene diamine aniline, α-naphthylamine, *p* and *m*-chloroaniline, indole, carbazole, and diphenylamine); and phenols (α-naphthol, *m*-nitrophenol, resorcinol, hydroquinone, and 8-hydroxyquinoline); on the separation of Ni^{2+} from Co^{2+} on S_7 using 1.0-M KSCN was also examined. The presence of most of the anions did not show any effect on the separation and the R_F values of Ni^{2+} and Co^{2+} remained unchanged. In the presence of $CrO_4{}^{2-}$, $Cr_2O_7{}^{2-}$, $MoO_4{}^{2-}$, $Mo_7O_{24}^{6-}$, Br^- $IO_3{}^{-}$, and $IO_4{}^{-}$, the detection of Ni^{2+} could not be realized and thus the separation is hampered by their presence in the mixture of nickel and cobalt. The presence of $Cr_2O_7{}^{2-}$ led to the formation of diffused spot for Co^{2+}. Amines and phenols have no effect on the separation. Although 3-chloroaniline caused tailing in the Ni^{2+} spot, its presence did not hamper the separation.

The chromatographic behavior of metal ions at different concentrations of HCl and KSCN using S_7 as stationary phase is depicted in Figs. 1 and 2. The R_F values for most of the metal ions (Bi^{3+}, $UO_2{}^{2+}$, VO^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, and Pb^{2+}) fluctuate in between 0.8 and 1.0 over the entire concentration range of aqueous HCl (1.0 to 7.0 M) showing the poor extraction of anionic chlorocomplexes of the metals by TBP. Conversely, Fe^{3+}, remained near the point of application in the concentration range of 3.0 to 7.0 M of HCl, indicating the strong extraction of chlorocomplex. However, at 1.0-M HCl, Fe^{3+} migrates with the solvent showing an R_F value of 0.75. The curves of R_F vs moles of HCl (see Fig. 1) pass through a minima either at 3.0 or 5.0 M of HCl. Interestingly, this was the concentration range where we found slightly more compact spots and we selected 5.0-M HCl for further study. Though, Fe^{2+} can be separated from Fe^{3+} on S_7 using 3 to 7 M HCl as a mobile phase, Ni^{2+} and Co^{2+} remain inseparable.

To understand the role of thiocyanate concentration on mobility, the metal ions were chromatographed on S_7 using aqueous developers containing varying molar concentrations of KSCN (0.10 M to 2.0 M). From the plot of R_F vs molar concentration of KSCN (Fig. 2), the following trends are noticeable:

1. Hg^{2+} and Tl^{+} remained near the point of application at all KSCN concentrations used. Conversely, Ni^{2+} moved with the solvent.

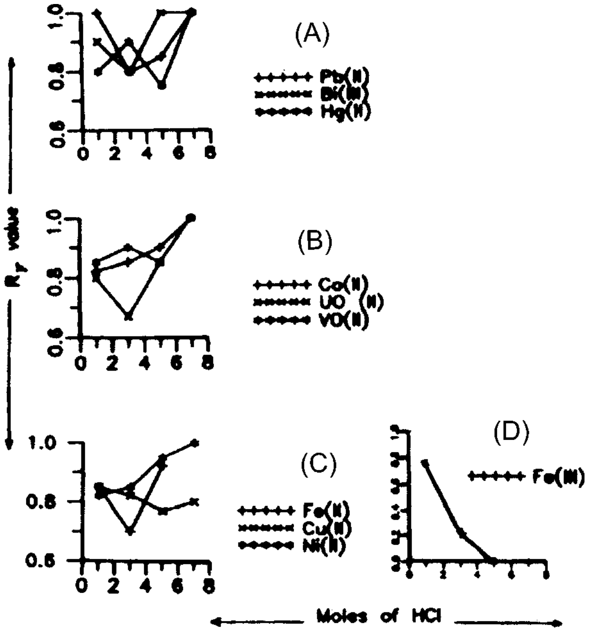

Figure 1. The mobility of metal ions on S_7 developed with molar concentrations of HCl.

2. The R_F of Pb^{2+}, Cu^{2+}, Ag^+, and Bi^{3+} increased with the increase in KSCN concentration. These results are analogous with those obtained on paper impregnated with high-molecular-weight amines using 0.5 to 7 M solutions of NH_4SCN as eluent.[40] A reverse trend, i.e., the decrease in R_F value with the increse in KSCN concentration was observed with Fe^{3+}, Co^{2+}, and Fe^{2+}. This variation of R_F values with the concentration of thiocyanate may be explained by a shift of the equilibrium of complex formation and the resulting shift in the partition of the complex between two phases. These changes may also be effected by the addition of HCl to thiocyanate solution. As is evident from Fig. B., the separation of Ni^{2+} from Co^{2+} is possible with aqueous thiocyanate system but the separation of Fe^{2+} from Fe^{3+} is not good.

It is clear from the previous discussion that while a thiocyanate system is capable of separating Ni^{2+} from Co^{2+}, the HCl system is most suitable for the separation of Fe^{2+} from Fe^{3+}. Thus, the use of thiocyanate in combination

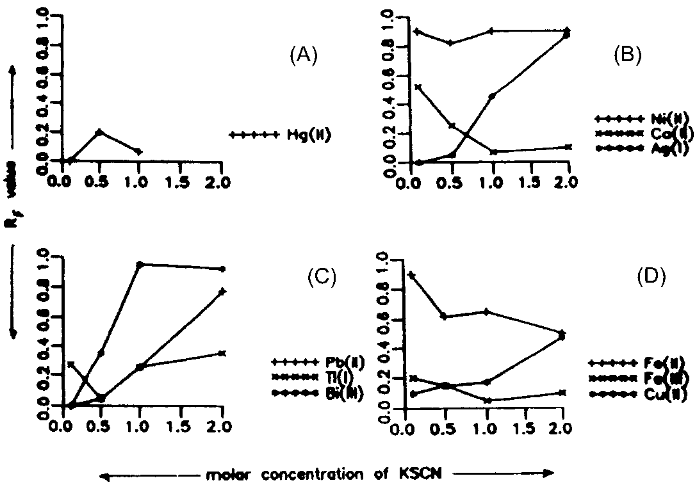

Figure 2. The mobility of metal ions on S_7 developed with molar concentrations of KSCN.

with HCl furnished a novel solvent system for reversed-phase TLC of metal ions on TBP-impregnated layers. As a result, we achieved a very clear, reliable, and reproducible separation of Ni^{2+}, Co^{2+}, Fe^{2+}, and Fe^{3+} from their mixtures. A mixture of 1.0-M KSCN and 5-M HCl is capable of producing a very reliable three-component separation of Ni^{2+}, Co^{2+}, and Fe^{3+}. It is also possible to separate Fe (II) from Fe (III) with this solvent on S_7 layers. However, the addition of 1.0-M NaCl in this solvent system further (5.0 M HCl + 1.0 M KSCN) improves the separation of Ni^{2+}, Co^{2+}, Fe^{2+}, and Fe^{3+} from their mixture. The results obtained after the variation of concentration of HCl (1 to 10 M) in a mixture of 1.0 M NaCl + 1.0 M KSCN and of KSCN (0.01 to 2.0 M) in a mixture of 1.0 M NaCl + 5.0 M HCl further confirms that a mixture consisting of 1.0 M NaCl, 1.0 M KSCN, and 5 M HCl in 1:8:1 ratio is the best solvent system for the separation of Ni^{2+}, Co^{2+}, Fe^{2+}, and Fe^{3+} (Figs. 3 and 4). The clarity of detection and compactness of spots increase with the increase in the concentration of KSCN in the mobile phase, yielding best the results with 1.0 M KSCN–5 M HCl–1.0 M NaCl (8:1:1) as mobile phase (M_1) and hence the chromatographic system, $S_7 - M_1$ was taken up as the best system for binary, ternary and quaternary separations of several metal ions including Ni^{2+}, Co^{2+}, Fe^{2+} and Fe^{3+} from their mixtures. At 2.0 M KSCN,

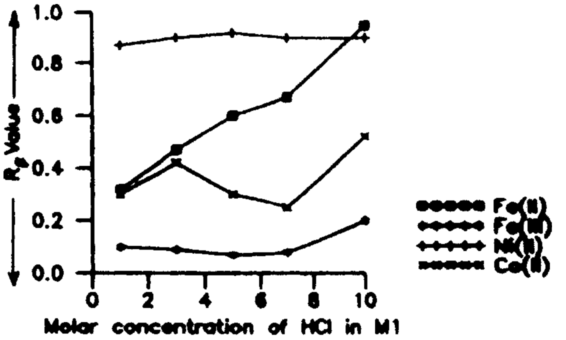

Figure 3. Mobility of metal ions on S_7 developed with mixtures of 1.0-M KSCN and 1.0-M NaCl containing different molar concentrations of HCl.

Fe^{2+} produces double spots with R_F values of 0.5 and 1.0 (Fig. 4) indicating the presence of two different species.

In addition to the separations achieved experimentally (Table 1), the separation of Ni^{2+} from Co^{2+} is very important because both of these ions have the same hydrated radii (3.0 Å), almost similar electronegativity (Ni = 1.75, Co = 1.70),[41] and nonspherical distribution of the d electrons, i.e., Co (d^7) and Ni (d^8). Although the chromatographic behavior of metal ions can hardly be generally connected with their structural properties but it seems that the electronic configuration of 3d-orbital is reflected on the mobility of Co and Ni in the present case. In spite of the fact that Co and Ni have a nonspherical distribution of d electrons, the R_F value of Ni ($R_F = 0.98$) is higher than that

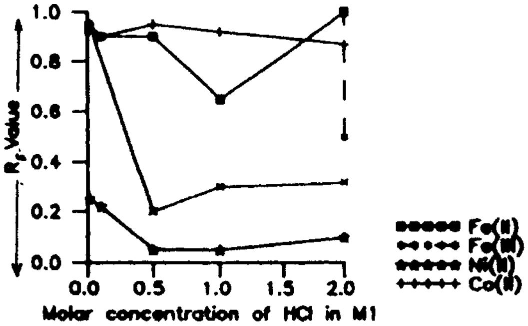

Figure 4. Mobility of metal ions on S_7 developed with mixtures of 5.0-M HCl and 1.0-M NaCl containing different molar concentrations of KSCN.

Table 1. Separations experimentally achieved with different mobile phases on S_5 and S_7 stationary phases.

Stationary phase	Mobile phase	Separation (R_F values)
S_5	M_5 (0.1 M)	Ag^{+} (0.00)–Pb^{2+} (0.85), Tl^{+} (0.15)–Pb^{2+} (0.85), Ag^{+} (0.00)–Bi^{3+} (0.85), Tl^{+} (0.15)–Bi^{3+} (0.85)
	M_8	Hg^{2+} (0.90)–Fe^{3+}/Cu^{2+}/Co^{2+}/Ni^{2+}/$UO_2{}^{2+}$/VO^{2+}/Ag^{+}/Pb^{2+} / Tl^{+}/Bi^{3+} (0.00)
	M_{12}	VO^{2+} (0.98)–Pb^{2+} (0.00), VO^{2+} (0.98)–Tl^{+} (0.10), Zn^{2+} (0.90)–Pb^{2+} (0.00)
		Zn^{2+} (0.90)–Tl^{+} (0.10), Ag^{+} (0.95)–Pb^{2+} (0.00), Ag^{+} (0.95)–Tl^{+} (0.10)
	M_{15}	Hg^{2+} (0.50)–Fe^{3+}/Cu^{2+}/Ni^{2+}/$UO_2{}^{2+}$/VO^{2+}/Cd^{2+}/Zn^{2+}/Pb^{2+}/Tl^{+} (0.00)
	M_{16}	Co^{2+} (1.00)–Pb^{2+} (0.00), Co^{2+} (1.00)–Ag^{+} (0.00), Co^{2+} (1.00)–Tl^{+} (0.00)
		Bi^{3+} (0.85)–Pb^{2+} (0.00), Bi^{3+} (0.85)–Ag^{+} (0.00), Bi^{3+} (0.85)–Tl^{+} (0.00)
	M_{17}	Ni^{2+} (1.00)–Pb^{2+} (0.00), Ni^{2+} (1.00)–Ag^{+} (0.00), Ni^{2+} (1.00)–Tl^{+} (0.00)
		Co^{2+}(1.00)–Pb^{2+} (0.00), Co^{2+} (1.00)–Ag^{+} (0.00), Co^{2+} (1.0)–Tl^{+} (0.00)
S_7	M_1[a]	Ni^{2+} (0.90)–Ag^{+} (0.55)–Pb^{2+} (0.05), Ni^{2+} (0.90)–VO^{2+} (0.50)–Pb^{2+} (0.01)
		Ni^{2+} (0.95)–Bi^{3+} (0.60)–Pb^{2+} (0.00), Ni^{2+} (0.98)–Ag^{+} (0.50)–Fe^{3+} (0.15)
		Ni^{2+} (0.90)–VO^{2+} (0.52)–Fe^{3+} (0.10), Ni^{2+} (0.85)–Bi^{3+} (0.60)–Fe^{3+} (0.10)
		Ni^{2+} (0.92)–Co^{2+} (0.20)–Pb^{2+} (0.00), Ni^{2+} (0.95)–Co^{2+} (0.30)–Fe^{3+} (0.10)
	M_2 (1.0 M)	Ni^{2+} (0.95)–Co^{2+} (0.07), Bi^{3+} (0.95)–Hg^{2+} (0.07)
	M_3 (5.0 M)	Fe^{3+} (0.10)–Cu^{2+} (0.77), Fe^{3+} (0.10)–Fe^{2+} (0.85)

[a] Development time ∼24 min.

for Co ($R_F = 0.30$). This is because Ni has more d electrons nonspherically distributed, i.e., 8, while Co has only 7, resulting in a greater shielding (causing higher mobility) in the case of Ni than in the case of Co.

Another important aspect of the present study is the separation of Ni^{2+}, Co^{2+}, Fe (II), and Fe (III) from their mixture. The order of R_F values and the separation sequence of these metal ions on S_7 with M_1 is as follows:

$$Ni^{2+}(0.98) > Fe\,(II)(0.65) > Co^{2+} + (0.30 > Fe^{3+}(0.1)$$

The approximate R_F values are given in parenthesis. The absence of sorption in the case of Ni^{2+} may be attributed to the lack of formation of anionic thiocyanate complex under the specified experimental conditions. In fact, we could not realize the characteristic green Ni–thiocyanate complex on mixing of nickel solution with the mobile phase (M_1). In the case of Co^{2+}, a blue-colored tetrathiocyanato cobaltate (II) ion $[Co(SCN)_4]^{2-}$ was formed, which showed maximum absorbance at λ_{max} 630 nm. This complex exhibits moderate extractability into TBP giving R_F value of 0.30. The blue color fades in the water but stabilized with thiocyanate solution. With Fe (II), a cationic dark red complex, Fe $(SCN)^{2+}$ is formed as expected in acidic aqueous medium,[42] which is strongly extracted by TBP and remains at the point of application ($R_F = 0.10$). Compared to Fe (III), Fe (II) shows higher R_F (i.e., poor extraction) facilitating another important separation of Fe (III) from Fe (II). This behavior may be explained on the basis of the relative stability of complexes of ions of different valency states. In the case of iron complexes with organic as well as inorganic anions, generally, the complex of Fe (III) has a higher formation constant.[43] Thus, Fe (III) complex being more stable shows less mobility (i.e. low R_F) compared to less stable complex of Fe (II), which shows higher R_F values ($R_F = 0.65$). The higher charge on Fe (III) also favors the smaller R_F for Fe (III).[44] A similar trend in R_F values for Fe (III) ($R_F = 0.24$) and Fe (II) ($R_F = 0.45$) was observed by Perisic-Janjic et al.[45] An inverse correlation between percent extraction (% E) and hR_F values of metal ions has been reported by Jain et al.[46]

The substitution of HCl in solvent M_1 by mineral or carboxylic acids hampered the four-component separation of Ni^{2+}, Co^{2+}, Fe^{2+}, and Fe^{3+} (Table 2). However, the tailing reducing nature of formic acid facilitates the formation of spots with increased compactness; and therefore, clearer detection and better binary separations of Ni^{2+} from Co^{2+} and of Fe^{2+} from Fe^{3+}. These separations could also be achieved with acetic acid instead of HCl or HCOOH. These acids can be put in the following preferred order if used as eluent in combination with KSCN and NaCl: $HCl > HCOOH > CH_3COOH > H_2SO_4$.

Table 2. Effect of mineral or carboxylic acids on the separation of Ni^{2+}, Co^{2+}, Fe^{2+}, and Fe^{3+} from their mixture on S_7.

	Mobile phase: I M KSCN + 5 M acid + 1 M NaCl (8:1:1) hR_F values ($R_F \times 100$)			
Metal ions	HCl	H_2SO_4	CH_3COOH	HCOOH
Fe^{2+}	60	82	55	60
Fe^{3+}	05	20 T[a]	00	00
Ni^{2+}	90	90	80	90
Co^{2+}	30	60	05	00

[a] T = tailed spot.

Similarly, the four-component separation is hampered if NaCl in M_1 is replaced with LiCl, NH_4Cl, $(NH_4)_2SO_4$, $NaNO_2$, or $NaNO_3$ (Table 3). The preferred order of using these salt solutions in combination with HCl and KSCN is: NaCl $>$ $NaNO_3$ $>$ LiCl $=$ $NaNO_2$ $>$ NH_4Cl $>$ $(NH_4)_2SO_4$. This particular observation is not in full agreement with Janjic et al.,[47] who, on the basis of literature data about the performance of aqueous salt solutions as mobile phases in salting out TLC, concluded that, "ammonium sulfate and to lesser extent sodium chloride, proved during the years to be better than other investigated salts." Further, the use of $NaNO_2$ with M_1 is not useful as it furnishes the color to the mobile phase and TLC plates are changed to yellow after development.

It is evident from Fig. 5 that R_F values of the cations are more or less independent of the pH of sample of mixtures of $Ni^{2+} + Co^{2+} + Fe^{3+}$ and

Table 3. Effect of different salts on the separation of Ni^{2+}, Co^{2+}, Fe^{2+}, and Fe^{3+} from their mixture on S_7.

	Mobile phase: I M KSCN + 5 M acid + 1 M salt (8:1:1) hR_F values ($R_F \times 100$)					
Metal ions	NaCl	LiCl	NH_4Cl	$NaNO_2$	$NaNO_3$	$(NH_4)_2SO_4$
Fe^{2+}	60	00	35 T[a]	00	60	80
Fe^{3+}	05	00	35 T	00	07	25t
Ni^{2+}	90	90	90	9	92	87
Co^{2+}	30	30	17 T	17 T	25 T	20 T

[a] T = tailed spot.

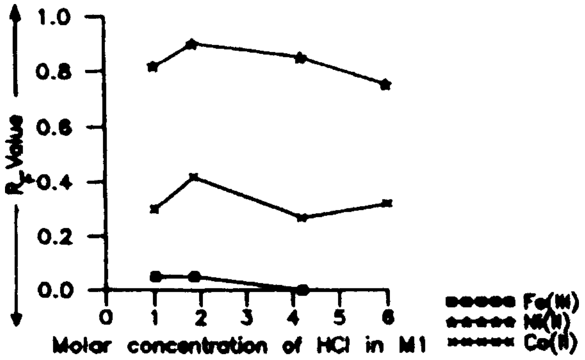

Figure 5. Mobility of metal ions at different pH values of sample solutions.

$Ni^{2+} + Co^{2+}$ between the pH limits of 1.0 to 4.2 and 1.0 to 6.0, respectively. Therefore Ni^{2+} can be separated from Co^{2+} and Fe^{3+} without the need for close control of the pH of the sample. At pH 4.2 of sample mixture, Fe^{3+} is partially hydrolyzed, while Ni^{2+} and Co^{2+} remains in the form of ions. At pH 7.6, Fe^{3+} and Ni^{2+} get precipitated along with partial hydrolysis of Co^{2+}. At pH 10, all three metals are completely converted into hydroxides. The precipitates obtained at pH 10.5 and 12.2 were dissolved in minimum amount of concentrated HCl, diluted with water and subjected to TLC. All three metal ions were clearly resolved on TLC plates in the identical separation sequence, i.e., Ni^{2+} ($R_F = 0.95$), Co^{2+} ($R_F = 0.3$), and Fe^{3+} ($R_F = 0.05$). Thus, this method can be applied for the separation of Ni^{2+}, Co^{2+}, and Fe^{3+} from acidic and alkaline sample solutions.

The effect of the loading amount on the R_F values was studied and the lowest possible detectable amount of metal ions on the chromatoplates was determined. As the amount of the metal ion loaded increases, the length of the spot increases. It is always possible to separate a reasonable amount of Ni^{2+} from microgram quantities of Fe^{3+} since 2.4 μg of Ni^{2+} gave R_F equal to 0.95, while it is 0.85 for 25.0 μg of Ni^{2+}. The proposed method is sensitive for the detection of Ni^{2+} (2.47 μg), Co^{2+} (2.02 μg), and Fe^{3+} (1.72 μg) as their chloride salts.

APPLICATION

The proposed method was applied to separate, detect, and identify nickel, cobalt, and iron (III) from various water samples. The detection of Ni^{2+} from electroplating waste water, Fe^{3+} from rock sample, and Fe^{3+} and Co^{2+} from high-speed steel sample was possible by directly spotting 0.01 mL of these samples on TLC plates. The TLC of spiked samples (acidic and ammoniacal) by this method yields clear detection, identification, and separation of Ni^{2+}, Fe^{3+}, and Co^{2+} on TLC plates. The limit of detection of Fe^{3+}, Co^{2+}, and Ni^{2+} was 3.4, 4.2, and 2.5 μg respectively. The nickel content in real samples of wastewater collected from different lock factories of Aligarh City, India before treatment was found in the range 4.6 to 5.6 g/L. Ni^{2+}, Fe^{3+}, and Co^{2+} were well detected in spiked samples giving R_F values of 0.92, 0.05, and 0.32 respectively.

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