Combined cation-exchange and extraction chromatographic method of preconcentration and concomitant separation of bismuth(III) with high molecular mass liquid cation exchanger

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ABSTRACT

A selective method has been developed for the extraction chromatographic separation of Bi^{III} with Versatic 10 coated on silanized silica gel (SSG). Bi^{III} has been quantitatively extracted from 0.1 M acetate buffer at the range of pH 5.0–5.5. The result showed that the solution pH, influent volume, flow-rate and solution temperature would affect the sorption of Bi^{III}. The sorbed Bi^{III} was eluted with 0.1 M H$_2$SO$_4$. The extractor system has got good values of exchange capacity (1.42 meq. of H$^+$ g^{-1} of dry exchanger at 25 °C), breakthrough capacity (19.75 mg g^{-1} at pH 5.5) and column efficiencies (300) with respect to Bi^{III}. The positive value of ΔH (12.63 kJ mol^{-1}) and ΔS (0.271 kJ mol^{-1} K^{-1}) and negative value of ΔG (−68.241 kJ mol^{-1}) indicated that the sorption process was endothermic, entropy gaining and spontaneous in nature. P.F. has been optimized at 76.4 ± 0.3 and the desorption constants $K_{desorption}$ (8 × 10^{-3}) and $K'_{desorption}$ (1.4 × 10^{-1}) have been determined. R_f values and selectivity factors for diverse metal ions with respect to that of Bi^{III} have been determined by ion-exchange paper chromatography. Bi^{III} has been separated from synthetic mixtures containing its congeners and other metal ions associated with it in ores and alloy samples. The method was found effective for removal of Bi^{III} from different water samples. A plausible mechanism for the extraction of Bi^{III} has been suggested.

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1. Introduction

Bismuth occurs in native in small amounts (0.008 g tone^{-1}) in minerals of silver, gold and tin. The principal ores are bismuth glance and bismite [1]. Bismuth and its compound are used in semiconductors, cosmetic preparations, alloys, medicines, metallurgical additives and in the preparation and recycling of uranium nuclear fuels [2]. Even in trace level Bi^{III} is nephrotoxic and neurotoxic [3]. Obviously trace level monitoring of metallic toxicant, Bi^{III} poses a challenging problem to the analytical chemists [2]. However, the preconcentration and separation of an analyte is usually necessary before its monitoring. During enrichment ultimately the target species is selectively gathered from a large volume of sample having relatively low concentration and small amounts of metal pollutant can, therefore, be quantified by coupling a preconcentration system to a sensitive, selective detection/estimation technique. In this regard, the most widely used techniques include solvent extraction [4], co-adsorption [5], ion-exchange chromatography [6], reverse flow adsorption [7], cloud point extraction [3], electrochemical

deposition [8] and extraction chromatography (EC) [9–13]. Extraction chromatography [14–16] is now one of the most interesting areas in analytical chemistry for the trace level separation and preconcentration of heavy metals because it is simple, selective, rapid and cost effective. EC is based on the utilization of a major constituent as the supporting phase with different coating liquid-materials, such as polyelectrolyte, high molecular mass carboxylic acid (HMMCA), chelating agent, surfactant, high molecular mass amine (HMMA), etc. Silica gel is found to act as a successful support since it does not swell or strain, has good mechanical strength and can undergo heat treatment [17]. In our laboratory, Versatic 10 on hydrophobic silica support has been effectively used [18] for the extraction, preconcentration and separation of Pb^{II}. But the systematic extraction chromatographic investigation of Bi^{III} with HMMCA, Versatic 10 has yet not been reported. Versatic 10, is a mixture of C$_{10}$ isomeric tertiary monocarboxylic acids, had the concentration and purity of 5.2 M and 99%, respectively. It is soluble in several solvents like benzene, toluene, n-hexane, xylene, butanol, carbon tetrachloride, chloroform, nitrobenzene, diisopropyl ether and has a good thermal and chemical stability and effectively extracts metal ions from aqueous over a wide range of pH [18]. The present work reports a rapid method for the extraction and preconcentration of microgram level Bi^{III} with HMMCA, Versatic 10 on hydrophobic silica support.

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2. Experimental

2.1. Apparatus and reagents

The pH measurements were carried out with a digital Elico L1-120 pH meter combined with glass electrode. The scanning electronic microscopy (SEM) image was obtained at 5.0 kV by JEoL JSM-6700-FESEM. Fourier transform infrared (FTIR) spectra of exchanger in its Bi[III] loaded and unloaded form were recorded on Shimadzu FTIR spectrophotometer (Model no FTIR-8400S) using KBr pellets. The amount of metal ion in the solution was measured by Simadzu atomic absorption spectrophotometer (Model no. AA 6300), with the measurement conditions like, wavelength: 217 nm, L233 Lamp: 10 mA, slit width: 0.7 nm, flame type: Air-C_2H_2, flow-rate: 2.2 L min^{-1}, support gas: 15 L min^{-1}, Burner H: 7 mm. A thermostat was used to carry out the extraction under controlled temperature. Chromatographic glass column (0.8×8 cm^2) with glass-wool plug at the bottom was used to prevent the loss of resin during the sample loading. The column was conditioned by acetate buffer solution before passing the sample solution. A liquid cation exchanger, Versatic 10 (Shell Chemical, London, England), a mixture of high molecular mass C_{10} isomeric tertiary mono carboxylic acid, was used without any further purification. Dimethyldichlorosilane (E Merck, Bombay, India) was used to make the silica gel (Qualigens, Mumbai, India) (120 mesh) hydrophobic. A standard stock solution of Bi[III] (3.13 mg mL^{-1}) was prepared by dissolving Bi(NO$_3$)$_3$ (E Merck, Bombay, India) in water and estimated complexometrically [19] with EDTA (E Merck, Bombay, India) using xylenol orange as indicator. The solution containing micro level of Bi[III] was prepared through appropriate dilution. Buffer solutions of different pH values were prepared from acetic acid (0.1 M) and ammonium acetate (0.1 M) in proper ratio. Lower pH values were adjusted with the help of 0.2 M chloro-acetic acid. All of these chemicals and solvents used in this work, unless otherwise stated, were of analytical grade (BDH, Mumbai, India/E Merck, Mumbai, India).

2.2. Preparation of ion-exchange material

Silica gel (120 mesh) was rendered hydrophobic by exposing it to vapor of dimethyldichlorosilane (DMDCS) in N$_2$ atmosphere. The DMDCS treated (silanized) silica gel was then washed with anhydrous methanol and dried at 100 °C. The silanized silica gel (SSG) was impregnated [20] with Versatic 10, diluted in diisopropyl ether and was dried in a rotary vacuum evaporator to achieve uniform coating. Excess benzene was removed by washing the exchanger with 4 M HCl. Each column could be used for at least 30 cycles without any loss of its exchange capacity. For ion-exchange paper chromatography, a strip of Whatman No 1 paper was immersed in a solution of Versatic 10 (0.5 mL in 20 mL benzene) to achieve uniform coating and then dried in air. Bi[III] at μg level was spotted on the paper strip and developed with acetate buffer of pH 5.5:acetone (25:1, v/v).

2.3. General extraction procedure

Ion exchanger (Versatic 10-SSG) was loaded in the chromatographic column and the pH of the exchanger bed was adjusted to the desired value with acetate buffer. An aliquot of Bi[III] in acetate buffer was passed through the column (pre-adjusted pH 5.5), at a flow-rate of 1.0 mL min^{-1}. After extraction Bi[III] was stripped with 0.1 M H$_2$SO$_4$. A number of fractions were collected and the amount of Bi[III] from each fraction was determined complexometrically.

3. Results and discussion

3.1. Physicochemical characteristics of the exchanger

The SEM image of the ion exchanger is shown in Fig. 1. The photograph confirms that the material is porous in nature. The pore volume, pore diameter and surface area of silica gel (60–120 mesh) are 0.35–0.45 cm^3, 20–30 A^0 and 600–800 m^2 g^{-1}, respectively. The surface area of Versatic 10 was determined by standard methylene blue method [21] ($\sim$132 m^2 g^{-1}), and is comparable to Versatic 911 ($\sim$120 m^2 g^{-1}) [22]. These correspond to the pore volume [23] of 0.5 cm^3. Pore diameters have been computed using the following equation (Eq. (1)) [23]. The pore diameters were found to be 1.1 μm for Versatic 10 and agreed well with the experimental result (SEM).

$$PD = \frac{4 \times PV}{SA} \times 10^4 \tag{1}$$

where PD is the pore diameter, PV the pore volume, and SA the surface area.

3.2. FTIR analysis

FTIR spectra (Fig. 2) of the exchanger containing –COOH group [24] show a strong absorption at 1720.8 cm^{-1}. However, the position of the peak is shifted to lower range (1627.8 cm^{-1}) in the spectra of Bi(NO$_3$)$_3$ loaded exchanger. This decrease in stretching frequency indicates the conversion of –COOH group to –COOH$^-$ ion [24] and rationalizes the chemisorptive nature of Bi[III] adsorption.

3.3. Exchange capacity, break-through capacity and preconcentration factor

The exchange capacity of the prepared exchanger was determined [18] and was found to be 1.42 meq. of H$^+$ g^{-1} of dry exchanger at 25 °C. It was found that the leakage of Bi[III] started at pH values 5.0, 5.25 and 5.5 after passing 342 mL (17.10 mg), 370 mL (18.5 mg) and 395 mL (19.75 mg) of Bi[III] solution (0.05 mg mL^{-1}) respectively and so the uptake of Bi[III] increases with the increase in pH. After extraction, Bi[III] was eluted with 10 mL 0.1 M H$_2$SO$_4$. Thus, the concentration of Bi[III] in the eluent has been increased from 0.05 mg mL^{-1} to 1.698, 1.84 and 1.961 mg mL^{-1} (average recovery percentage: 99.3; standard deviation: 0.32) with a preconcentration factor (P.F.) of $\sim$34.0, 36.7 and 39.2 at the corresponding pH.

3.4. Effect of temperature on extraction

The extraction equilibrium constant (K_{ex}) has been computed at different temperatures using the following equation (Eq. (2))
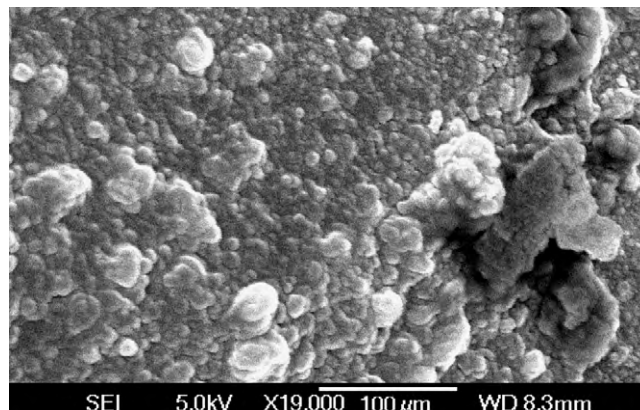

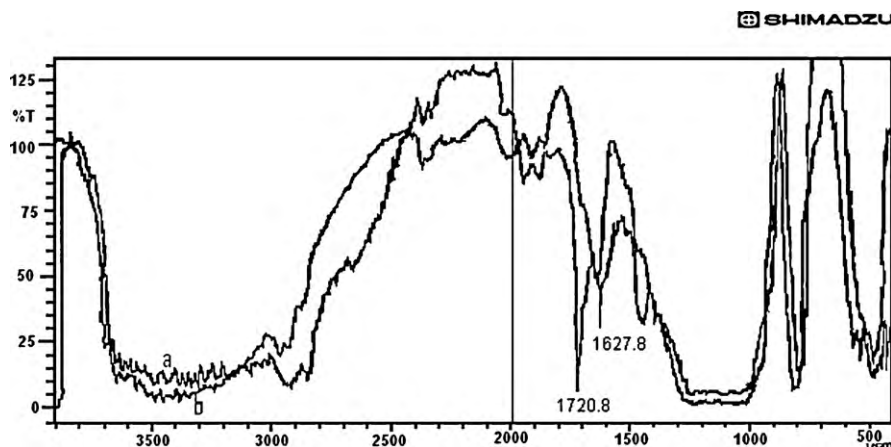**Fig. 1.** SEM image of Versatic 10.

⊕ SHIMADZU

Fig. 2. FTIR spectra of (a) the ion exchanger and (b) Bi[III] loaded ion exchanger.

[18] and plot of $\log K_{ex}$ vs. $1000/T$ gives a linear relationship ($y = -0.6598X + 14.178$; $R^2 = 0.977$) (Fig. 3).

$$K_{ex} = \frac{E_R}{[RCOOH]^2} \times [H^+]^2 \qquad (2)$$

where [RCOOH] denotes the concentration of Versatic 10 and ER is the ratio of extracted metal ion to its un-extracted portion.

The effect of temperature on extraction of Bi[III] has been made for the determination [22] of different thermodynamic parameters at pH 5.5 using the standard Van't Hoff equation [25]. The positive value of ΔH (12.63 kJ mol^{-1}) and positive ΔS (0.271 kJ mol^{-1} K^{-1}) rationalizes the endothermic nature of the extraction process [25]. During adsorption H$^+$ is released in the solution phase and combines with acetate ion produce neutral CH$_3$COOH molecule. The formation of neutral CH$_3$COOH molecule enhances ΔS values. The negative value of ΔG (-68.241 kJ mol^{-1}) suggests the spontaneity and tendency of chemisorptions of the equilibrium.
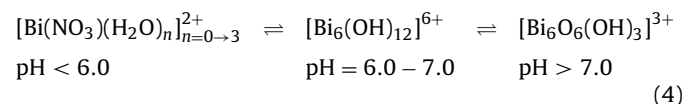
3.5. Effect of pH on extraction and distribution co-efficient

Systematic studies on extraction chromatographic behavior of Bi[III] across the pH range 3.5–6.0 ensured its quantitative extraction at pH range 5.0–5.5. The distribution co-efficient (K_d) at different pH values has been computed (Eq. (3)) and the effect of pH on $\log K_d$ is shown in Fig. 4. At pH higher than 6.0, Bi[III] salt hydrolyses and does not participate in the exchange process. At low pH values (<5.0), the lower extractions were attributed to the difficult deprotonation of the carboxylic acid moiety which eliminates the ability of acetate ion to chelate with Bi[III]. At the low pH, the solubility of Bi[III] was also increased in aqueous solution. Complete retention of Bi[III] in the column was found up to a flow-rate of 2 mL min^{-1}. Anions like NO$_3$$^-$

and SO$_4$$^{2-}$ did not interfere in the extraction. In aq. solution Bi[III] exist as different forms [26] at different pH values as per following equilibrium (Eq. (4)).

$$K_d \left(mL\, g^{-1} \right) = \frac{C_s (mg\, g^{-1})}{C_{sol} (mg\, g^{-1})} \qquad (3)$$

where, C_s and C_{sol} are concentrations of Bi[III] in solid phase and in solution phase, respectively.

$$[Bi(NO_3)(H_2O)_n]^{2+}_{n=0\to3} \;\rightleftharpoons\; [Bi_6(OH)_{12}]^{6+} \;\rightleftharpoons\; [Bi_6O_6(OH)_3]^{3+}$$
$$pH < 6.0 \qquad\qquad pH = 6.0 - 7.0 \qquad pH > 7.0$$
$$(4)$$

3.6. Plausible mechanism of the extraction

The surface of the silica gel becomes methylated (hydrophobic) during silanization (Eq. (5)) [27]. The silanized silica surface immobilizes the hydrophobic part of the exchanger through weak hydrophobic interaction [27] and the –COOH group directed towards the mobile phase (Fig. 5). At the range of pH 4.5–6.5, the exchanger exists as a dimmer through inter molecular hydrogen bonding (Fig. 6) [18]. Taking O···H···O bond length 258 pm, C–O bond length 132 pm and ∠OCO 1200 [28], the calculated core radius of the dimmer (114 pm) is comparable to the radius of Bi[III] (117 pm). To elucidate the hardness behavior, the structure of Versatic 10 was optimized by semi empirical method and from HOMO (-11.10 ev) – LUMO (1.03 ev) gap the global hardness was calculated [29] ($\eta = 6.03$ ev). Here, the presence of a number of hard
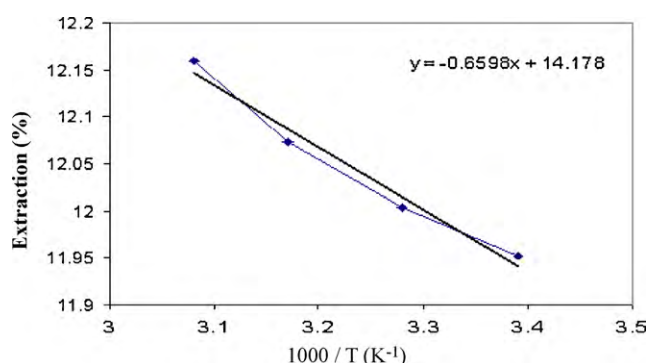

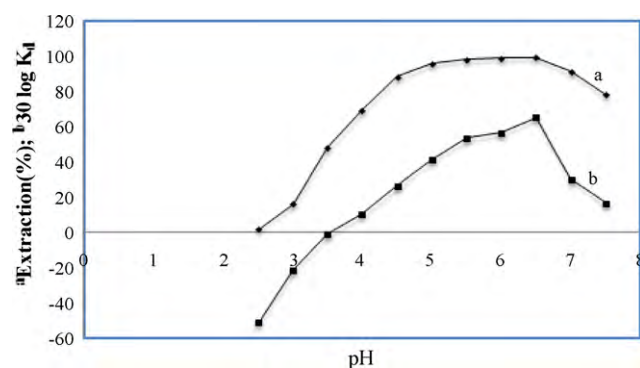**Fig. 3.** Effect of temperature on the extraction of Bi[III].

Fig. 4. Plot of (a) extraction (%) vs. pH and (b) distribution co-efficient (30 log K_d) vs. pH.
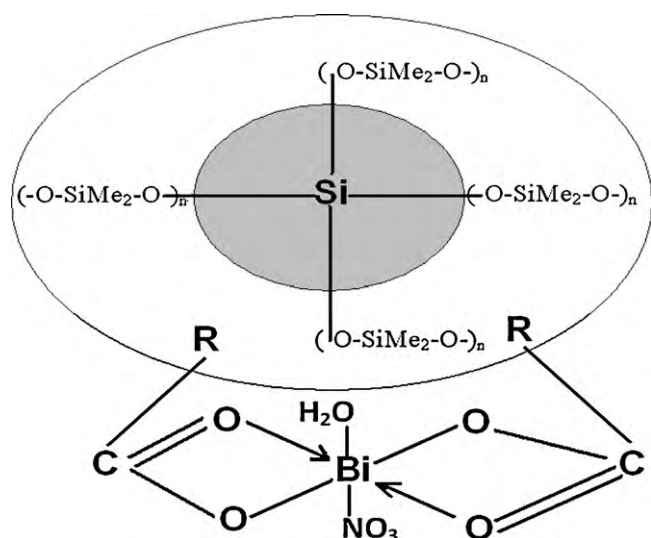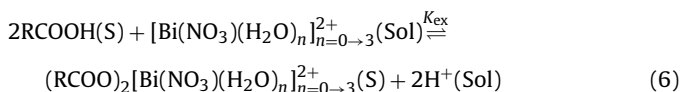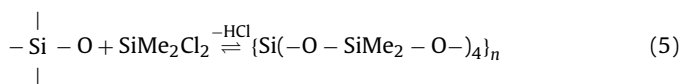
Fig. 5. Probable attachment of Bi^{III} at the hydrophilic part of the exchanger.

donor O-sites in the co-ordination sphere (Fig. 5), symbiotic effect enhanced the global hardness of Bi^{III}, trapped in the exchanger core (inherent η = 3.96 ev). The enhanced η-value possibly approached to that of the exchanger (calculated η = 6.03 ev).

At pH 5.0, plot of $\log K_{ex}$ against $\log K_{[Versatic\ 10]}$ gives a linear relationship (y = 1.896x + 1.659; R^2 = 0.9895) with a slope of 1.896 at fixed concentration acetate and fixed concentration of Bi^{III}. Thus the exchange process can be systematically represented as per the following suggested path (Eq. (6)).

$$-\overset{|}{\underset{|}{Si}} - O + SiMe_2Cl_2 \overset{-HCl}{\rightleftharpoons} \{Si(-O-SiMe_2-O-)_4\}_n \quad (5)$$

$$2RCOOH(S) + [Bi(NO_3)(H_2O)_n]^{2+}_{n=0\rightarrow3}(Sol) \overset{K_{ex}}{\rightleftharpoons}$$

$$(RCOO)_2[Bi(NO_3)(H_2O)_n]^{2+}_{n=0\rightarrow3}(S) + 2H^+(Sol) \quad (6)$$

where K_{ex} denotes the extraction equilibrium constant of Eq. (6).

3.7. Selection of stripping agents

The systematic studies on stripping behavior gave the quantitative elution of Bi^{III} with 10 mL H$_2$SO$_4$ ($\geq$0.1 M), 30 mL HCl ($\geq$1.0 M), 20 mL HNO$_3$ ($\geq$0.2 M) and 70 mL CH$_3$COOH ($\geq$2 M). Column efficiency (N) has been calculated [30] with respect to these eluents ($N_{H_2SO_4}$: 300; N_{HCl} : 256; N_{HNO_3} : 222; N_{CH_3COOH} : 248) (Eq. (7)).

$$N = 4 \times \left[\frac{y}{x}\right]^2 \quad (7)$$

where y = distance for peak elution, x = 1/2$W_{0.6065}$ and $W_{0.6065}$ = width of the peak height at 0.6065 times of the peak height.
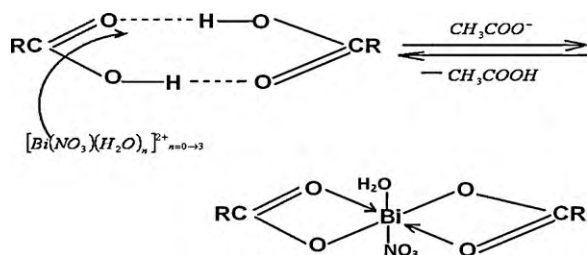

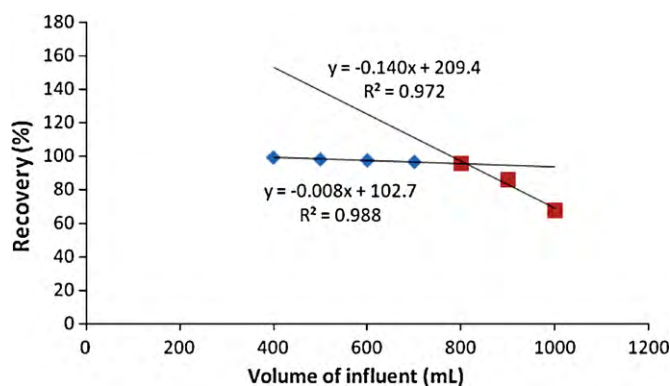**Fig. 6.** Probable mechanism of Bi^{III} trapping in the dimeric cavity of the exchanger.

Fig. 7. Effect of influent volume on recovery.

0.1 M H$_2$SO$_4$ with least elution volume (10 mL) and highest column efficiency ($N_{H_2SO_4}$: 300) gave the best stripping. The elution process (back extraction) follows the reverse reaction of extraction (Eq. (6)). Efficiency of organic acid (CH$_3$COOH) is less than the inorganic acids (H$_2$SO$_4$, HNO$_3$, and HCl) due to its lower degree of dissociation. Low level of inorganic acids effectively shifts the equilibrium (Eq. (6)) to left hand side and elutes Bi^{III} from the exchanger bed through the formation of chloro, sulfato and nitro complexes.

3.8. Effect of pH, concentration and volume of the influent on preconcentration factor

The extraction of 0.018–0.023 mg mL^{-1} of Bi^{III} on exchanger in the pH range 5.0–5.5 (Table 1) showed that P.F. (C_f/C_s) has been increased with increase in volume of the influent as expected. Also the P.F. at a constant volume of influent turns out to be independent of variation in pH and influent concentration. The recovery decreased with increase in sample volume. Up to an influent volume of 800 mL, recovery of Bi^{III} was quantitative (>95%) with P.F. 76.4 $\pm$ 0.3. To reach the break-through values 17.1 mg g^{-1} (at pH 5.0), 18.5 mg g^{-1} (at pH 5.25) and 19.7 mg g^{-1} (at pH 5.5), respectively 950 mL of 0.018 mg mL^{-1}, 925 mL of 0.02 mg mL^{-1} and 859 mL of 0.023 mg mL^{-1} of Bi^{III} solution were passed through the column. Due to volume effect [18], the recoveries (%) were much poor (<75%) and P.F. did not attend the maximum possible values 95, 92.5 and 85.9. But, the P.F. value was optimized at 76.4 $\pm$ 0.3. Plot of V_s (volume of influent sample) vs. $R_{Bi^{III}}$ (recovery of Bi^{III}) indicates two linear segments (y = $-$0.008x + 102.7; R^2 = 0.988 and y = $-$0.140x + 209.4; R^2 = 0.972) intersecting at about a influent volume of 800 mL (Fig. 7). The slopes of the corresponding linear segments yield desorption constants $K_{desorption}$ = 8 $\times$ 10^{-3} and $K'_{desorption}$ = 1.4 $\times$ 10^{-1}, respectively. The slope is a measure of desorption efficiency and at higher slope it needs the smaller volume for 100% desorption. It shows that the recovery would become zero at an influent volume of 1.5 L (approx.). That is, at that very condition the influent will also act as an eluent for Bi^{III}.

3.9. Ion-exchange paper chromatography

At pH 5.5, the R_f values and the selectivity factor were determined in acetate buffer–acetone mixture (25:1, v/v) on chromatogram (Table 2). Result shows that under this recommended condition Sn^{II}, Zn^{II}, Mg^{II}, Ca^{II}, Cr^{III} are very weakly bound ($R_f \sim$ 0.9), metal ions like Cd^{II}, Al^{III}, Pb^{II}, Cu^{II}, Ga^{III}, Bi^{III} are moderately bound ($R_f \sim$ 0.3–0.6) while Tl^{III} is tightly bound with the stationary phase (R_f < 0.1). At pH 2.5 binding strength of Zr^{IV} is very much higher than Fe^{III} and under this condition Bi^{III} is very weakly bound with the stationary phase. Higher values of selectivity factors [31] ($\alpha \geq$ 1.5) suggest easy separation of

Table 1
Effect of volume, sample concentration and pH on preconcentration factor [flow-rate = 1.0 mL min^{-1}; pH 5.5; Bi^{III} = 0.018–0.023 mg mL^{-1}; standard deviation < 0.07].

pH	Sample conc. (C_s) (mg mL^{-1})	Sample volume, V_s (mL)	Amount of Bi^{III} (mg)		Effluent conc. (C_f) (g L^{-1})	Recovery[a] $R_{Bi^{III}}$ (%)	P.F.[s] (C_f/C_s)
			Added	Recovered			
5.0	0.018	400	7.2	7.11	0.71	98.8	39.4
		500	9.0	8.83	0.88	98.1	48.9
		600	10.8	10.55	1.06	97.7	58.9
		700	12.6	12.15	1.22	96.4	67.8
		800	14.4	13.78	1.38	95.7	**76.7**
		900	16.2	13.88	1.38	85.6	76.7
		950	17.1	13.44	1.34	78.6	74.4
5.2	0.02	400	8.0	7.95	0.79	99.4	39.5
		500	10.0	9.81	0.98	98.2	49.0
		600	12.0	11.68	1.17	97.3	58.5
		700	14.0	13.51	1.35	96.5	67.5
		800	16.0	15.25	1.53	95.3	**76.5**
		900	18.0	15.39	1.53	85.5	76.5
		925	18.5	14.49	1.45	78.3	72.5
5.5	0.023	400	9.2	9.15	0.92	99.5	40.0
		500	11.5	11.26	1.13	97.9	49.1
		600	13.8	13.46	1.35	97.5	58.7
		700	16.1	15.62	1.56	97.0	67.8
		800	18.4	17.55	1.75	95.4	**76.1**
		859	19.7	16.63	1.66	84.4	72.2

[a] Average of five determinations; P.F. = ratio of effluent conc. to sample conc. (C_f/C_s); optimized value of P.F. has been highlighted as bold.
[s] Synthetic samples.

Bi^{III} from these diverse metal ions except Ga^{III}. At ∼pH 5.5 Sn^{II} exists as an anionic complex [32], [Sn(CH$_3$COO)$_3$]$^-$ and moves at a fastest rate with the mobile phase. With acetate ion the complexity constant [26] for Ca^{II} is much higher than that for Mg^{II}. So Ca^{II} moves at a faster rate than Mg^{II}. The affinity order of Tl^{III}, Ga^{III}, Cr^{III} and Al^{III} with the exchanger is directly related to the order of ease of formation of monohydroxo-species [26], i.e., [Tl(OH)(H$_2$O)$_5$]$^{2+}$ ≫ [Ga(OH)(H$_2$O)$_5$]$^{2+}$ > [Cr(OH)(H$_2$O)$_6$]$^{2+}$ > [Al(OH)(H$_2$O)$_5$]$^{2+}$. The increasing affinity order is directly related to decreasing order of the hydrated radii [33] of Zn^{II}, Cd^{II} and Hg^{II}.

3.10. Separation of Bi^{III} from binary mixtures

Bi^{III} was separated from several metal ions in binary mixtures (Table 3). The separations were achieved either by exploiting the difference in pH for extraction or by using suitable stripping agent utilizing the R_f values. When, Bi^{III}–Fe^{III} and Bi^{III}–Zr^{IV} binary mixtures were passed through the column at pH 2.5, only Bi^{III} (R_f > 0.9) from the said mixtures was percolated through the column with the mobile phase. The extracted Fe^{III} and Zr^{IV} were eluted with

0.5 M H$_2$SO$_4$ and 6 M HNO$_3$, respectively. Binary mixtures containing Bi^{III} with Cr^{III}, Zn^{II} and Sn^{II} when passed through the column at pH 5.5, the diverse ions (R_f > 0.9) were passed through the column with mobile phase. Under this condition only Bi^{III} was extracted at the column and was eluted with 0.1 M H$_2$SO$_4$. However at pH 5.5 from the binary mixtures the diverse ions like Pb^{II}, Cd^{II}, Hg^{II}, Al^{III}, Cu^{II} and Tl^{III} were extracted along with Bi^{III} (R_f < 0.6). For Bi^{III}–Pb^{II}, Bi^{III}–Cd^{II}, Bi^{III}–Al^{III}, Bi^{III}–Cu^{II} and Bi^{III}–Tl^{III} mixtures, the diverse ions were eluted first with different specific eluents, e.g., Pb^{II} with 0.005 M HNO$_3$, Cd^{II} with 0.5 M CH$_3$COOH, Al^{III} and Cu^{II} with 0.05 M CH$_3$COOH and, Tl^{III} with 0.01 M HCl, followed by Bi^{III} with 0.1 M H$_2$SO$_4$. For Bi^{III}–Hg^{II} mixture, Bi^{III} was first extracted with 0.2 M HNO$_3$, followed by Hg^{II} with 0.5 M HNO$_3$.

3.11. Separation of Bi^{III} from multi-component synthetic mixture

In order to assess the possible analytical applications the proposed method was applied to separate Bi^{III} from multi-component synthetic mixtures containing Bi^{III} with different metal ions commonly associated with it in same analytical group, ores and alloy

Table 2
R_f values and selectivity factors of different metal ions on Whatman No 1 impregnated with Versatic 10 [time = 2.5 h; pH 5.5; [b]pH 2.5; developing solvent = acetate buffer:acetone (25:1) v/v].

Cations	R_f[d] values	Affinity order (increasing) ↓	Selectivity factor, $\alpha = \frac{(R_f)_i}{(R_f)_{Bi}}$
Mg^{II}	**0.93**	Sn^{II}	3.30
Ca^{II}	**0.94**	Zn^{II}	3.23
Zn^{II}	**0.97**	Ca^{II}	3.13
Cd^{II}	**0.56**	Mg^{II}	3.10
Hg^{II}	**0.28**	Cr^{III}	3.06
Sn^{II}	**0.99**	Cd^{II}	1.86
Cr^{III}	**0.92**	Pb^{II}	1.77
Pb^{II}	**0.53**	Al^{III}	1.63
Cu^{II}	**0.47**	Cu^{II}	1.57
Al^{III}	**0.49**	Ga^{III}	1.00
Ga^{III}	**0.30**	Bi^{III}	
Tl^{III}	**0.08**	Hg^{II}	2.50
Bi^{III}	**0.30**	Tl^{III}	3.75
Bi^{III}[b]	**0.92**	Bi^{III}[b]	
Fe^{III}[b]	**0.36**	Fe^{III}[b]	2.44
Zr^{IV}[b]	**0.04**	Zr^{IV}[b]	22.00

[d] R_f values highlighted as bold.

Table 3
Important binary separations of Bi^{III} [flow-rate = 1.0 mL min^{-1}; pH 5.5, ^{b}pH 2.5; Bi^{III} = 3.13 g].

Cations	Wt. of the cations added (mg)	Recovery (%)[a]	R.S.D. (%)[r]	Eluent used	Eluent volume (mL)
Bi^{III}	3.13	99.24	**1.83**	–	30
$Fe^{III\,b}$	2.87	100.2	**2.45**	$0.5\,M\,H_2SO_4$	50
Bi^{III}	3.13	98.64	**1.65**	–	30
$Zr^{IV\,b}$	3.02	100.5	**2.08**	$6\,M\,HNO_3$	30
Sn^{II}	3.75	99.18	**1.33**	–	30
Bi^{III}	3.13	100.4	**1.54**	$0.1\,M\,H_2SO_4$	10
Cr^{III}	2.94	98.74	**2.08**	–	30
Bi^{III}	3.13	101.2	**1.56**	$0.1\,M\,H_2SO_4$	10
Zn^{II}	3.26	99.45	**1.62**	–	30
Bi^{III}	3.13	100.8	**2.04**	$0.1\,M\,H_2SO_4$	10
Pb^{II}	3.07	98.25	**1.80**	$0.005\,M\,HNO_3$	40
Bi^{III}	3.13	101.0	**1.94**	$0.1\,M\,H_2SO_4$	10
Cd^{II}	3.52	99.32	**1.86**	$0.5\,M\,CH_3COOH$	20
Bi^{III}	3.13	99.37	**1.72**	$0.1\,M\,H_2SO_4$	10
Bi^{III}	3.13	101.6	**1.96**	$0.2\,M\,HNO_3$	20
Hg^{II}	2.72	98.68	**1.60**	$0.5\,M\,HNO_3$	20
Al^{III}	3.56	98.96	**1.45**	$0.05\,M\,CH_3COOH$	50
Bi^{III}	3.13	101.3	**2.06**	$0.1\,M\,H_2SO_4$	10
Cu^{II}	3.06	100.8	**2.24**	$0.05\,M\,CH_3COOH$	40
Bi^{III}	3.13	99.14	**2.04**	$0.1\,M\,H_2SO_4$	10
Tl^{III}	3.00	101.2	**2.44**	$0.01\,M\,HCl$	50
Bi^{III}	3.13	100.5	**2.33**	$0.1\,M\,H_2SO_4$	10

[a] Average of five determinations.
[r] Relative standard deviation has been highlighted as bold.

samples (Table 4). Separation of Bi^{III} from diverse metal ions in binary and multi-component synthetic mixtures follows the R_f values and Kielland principle [32], 'affinity order of the cations for cation-exchange resin is approximately the inverse order of their hydrated ionic radii (order of their radii)'. Low R_f values (<0.6 at the recommended pH) indicate strong exchanger–metal ion interaction, i.e., chemisorptions.

3.11.1. Sequential separation of Bi^{III}, Sn^{II}, Pb^{II} and Cd^{II}

Separation of Bi^{III}, Pb^{II}, Sn^{II} and Cd^{II} was achieved by passing the mixed solution at pH 5.5, when except Sn^{II}, all the metal ions were co-extracted and then they were eluted by selective eluting agent. Pb^{II} was first eluted by $0.005\,M\,HNO_3$, then Cd^{II} by $0.5\,M\,CH_3COOH$ and Bi^{III} finally by $0.1\,M\,H_2SO_4$.

3.11.2. Sequential separation of Bi^{III}, Sn^{II}, Cu^{II} and Hg^{II}

When the mixture of Bi^{III}, Sn^{II}, Cu^{II} and Hg^{II} was passed through the exchanger at pH 5.5, Sn^{II} was percolated through the column with the mobile phase and other metal ions were co-extracted. Then they were eluted by selective eluting agent. Cu^{II} was first eluted by $0.05\,M\,CH_3COOH$, Bi^{III} by $0.2\,M\,HNO_3$ and Hg^{II} finally by $0.5\,M\,HNO_3$.

3.12. Effectiveness and utility of the proposed method

The effectiveness and the feasibility of the process were tested with the effluent (waste, thermal and tap water) (Table 5). High degree of preconcentration (600–10 mL) (>57.5 ± 0.3 fold) with subsequent recovery of 93.6 ± 0.8% and 93.4 ± 0.6% for Bi^{III} and Hg^{II}

Table 4
Separation of Bi^{III} from multi-component synthetic mixtures [flow-rate = 1.0 mL min^{-1}; pH 5.5, ^{b}pH 2.5; Bi^{III} = 3.13 g].

Metal Ions	Weight of the metal ions (mg) Added	Recovery (%)[a]	R.S.D. (%)[r]	Eluent used	Eluent volume (mL)
$Fe^{III\,b}$	2.87	100.8	**1.68**	$0.5\,M\,H_2SO_4$	50
Cu^{II}	3.06	100.9	**1.54**	$0.05\,M\,CH_3COOH$	20
Bi^{III}	3.13	98.26	**1.62**	$0.1\,M\,H_2SO_4$	10
$Fe^{III\,b}$	2.87	101.2	**2.46**	$0.5\,M\,H_2SO_4$	50
Zn^{II}	3.26	99.46	**1.85**	–	30
Bi^{III}	3.13	100.6	**2.35**	$0.1\,M\,H_2SO_4$	10
$Fe^{III\,b}$	2.87	101.5	**2.24**	$0.5\,M\,H_2SO_4$	50
Cr^{III}	2.94	98.93	**1.83**	$-0.1\,M\,H_2SO_4$	30
Bi^{III}	3.13	99.27	**1.50**	–	10
$Fe^{III\,b}$	2.87	101.4	**1.61**	$0.5\,M\,H_2SO_4$	50
Al^{III}	3.56	99.27	**1.69**	$0.05\,M\,CH_3COOH$	50
Bi^{III}	3.13	98.78	**1.83**	$0.1\,M\,H_2SO_4$	10
Pb^{II}	3.07	101.0	**1.84**	$0.005\,M\,HNO_3$	40
Cd^{II}	3.52	98.92	**1.51**	$0.5\,M\,CH_3COOH$	20
Bi^{III}	3.13	100.6	**2.35**	$0.1\,M\,H_2SO_4$	10
Sn^{II}	3.06	101.20	**1.84**	–	30
Pb^{II}	3.07	99.22	**1.56**	$0.005\,M\,HNO_3$	40
Cd^{II}	3.52	98.69	**1.51**	$0.5\,M\,CH_3COOH$	20
Bi^{III}	3.13	99.26	**1.67**	$0.1\,M\,H_2SO_4$	10
Sn^{II}	3.75	101.3	**1.22**	–	30
Cu^{II}	3.06	99.78	**2.51**	$0.05\,M\,CH_3COOH$	40
Bi^{III}	3.13	100.7	**1.42**	$0.2\,M\,HNO_3$	20
Hg^{II}	2.72	98.85	**1.94**	$0.5\,M\,HNO_3$	20

[a] Average of five determinations.
[r] Relative standard deviation has been highlighted as bold.

Table 5
Removal of Bi^{III} and Hg^{II} in water samples [sample volume = 600 mL; elution volume = 10 mL (Bi^{III}); 20 mL (Hg^{II})].

Sample	Water				
	Metal ion	Added ($\mu g\,mL^{-1}$)	Found ($\mu g\,mL^{-1}$)[a]	Recovery (%)	P.F.[r]
Waste water	Bi^{III}	–	ND	–	
		16.4	917.1	93.2	55.9
	Hg^{II}	–	ND	–	
		15.2	843.7	92.5	55.5
Thermal water	Bi^{III}	–	ND	–	
		16.4	913.2	92.8	55.7
	Hg^{II}	–	ND	–	
		15.2	852.1	93.4	56.1
Well water	Bi^{III}	–	ND	–	
		16.4	928.9	94.4	56.6
	Hg^{II}	–	ND	–	
		15.2	858.2	94.1	57.1

[a] Average of five determinations.
[r] Real samples.

Table 6
Comparison of the observed concentration (AAS) of Bi^{III} with the preconcentration technique.

Sample	Concentration (AAS) ($\mu g\,mL^{-1}$)	Concentration (predicted) ($\mu g\,mL^{-1}$)	Error (%)
Waste water	16.40	15.68	4.39
Thermal water	16.40	15.61	4.82
Well water	16.40	15.88	3.17

respectively with low standard deviation (<0.4) find its analytical applicability. The recovered Bi^{III} were equated with the average recovery of 97.5% for a sample volume of 600 mL (Table 1) and the projected concentrations were calculated to have an idea about the concentration of the mother solution. The predicted values were highly compatible with observed values obtained by AAS (4.0 ± 0.8% error) (Table 6). Having suitable size, charge and hardness, Bi^{III} has been effectively extracted from a solution of large volume of relatively low concentration. At the same time, H_2SO_4 being a strong inorganic acid elute Bi^{III} with its very small volume by efficiently shifting the equilibrium (Eq. (6)) towards left. Both these factors favor the enhancement of the preconcentration factor. In comparison to other matrices (except very few matrices [2,37]) such as, Bromopyrogallol red-Triton X-114 (P.F.: 20) [3], SP Sephadex C-25 cation-exchange resin (P.F.: 33.4) [6], SRS 100-Silanised Silica Gel (P.F.: 42) [13], polyacrylacylisothiourea chelating fiber (P.F.: 20) [34], dithiocarbamates-coated amberlite XAD-7 (P.F.: 150) [2], 2,5-dimercapto-1,3,4-thiadiazole loaded on silica with gel (P.F.: 50) [35], nylon fiber-packed microcolumn (P.F.: 20) [36], thionalide-loaded silica gel (P.F.: 100) [37] the present exchanger has got much higher value of preconcentration factor (P.F.: [s]76.4 ± 0.3; [r]57.5 ± 0.3).

4. Conclusions

The outcomes of the proposed method are summarized as follows: Bi^{III} is trapped as an extracted species, $(RCOO^-)_2[Bi(NO_3)(H_2O)](S)$ in the dimeric core of hard donor O-sites. (1) Quantitative extraction was achieved at the range of pH 5.0–5.5. (2) The extraction was an endothermic one. (3) With respect to 0.1 M H_2SO_4 as an eluent column efficiency was good ($N = 300$). (4) With respect to Bi^{III}, the values of selectivity factors (α) for individual metal ions are: Sn^{II} (3.30), Zn^{II} (3.23) Ca^{II} (3.13), Mg^{II} (3.10), Cr^{III} (3.06), Cd^{II} (1.86), Pb^{II} (1.77), Al^{III} (1.63), Cu^{II} (1.57), Ga^{III} (1.00), Hg^{II} (2.50), Tl^{III} (3.75), Fe^{III} (2.44), Zr^{IV} (22.0). For the selectivity factors, $\alpha \geq 1.5$ which is attained for all other metal ions (except Ga^{III}: 1.00), clean separations were achieved from several toxic and heavy metal ions present

in their synthetic mixtures. (5) The method of optimization for preconcentration factor was developed. The preconcentration factor was optimized at 76.4 ± 0.3 and value is comparable to other matrices [2,3,13,33–36]. (6) For the synthetic multi-component mixtures, in most of the cases recoveries were quantitative (>99%) and the relative standard deviations were <2%. (7) The proposed method is simple, rapid, selective, eco-friendly and cost effective as each column could be used for at least 30 cycles without any loss of its exchange capacity. (8) The method effectively permits sequential separation of Bi^{III} from synthetic quaternary mixture containing its congeners Cu^{II}, Sn^{II}, Hg^{II} and Sn^{II}, Cd^{II}, Pb^{II} of same analytical group. (9) As an alternative to AAS, the technique shows its acceptability in a very low level quantification (in ppm level) by coupling its preconcentration process.

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