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CHELATING RESIN-IMPREGNATED PAPER CHROMATOGRAPHY, APPLICATIONS TO TRACE ELEMENT COLLECTION OF FERROUS AND FERRIC IONS, AND DETERMINATION BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

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Summary—An ion-exchange approach to the preparation of chelating resin is demonstrated whereby a typical sulfonated chelating agent, 7-iodo-8-hydroxy quinoline-5-sulfonic acid, is immobilized as counterions on a piperazinium polyelectrolyte matrix. The resulting chelate forming resin has been used to effect the selective separation of ferrous as well as ferric ion from a known mixture containing other trace elements without any complication of the leaching of either chelating ligand or resin from the stationary support. The chelating resin-impregnated paper chromatographic technique followed with differential pulse anodic stripping analysis is described for the preconcentration, separation, and recovery of divalent and trivalent ions of iron from the various heavy metals in aqueous phases. The combination of chelation and paper chromatography involves a differential migration procedure which provides a technique for the separation of analyte ions quantitatively without any interference from the complex matrices.

Of several chromatographic techniques extensively used for the selective and quantitative separation of metal ions from aqueous matrix of macroamounts of other metals, the applications of chelating resins/immobilized (adsorbed or chemically bound) chelating functional groups on polymeric supports in ion-chromatographic separations are found to be potentially more selective than ordinary cation-exchange resins.[1-10] Several chelating agents have been evaluated as precolumn derivatizing agents for reversed-phase liquid chromatographic determination of metal ions.[11-13] An extensive review on separation of metal chelates by high pressure liquid chromatography covering both normal-phase and reversed-phase separations[14-21] indicates that improved efficiency could be attained exclusively by the reversed-phase separation of metal chelates. However, severe problems of bleeding, swelling and cracking of the sorbent under the influences of medium effect, mechanical shaking and/or the elution process[22-24] and above all, the 'incomplete' chemical reaction for immobilization of suitable chelating functional groups[25-27] on common supports have encouraged much investigation to determine a better method of immobilization of chelating agent on the polymer or resin supports. The Donnan equilibrium concept[28] is found convenient, simpler and less time consuming, where the electroneutrality is maintained by the exchange of counterions with the active chelating anions along polycationic resin instead of being chemically bound. Unfortunately, such sorbents are prone to leaching of chelating agent to some extent from the loaded resin with mineral acids of the concentrations required for elution.[29]

Keeping abreast with the problems stated above, the present paper evolves a very simple technique in which a chelating resin-impregnated paper chromatography/differential pulse anodic stripping voltammetry is investigated to discover how selective it is for free ferrous (Fe^{2+})/ferric (Fe^{3+}) ions from the many competing metals of prime environmental concern. The ions Fe^{2+} and Fe^{3+} were chosen for the study because there is no easily serviceable ion selective electrode for these ions,[30] and also because of the concern that Fe^{2+} and Fe^{3+} pose severe interference in the determination of other heavy metals in stripping voltammetry and vice versa.[31] Several approaches such as electrochem-

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ical,[32] chromatographic[33] and spectrophotometric[34,35] methods have been adopted for the analysis of Fe^{2+} and Fe^{3+}. In chromatographic separations through precolumn[36–38] and on-column[12] chelation, most of chelating agent used for iron analyses are found lacking specificity due to interferences with diverse metal ions in aqueous matrix. For instance, iron separation through 4-(2-pyridylazo) resorcinol (PAR) complexation, which provides ideal conditions for separation with a model suitable for ion chromatograph (Dionex model, for example), is likely to be dependent on the mobile phase pH and the type of the stationary phase used. A proper selection of either of these factors is recommended to attain the requisite chromatographic selectivity, since most of the metal–PAR complexes are strongly retained in the column beyond pH 4.[13] Insofar as postcolumn derivatization with non-specific metallochromic indicator PAR is concerned, the prospect of chelation ion chromatography using a macroporous poly(styrene divinyl benzene) (PSDVB) column with iminodiacetate functional groups (Dionex, Corp.) is also problematic owing to the overlapping absorption band and allowing all complexes to be detected at the same wavelength.[8–10] Moreover, the specification aspect would also be hampered severely.

As an approach to provide a solution for these problems, a new, poly[*N*-*p*-xylylene piperazinium di-iodohydroxyquinoline-sulfonate] system (PXPi(IHQS)$_2$; structure shown in Fig. 1) which incorporates the chelating agent, 7-iodo-8-hydroxyquinoline-5-sulfonic acid (Ferron, IHQS), seems more promising. In the present work, PXPi(IHQS)$_2$-impregnated paper chromatography fortuitously obviates the problems of leaching as well as hydrolysis of metal chelates. The desired selectivity is achieved, without any interference of diverse metal ions and natural matrix, via a differential migration procedure where distribution occurs between the non-mobile precipitate and mobile ions in the aqueous solution on the basis of the differences in solubility product equilibria.[39]

EXPERIMENTAL

Materials

All chemicals were analytical reagent grade or better. Solutions of the metal ions of interest were prepared by sequential dilution of 100 mg/l. solutions of the pure metal in conductivity grade (0.06–0.07 μmho/cm, 25°C) water.

Preparation of poly[N-p-*xylylene piperazinium dibromide*] *(PXPiBr$_2$)*

Equimolar solutions of α, α′-dibromo-*p*-xylene (1.0032 g/15 ml acetonitrile) and piperazine hexahydrate (Merck) (0.7375 g/15 ml acetonitrile) were refluxed in a water bath for ~6 hr. The resulting white polymer, which was kept overnight in the reaction mixture, was filtered and washed several times with hot acetonitrile and finally dried in vacuo. The product was found insoluble in almost all organic and aqueous solvents. Elemental analysis ($C = 40.95\%$, $H = 5.30\%$, and $N = 8.23\%$) and conductometric titration in acidified aqueous suspensions of PXPiBr$_2$ [5.65 mol Br^-/1000 g PXPiBr$_2$] confirmed the structure (Fig. 1, $X^- = Br^-$) of the polyelectrolyte with total degree of polymerization, $n = 40$.

Preparation of chelating agent loaded resin poly[N-p-*xylene piperazinium di-iodohydroxyquinoline-sulfolanate*] *(PXPi($_I$HQS)$_2$)*

To obtain the modified polymer matrix, a weighed amount (1 mol) of the PXPiBr$_2$ was

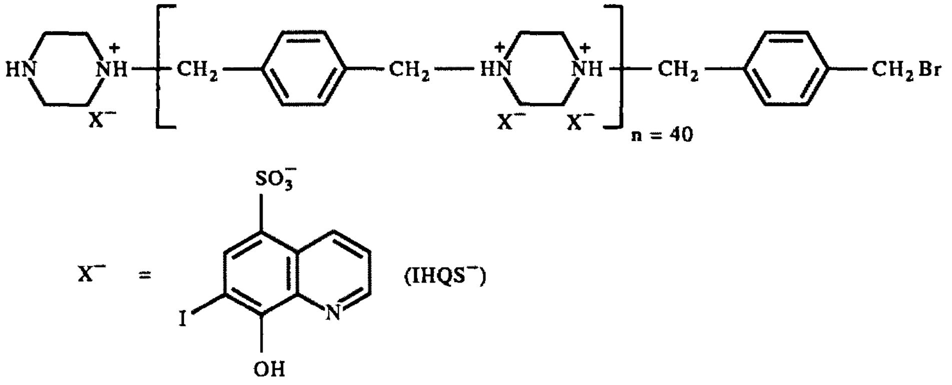

Fig. 1. Structure of chelating resin.

moistened with dimethylformamide (DMF), and then shaken with DMF solution containing the required amount ($2n + 1$ mol) of 7-iodo-8-hydroxyquinoline-5-sulfonic acid (IHQS) for 3 days followed by a brief heating (10 min) of the reaction mixture. The yellow coloured amorphous loaded resin was filtered off, washed several times with deionized water to remove the excess reagent and then dried at ~80° *in vacuo* for a day. The modified resin did not give any Br^- test. However, the total amount of chelating agent ($IHQS^-$ anions) bound onto $PXPiBr_2$ matrix was obtained spectrophotometrically as 3.28 mmol/g of $PXPi(IHQS)_2$ which is higher than the theoretical value of 2.23 mmol/g for $PXPi(IHQS)_2$ (mol. wt = 36310). This indicates that the mechanism of the absorption of the chelating agent by the resin is involved in some molecular absorption[29] in addition to the ion-exchange between bromide ion and the anionic sulfonate of the chelating agent. The loaded resin was identified by the IR (KBr) frequencies (only key bands) at 3441 cm^{-1} (—OH group), 1350, 1143, 652 cm^{-1} (S═O stretching vibrations of sulfonic group) 544 cm^{-1} (C—I vibration of iodo groups) corresponding to $IHQS^-$ anions.

Procedures

Chelating resin-impregnated paper chromatography. Chromatography was performed on 25 × 1.5 cm Whatman No. 1 paper strips in 30 × 5 cm glass jars. Whatman No. 1 paper strips were impregnated in DMF suspension with finely powdered $PXPi(IHQS)_2$ ($5.5 \times 10^{-5}M$) for 3–5 sec and excess reagent was removed by placing the strips on filter paper sheets. The strips were allowed to dry for 15 min in hot air.

Test solution consisting of metal ions (60 ppm each) was placed as one spot (0.02 ml) on the paper with the help of a microsyringe pipette. The paper was then conditioned for 15 min and dried. Fe^{3+} gave a visible green spot on the strip. It was dipped into solvent (triple distilled water) until the solvent ascent was 17–19 cm. The green spot of Fe^{3+} (or Fe^{2+}) did not move from its position but the other cations moved upward. The front (R_L) and rear (R_T) R_f values for the stationary iron spot were measured. The lower portion containing the green spot was cut apart from the strip containing mobile metal ions, which were detected by PAN indicator, and both parts were digested in 2 ml of concentrated nitric acid (suprapur, ExcelaR Glaxo). The resulting solutions were diluted to 25 ml, maintaining pH 7 for the solution made from the lower part of the strip and pH 3 for the upper part of the strip using $1M$ KOH solution.

In the ascending chromatographic analysis of mixture containing four heavy metals (Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}) with Fe^{3+} or Fe^{2+}, it was found that all four upward moving metal ions had formed a 'diffused' zone of length ~2 cm behind a well-separated Fe^{3+} (or Fe^{2+}) spot at the bottom of the paper strip. After digestion of both parts separately as indicated above, iron could be estimated quantitatively in the lower part, whereas the remaining metals in the upper strip portion were determined simultaneously by the process of standard addition method of voltammetric analysis.

Differential pulse anodic stripping voltammetry. Anodic stripping voltamperograms were obtained in the conventional manner with an EG & G Princeton Applied Research model 264A polarographic analyser in a conjunction with a model 303 static mercury drop electrode at room temperature (~20°C). In each run, 1 ml of the digested solutions was added to 10 ml of buffer containing background electrolytes sodium tartrate buffer ($\mu = 0.001M$, pH 11) for lower digested parts and ammonium citrate buffer ($\mu = 0.2M$, pH 3) for upper digested parts. For estimation of cobalt and nickel, $0.01M$ KCl solution was used as supporting electrolyte.

RESULTS AND DISCUSSION

Chelating resin-impregnated paper chromatography

Unlike the usual method to prepare chelating resins where ligands are diazo-coupled to a modified carboxymethyl cellulose matrix in powder form[40], the firm adherance of chelating resin may be due to the specific adsorption of the large polycations ($PXPi^{n+}$) onto a non-ionic paper matrix. The gegenion ($IHQS^-$) would serve as a 'potential determining' ion in the present case somewhat similar to the proposed mechanism[41] of Cantwell and Puon for the retention of organic ions on a non-ionic sorbent suggested on the basis of Grahame's modification[42] of the Stern–Gouy–Chapman electrical double layer theory. It may be noted that similar adsorption of $PXPi(IHQS)_2$ resin on any other solid support such as silica gel, glass, molecular sieves and amberlite XAD-2 did not work for batch equilibrium or dynamic (column) methods probably because of the finely powdered amorphous and predominating non-solvating character of the chelating resin. During the course of shaking the loaded PXPi(IHQS)$_2$ with solution containing Fe^{3+} ions, a major portion of $IHQS^-$ was found removed from the loaded resins, presumably because of ion-exchange between anionic sulfonate of the chelating agent and anion(s) (ClO_4^-, NO_3^-, Cl^-, SO_4^{2-}, CH_3COO^-, *etc.*) in the media. The extent of leaching was also observed from the intensity of the solution in the order $1 > 3 > 5 > 7$ of pH values. At pH 1, the entire polycation matrix turned white whilst the solution appeared intense green due to Fe^{3+}–$IHQS^-$ complex. For other divalent metal ions such as Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+}, the extent of removal of $IHQS^-$ was found maximum at lower pH values and in the neutral medium. However, it was minimum in the middle range of pH 2.5–4. This problem has also been noticed earlier.[29] In the present work, the leaching of chelating resin is largely circumvented with the use of an ascending paper chromatographic procedure where the chelating ligand anion ($IHQS^-$) is immobilized by electrostatic forces to the polymer matrix impregnated over cellulose. It has been observed that when $IHQS^-$ is doped alone on the paper, the entire ligand moved upward leaving the lower part of the strip completely colourless. Also, the green spot of Fe^{3+}–$IHQS^-$ largely diffused downward owing to the solubility of $IHQS^-$ in water in this case.

It was found, that the loaded Fe^{3+} selective $IHQS^-$ onto polypiperazinium matrix did not distinguish between ferrous and ferric ion in contrast to its independent function.[43] The possible reason could be the presence of quaternary nitrogen centres in the polymer matrix which readily oxidise ferrous into ferric ions. Therefore PXPi(IHQS)$_2$ resin could be used for the separation and estimation of Fe^{2+} and/or Fe^{3+} from the host metal ions. It may be pointed out that Fe^{2+} separation from Fe^{3+} in total iron content could only be achieved by the present method provided a proper masking of either of the two elements, such as Fe^{2+} by α,α'-dipyridyl, dimethylglyoxime or *o*-phenanthroline reagent and Fe^{3+} by ammonium thiocyanate, is made prior to the chromatographic separation. The complexing properties of PXPi(IHQS)$_2$ are not changed if it is immobilized on a paper. Ferric iron (or ferrous iron) is firmly retained on PXPi(IHQS)$_2$ paper matrix over a wide pH range (1–7), whereas all other accompanying metal ions move upward without any further resolution among themselves. Insofar as binary mixtures are concerned, iron could be separated from almost all divalent ions depending on their R_f values (Table 1). However, for ternary or quaternary mixtures; the non-ferrous ions migrated upward with the solvent front and could not be separated in the course of ascending dynamic motion. This is because of non-compliance of the factors responsible for chelation (such as equilibrium kinetics, stability constant and pH) and moreover, owing to the intermetallic interactions and restricted chelation property of ferron. In aqueous acidic and organic media, the iron spot was slightly diffused both upward and downward and good separations of binary mixtures were not achieved. Therefore, triple distilled water (pH 7) was found to be the most suitable carrier solvent for better resolutions of spots on the paper strip.

Differential pulse anodic stripping voltammetry

The combination of differential pulse anodic stripping voltammetry (DPASV) with a preliminary concentration step in our work appears to be an advantageous approach to the previously reported influences of diverse metal ions,[31] sur-

Table 1. Separation of heavy metal ions achieved experimentally on PXPi(IHOS)$_2$-impregnated paper (all take 30 *min*) by triple distilled water (pH 7)

	Distance travelled (*cm*)		Separation achieved	
Mixtures	Fe-spot	Solvent front	Lower strip ($R_T R_L$)	Upper strip (R_f)*
Fe^{3+}/Cu^{2+}	3	17	Fe^{3+} (0.00–0.18)	Cu^{2+} 0.60
Fe^{3+}/Zn^{2+}	2	17	Fe^{3+} (0.00–0.12)	Zn^{2+} 0.76
Fe^{3+}/Cd^{2+}	2	17	Fe^{3+} (0.00–0.12)	Cd^{2+} 0.82
Fe^{3+}/Pb^{2+}	2	17	Fe^{3+} (0.00–0.12)	Pb^{2+} 0.79
Fe^{3+}/Co^{2+}	3	18	Fe^{3+} (0.00–0.17)	Co^{2+} 0.78
Fe^{3+}/Ni^{2+}	3	18	Fe^{3+} (0.00–0.17)	Ni^{2+} 0.66
$Fe^{3+}/Zn^{2+}/Pb^{2+}$	2	16	Fe^{3+} (0.00–0.13)	Zn^{2+}/Pb^{2+} 0.75
$Fe^{3+}/Pb^{2+}/Cu^{2+}$	1	19	Fe^{3+} (0.00–0.05)	Pb^{2+}/Cu^{2+} 0.74
$Fe^{3+}/Co^{2+}/Ni^{2+}$	2	16	Fe^{3+} (0.00–0.13)	Co^{2+}/Ni^{2+} 0.75

*R_f calculations based on the distance measured from the centre of the 'diffused' spot.

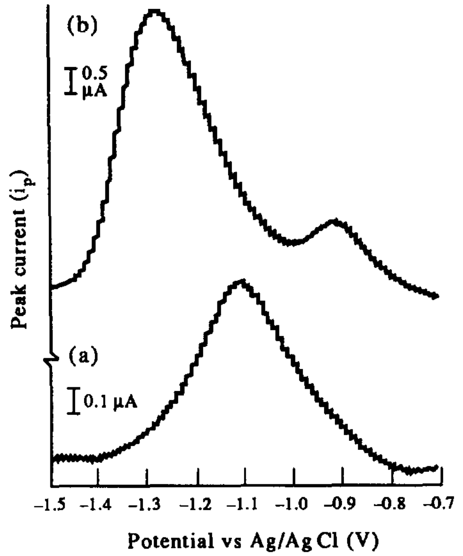

Fig. 2. Typical differential pulse voltamperograms of ferric ions: (a) [Fe^{3+}] = 20.10 μg/l.; (b) spiked curves by 81.3 ppm 0.2 ml Fe^{3+}. Scan rate 10 mV/sec; pulse amplitude, 25 mV; drop size small; deposition potential = -1.5 V *vs.* Ag/AgCl; deposition time = 240 sec, equilibration time = 15 sec. sodium tartarate buffer ($\mu = 0.001M$, pH 11).

factants[44] and organic colloids[45] on the stripping peaks.

The representative DPASV runs for ferric ions and other diverse metal ions are shown in Figs 2 and 3, respectively and the optimized DPASV operation conditions are indicated therewith. The results of determination of Fe^{2+} or Fe^{3+} in binary mixtures are presented in Tables 2 and 3, respectively. The recovering of Fe^{3+} from the heavy metals (Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+}) present in larger amounts (>19 μg/l.) in synthetic multicomponent mixtures and their simultaneous determinations are also portrayed in Table 3 (larger amounts of constituent metals were deliberately taken as their natural occurrence in river sediments are generally high).

In Fig. 2(b), where ferric ion is deposited on HMDE from alkaline solutions (pH 11), a second current maximum appeared at approximately -0.9 V on the anodic polarization curves when spiking was made with 0.2 ml of 81.3 ppm Fe^{3+} ions. This is a known phenomenon[31] of an easier oxidation in anodic polarization curve through $Fe(OH)_2$ intermediate, with a higher concentration of iron (III). The first peak height of the spiked sample, which was negatively shifted at -1.33 V, was taken as an analytical peak current for the application in the standard addition method.

In order to find out the detection limit[46] and a suitable quantitative parameter for the multicomponent mixture involving the influence of different variables, sensitivity was defined as: $S = i_p/Ct_e$ (nA.l.μg^{-1}. min^{-1}), where i_p is in nA, C is the concentration (μg/l), and t_e is

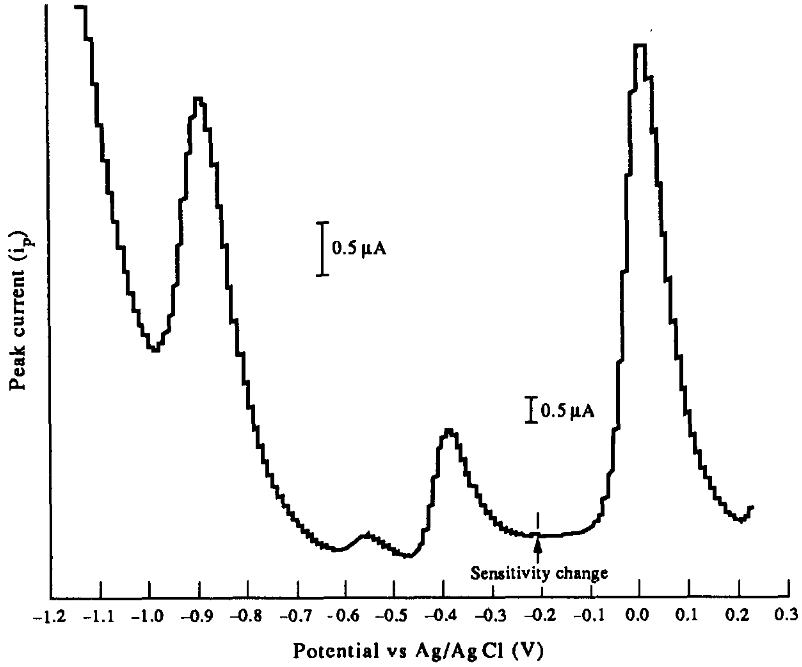

Fig. 3. Voltamperograms of Zn^{2+}, Cd^{2+}, Pb^{2+} and Cu^{2+} digested from upper parts of the paper strip at pH 3 containing 0.2*M* ammonium citrate buffer, deposition potential = -1.2 to -1.5 V *vs.* Ag/AgCl, other conditions as for Fig. 2.

Table 2. Determination of ferrous ions in synthetic mixture by DPASV after PXPi(IHQS)$_2$-resin impregnated paper chromatographic separation and preconcentration

	Lower strip containing Fe^{2+} ion ($\mu g/l.$)		Upper strip containing diverse metal ion ($\mu g/l.$)	
Mixtures	Applied	Found*	Applied	Found*
Fe^{2+}/Cu^{2+}	2.20	2.30 ± 0.04	4.35	4.28 ± 0.05
Fe^{2+}/Zn^{2+}	2.20	2.20 ± 0.025	2.10	1.88 ± 0.02
Fe^{2+}/Cd^{2+}	2.20	2.30 ± 0.03	2.10	2.00 ± 0.05
Fe^{2+}/Pb^{2+}	2.20	2.20 ± 0.04	2.30	2.00 ± 0.10
Fe^{2+}/Co^{2+}	2.20	2.20 ± 0.05	2.30	2.00 ± 0.06
Fe^{2+}/Ni^{2+}	2.20	1.80 ± 0.15	4.40	4.00 ± 0.01
$Fe^{2+}/Zn^{2+}/Cd^{2+}$	2.20	2.20 ± 0.10	—	—
$Fe^{2+}/Cu^{2+}/Pb^{2+}$	2.20	1.85 ± 0.20	—	—
$Fe^{2+}/Ni^{2+}/Co^{2+}$	2.20	2.30 ± 0.18	—	—

*Mean and range of three determinations (SD).

Table 3. Determination of ferric ions in synthetic mixtures by DPASV after PXPi(IHQS)$_2$-resin impregnated paper chromatographic separation and preconcentration

	Lower strip containing Fe^{3+} ion ($\mu g/l.$)		Upper strip containing diverse metal ions ($\mu g/l.$)	
Mixtures	Applied	Found*	Applied	Found*
Fe^{3+}/Cu^{2+}	1.44	1.47 ± 0.03	4.35	4.17 ± 0.05 (Cu^{2+})
Fe^{3+}/Zn^{2+}	4.35	4.30 ± 0.06	1.40	1.30 ± 0.10 (Zn^{2+})
Fe^{3+}/Cd^{2+}	2.20	2.30 ± 0.17	4.40	4.16 ± 0.10 (Cd^{2+})
Fe^{3+}/Pb^{2+}	4.30	4.10 ± 0.05	4.30	4.10 ± 0.05 (Pb^{2+})
Fe^{3+}/Co^{2+}	4.78	4.60 ± 0.01	2.30	2.30 ± 0.06 (Co^{2+})
Fe^{3+}/Ni^{2+}	2.20	1.90 ± 0.01	4.40	4.30 ± 0.01 (Ni^{2+})
$Fe^{3+}/Zn^{2+}/Pb^{2+}$	1.44	1.50 ± 0.03	—	—
$Fe^{3+}/Co^{2+}/Ni^{2+}$	1.44	1.40 ± 0.02	—	—
$Fe^{3+}/Cu^{2+}/Cd^{2+}/Zn^{2+}/Pb^{2+}$	20.10	20.40 ± 0.15	37.52	37.51 ± 0.05 (Cu^{2+})
			18.90	18.80 ± 0.015 (Cd^{2+})
			20.04	20.04 ± 0.15 (Zn^{2+})
			20.93	20.80 ± 0.09 (Pb^{2+})

*Mean and range of three determinations (SD).

deposition time in min. The detection limit was calculated from the expression, $DL = 2.5\sigma B/st_e$, where σB is the absolute standard deviation of the blank (in nA) obtained at t_e. The detection limit calculated for the best conditions: (pH 11, $t_e = 4$ min, $\sigma B = 2$ nA, $S = 9.2$ nA.l.μg^{-1}. min^{-1}) for Fe^{3+} ion was 0.13 μg/l. (Fig. 2a).

CONCLUSIONS

The proposed method is based on chelating resin-impregnated paper chromatographic separation of trace iron ions prior to the application of DPASV, at a HMDE in alkaline medium (pH 11). This provides a simple, fast and reliable way of dealing with interferences caused by other diverse ions and organic materials in water samples, and also for combating the leaching complications of sorbent and/or the chelating ligand.

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