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SYNTHESIS, ION-EXCHANGE BEHAVIOUR AND COMPOSITION OF TIN(IV) HEXACYANOFERRATE(II)*

MOHSIN QURESHI, K. G. VARSHNEY AND A. H. ISRAILI

Z.H. College of Engineering and Technology and Department of Chemistry, Aligarh Muslim University, Aligarh, U.P. (India)

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SUMMARY

Tin(IV) hexacyanoferrate(II) as an inorganic ion exchanger has been prepared in thirteen different ways by varying the pH, the mole ratios mixed and the concentration. Exhaustive analytical studies of a sample having a Sn/Fe mole ratio of 3:1 and an ion-exchange capacity of 2.02 mequiv./g dry weight have been made. These include investigation of its stability in different solvents and its composition, pH-titrations, ion distribution studies, thermogravimetry, and X-ray diffraction measurements. On the basis of all these experimental data a tentative approach to the formula of the compound was made. The potentiality of its use as an ion exchanger has been demonstrated by the achievement of some important and difficult separations.

INTRODUCTION

Metal ion complexes formed with ferrocyanides have recently shown very interesting properties as synthetic inorganic ion exchangers[1]. They are easily prepared and are comparatively less prone to the adverse effects of acids[2] and heat than organic ion exchangers. A high exchange capacity and the fact that they can be used for the separation of radioactive waste and fissionable materials[3] with less damage by radiation than their organic counterparts is indicative of their usefulness. The work on these ion exchangers reported so far mostly concerns their preparation, radiochemical properties, crystallography[4] and the adsorption behaviour of alkali metal ions or alkaline earths[5,6]. The ion-exchange adsorption of other ions has received less attention.

Tin(IV) ion exchangers prepared in these laboratories[7-11] have been found to show very good ion-exchange properties and a few very important and difficult separations have been achieved on papers impregnated with these materials[12,13]. So far, no systematic work on tin(IV) hexacyanoferrate(II) seems to have been reported in the literature. The formation of a yellow precipitate on the addition of

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potassium ferrocyanide solution to stannic chloride solution has been mentioned (see MELLOR[14]) but a detailed study of its use as an ion exchanger is lacking. The preparation and study of the properties of this material were undertaken and the results of such a study are summarized here.

EXPERIMENTAL

Reagents

Stannic chloride pentahydrate (Poland) and potassium ferrocyanide (B.D.H. Analar) were used. All other chemicals were of reagent grade.

Apparatus

Spectrophotometric studies were performed on a Bausch and Lomb spectronic-20 colorimeter. pH-measurements were made on Beckman model-G and Elico Model LI-10 pH-meters. A Philips Camera with an X-ray unit was used for the X-ray studies while thermogravimetry was performed with Stanton thermobalance type H-4.

Synthesis

Thirteen samples were prepared by mixing stannic chloride with potassium ferrocyanide solution under different conditions. The gels formed were digested at room temperature for 24 h. The supernatant liquid was then decanted and the gels were washed several times with distilled water to remove the unreacted reagents. They were filtered and dried at 40–45°. The dry gels were immersed in cold water. They broke down to small particles with cracking and slight evolution of heat. The exchanger was washed with hot distilled water at pH 6–7 to get rid of occluded tin ions or ferrocyanide. It was, then, immersed in 1–2 M HNO_3 or HCl for 24 h to convert it to the H^+ form. The exchanger in the H^+ form was washed with distilled water to remove excess acid. When the wash solution had a pH of 6–7 the samples were dried at 40–45°. The particles of desired size were then obtained by passing the ion-exchange material through appropriate sieves. The methods of preparation and some important properties of the different samples are summarized in Table I.

RESULTS

In order to prepare an ion exchanger having a high ion-exchange capacity and low solubility, all the samples prepared were studied on a comparative basis. Their ion-exchange capacity, solubility in distilled water, and compositions are given in Table II.

As is clear from Table II, the ion exchange capacity increases with an increase of the ferrocyanide content in the product. However, the gel character improves with an increase in the tin content of the compound. S-11 was, therefore, selected for detailed study.

Properties

Tin(IV) hexacyanoferrate(II) (Sample S-11) is in the form of blue black, hard, shining granules, suitable for column operation.

TABLE I

SYNTHESIS OF DIFFERENT SAMPLES UNDER DIFFERENT CONDITIONS

Sample No.	Method of preparation	Remarks
S-1	0.1 M SnCl$_4$ + 0.1 M K$_4$Fe(CN)$_6$, (1:1), pH 4	Green product
S-2	0.1 M SnCl$_4$ + 0.1 M K$_4$Fe(CN)$_6$, (2:1), pH 4	Blue product
S-3	0.1 M SnCl$_4$ + 0.1 M K$_4$Fe(CN)$_6$, (1:2), pH 4	Blue product which dissolved during washing
S-4	0.1 M SnCl$_4$ + 0.1 M K$_4$Fe(CN)$_6$, (1:3), pH 4	Blue product which dissolved during washing
S-5	0.1 M SnCl$_4$ + 0.1 M K$_4$Fe(CN)$_6$, (1:1), pH 1	Blue product
S-6	0.1 M SnCl$_4$ + 0.1 M K$_4$Fe(CN)$_6$, (1:1), pH 6.9	Brown product having shiny particles
S-7	0.1 M SnCl$_4$ + 0.1 M K$_4$Fe(CN)$_6$, (1:1), pH 9.9 (ammonia)	Brown product which dissolved in 1-2 M HCl in 24 h
S-8	0.1 M SnCl$_4$ + 0.1 M K$_4$Fe(CN)$_6$, (1:1), pH 13 (NaOH)	Very small white precipitate which dissolved during digestion
S-9	0.02 M SnCl$_4$ + 0.02 M K$_4$Fe(CN)$_6$, (1:1), pH 1	Blue product
S-10	0.01 M SnCl$_4$ + 0.01 M K$_4$Fe(CN)$_6$, (1:1), pH 1	Blue product
S-11	0.1 M SnCl$_4$ + 0.1 M K$_4$Fe(CN)$_6$, (3:1), pH 0.8	Blue black, shiny particles
S-12	0.04 M SnCl$_4$ + 0.04 M K$_4$Fe(CN)$_6$, (3:2), pH 1.3	Blue black, shiny particles
S-13	0.02 M SnCl$_4$ + 0.02 M K$_4$Fe(CN)$_6$, (2:1), pH 1.6	Blue black, shiny particles

Chemical stability

To test the chemical stability visually, 0.2–0.5 g of the exchanger was kept in 25 ml of various solutions at room temperature with the following results:

(a) In 12 h there was no change with sulphuric acid, nitric acid, formic acid and acetic acid of all possible concentrations; 4 M hydrochloric acid, 0.02 M sodium hydroxide and 10% aqueous oxalic acid solutions.

TABLE II

A COMPARISON OF THE ION-EXCHANGE CAPACITY, SOLUBILITY AND COMPOSITION OF THE DIFFERENT SAMPLES

Sample No.	Composition (Sn:Fe) (mole ratio)	Ion-exchange capacity mequiv./dry g	Solubility in water	
			mg Sn/50 ml	mg Fe/50 ml
S-1	9.2:1	0.60	0.112	0.50
S-2	3.2:1	1.30	0.112	0.60
S-5	3:5	2.29	0.084	0.50
S-6	100:1	0.11	0.120	0.00
S-9	4:5	3.40	0.240	0.60
S-10	4:5	2.95	0.056	0.70
S-11	5:2	2.02	0.068	0.50
S-12	7:5	2.5	0.120	0.45
S-13	5:2	1.97	0.068	0.70

(b) In 15 min the exchanger dissolved in concentrated hydrochloric acid and 10% ammonium hydroxide.

A detailed study of the chemical stability of the exchanger in water and acids was made as follows:

It was first washed with hot water to remove any tin ions or ferrocyanide remaining adsorbed on the beads. 500 mg of this washed material were then refluxed with 50 ml of distilled water at different time intervals ranging from 1 to 8 h. On quantitative determination of tin and iron in all the filtrates it was noticed that there was a gradual increase in the amount of the dissolved ion exchanger in all cases and after heating for 8 h the exchanger had dissolved almost completely, giving a turbid blue solution. The solubility was determined in different solvents by taking 500 mg of the exchanger in 50 ml of the solvent, and refluxing it with an air condenser for 1 h in each case. After cooling, the solution was filtered and the tin and iron in the filtrate were determined spectrophotometrically by the procedures given below:

Determination of tin. 25 ml of the filtrate were distilled[15] to separate tin from iron. The distillate was diluted to 100 ml with distilled water in a standard flask. 0.5 ml (2:1) sulfuric acid and 5 ml conc. nitric acid were added to a 25 ml portion of the dilute distillate in a 100 ml beaker which was covered with a watch glass and heated to evaporate the liquid completely to dryness. The residue was then cooled and tin was determined with phenyl fluorone as usual[16] against a blank prepared in an identical manner.

Determination of iron. 10 ml of the filtrate were heated in a beaker with 1 ml of conc. H_2SO_4 and 1 ml of conc. HCl to decompose ferrocyanide and cyanide ions. The volume was reduced to about 1 ml and the solution was finally evaporated to dryness. The residue was taken up in a little distilled water and was transferred to a 10 ml standard flask. Iron was determined with 1,10-phenanthroline against a blank[17].

The results of the solubility determinations in water and acids are given in Table III.

Composition

200 mg of the exchanger were heated with 10 ml of H_2SO_4 and 50 ml of HCl. First the solution was blue (ferrocyanic acid) then it turned yellow. It was cooled and stannous chloride solution (60 g $SnCl_2$ in 600 ml HCl and 400 ml H_2O) was added

TABLE III

SOLUBILITY OF TIN(IV) HEXACYANOFERRATE(II) IN WATER AND ACIDS

Solvent	Amount of tin dissolved in 50 ml (mg)	Amount of iron dissolved in 50 ml (mg)
Distilled water	0.07	0.50
0.1 M HCl	0.42	1.75
0.1 M HNO₃	0.11	0.35
0.5 M HNO₃	0.19	0.35
1 M HNO₃	0.32	0.58
0.1 M H₂SO₄	0.38	1.58

TABLE IV

COMPOSITION OF TIN(IV) HEXACYANOFERRATE(II)

Wt. of the exchanger (mg)	Volume of $0.1\ N\ K_2Cr_2O_7$ used for iron (ml) (a)	Volume of $0.1\ N\ K_2Cr_2O_7$ used for iron and tin (ml) (b)	Volume of $0.1\ N\ K_2Cr_2O_7$ used for tin only (ml) (b−a)	Molar ratio (Sn:Fe) $\left[\dfrac{b-a}{2}:a\right]$
200	2.25	15.00	12.75	2.7:1
200	2.30	15.95	13.65	2.9:1
200	2.35	14.35	12.00	2.5:1
200	2.35	15.35	13.50	2.9:1
200	2.35	15.40	13.55	2.9:1

dropwise to the cold solution until the colour of iron was no longer evident. The excess of $SnCl_2$ was destroyed with mercuric chloride (saturated solution) as usual. 15 ml of a phosphoric acid–sulphuric acid mixture (150 ml H_3PO_4 + 150 ml H_2SO_4 diluted to 1000 ml) were then added and the volume was made up to about 200 ml with distilled water. Iron was determined by titration against a $K_2Cr_2O_7$ solution using diphenylamine as indicator[18].

For the simultaneous determination of tin and iron in the exchanger 200 mg were dissolved in the sulphuric acid–hydrochloric acid mixture as above. 10 ml of conc. H_2SO_4, 100 ml of conc. HCl and about 2–3 g of test lead in a 500 ml conical flask were added to this solution. The volume was made up to 300 ml with distilled water and the solution was heated for 1 h in an atmosphere of CO_2. It was then cooled to 10° in an ice bath. Tin and iron in the reduced state were titrated against $0.1\ N\ K_2Cr_2O_7$ using diphenylamine as the indicator[19]. The total quantity of tin and iron in the exchanger was thus determined. The amount of tin was then obtained by subtracting the quantity of iron from the total amount of tin and iron. The results for sample S-11 are summarized in Table IV.

Ion-exchange capacity

The gel was found to have cation-exchange properties. Its ion-exchange capacity was therefore determined by testing different mono- and bivalent metal ions in the usual manner[7,8]. A column was prepared in a glass tube of I.D. 6 mm and the flow rate of the effluent was kept at 10–12 drops (approx. 0.5–0.6 ml) per min. Table V summarizes the results.

TABLE V

ION EXCHANGE CAPACITY OF TIN(IV) HEXACYANOFERRATE(II)

Metal ion	Capacity (mequiv./g dry exchanger)
Na(I)	2.02
K(I)	2.08
Ba(II)	2.028
Mg(II)	1.88

Titration curve

Several 250 ml conical flasks, each containing 0.5 g of the exchanger, were taken. 0.1 M sodium hydroxide and 0.1 M sodium chloride were added in different ratios keeping the final volume at 100 ml in all cases. The flasks were kept for 3 days at $25° \pm 1°$ with intermittent shaking. After attainment of equilibrium the pH values of all the solutions were measured. The results are shown in Fig. 1.
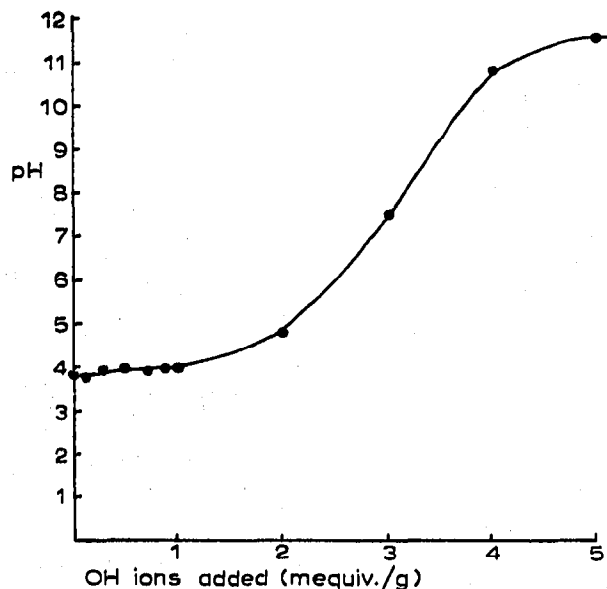

Fig. 1. Titration curve for stannic ferrocyanide.

Distribution coefficients

The usefulness of this exchanger for analytical separations was examined by determining the distribution coefficient with different metal ions in distilled water and 0.1 M nitric acid. The following method was used:

2 ml of the metal solution and 98 ml of either water or 0.1 M nitric acid were taken in a 250 ml conical flask. The concentration of the solution was adjusted so that the amount of the metal did not exceed 3% of the total capacity of the exchanger[20]. Then 0.5 g of the exchanger in H+ form was added. The flask was kept at room temperature ($25° \pm 1°$) for 48 h with occasional shaking. 40 ml of this solution were titrated against 0.002 M EDTA solution and K_d values of the metal ion were determined using the formula:

$$K_d = [M_R]/[M_{Sol.}]$$

where $[M_R]$ = amount of the metal ion adsorbed per gram of the exchanger,

$[M_{Sol.}]$ = amount of the metal ion left per unit volume of the solution.

Sodium and potassium were determined in the solution using radioactive tracers. Table VI summarizes all the K_d values.

Thermogravimetry

The results of thermogravimetric analysis of sample S-11 are given in Fig. 2. To check the effect of heat on the colour of the exchanger and on its ion-exchange

TABLE VI

DISTRIBUTION COEFFICIENTS OF SOME METAL IONS

Metal ion	Compound used	K_d value	
		In water	In 0.1 M HNO_3
As(III)	Arsenite	0.0	0.0
Pb(II)	Nitrate	Total adsorption	1693
Cd(II)	Chloride	Total adsorption	1600
Cu(II)	Sulfate	2520	2520
Al(III)	Chloride	Total adsorption	236.4
Ga(III)	Chloride	1680	176
Ni(II)	Sulfate	Total adsorption	840
Co(II)	Chloride	Total adsorption	588.5
Mn(II)	Sulfate	Total adsorption	622.2
Zn(II)	Chloride	Total adsorption	1360.0
Ba(II)	Chloride	704.5	19.4
Sr(II)	Nitrate	1465.2	9.5
Ca(II)	Nitrate	484	0.0
Mg(II)	Nitrate	2470	5.3
K(I)	Chloride	52.6	17.4
Na(I)	Chloride	20.6	—
In(III)	Sulfate	21.4	0.0
Y(III)	Nitrate	8800	362.5
Fe(III)	Alum	156.9	10.9
Bi(III)	Nitrate	Total adsorption	120.0
Sm(III)	Chloride	1905.2	66.6
Nd(III)	Chloride	813.3	8.5
Pr(III)	Chloride	486.3	10.9

capacity 1 g portions of S-11 were heated at 100, 200, 300 and 400° for 1 h in each case. Capacities of all the samples after heating were determined in the usual way. The results are shown in Table VII.
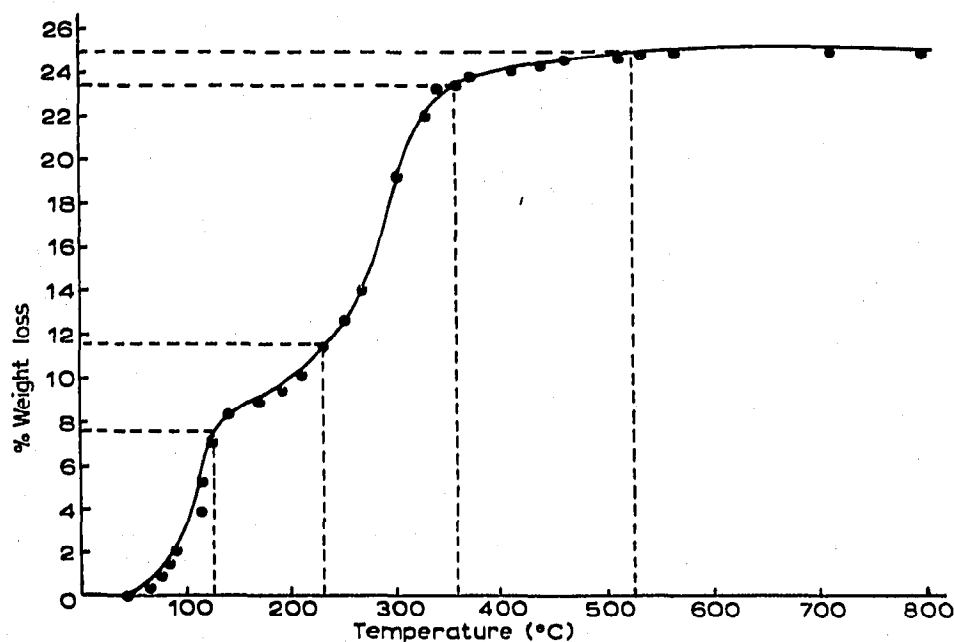

Fig. 2. Thermogram for stannic ferrocyanide.

TABLE VII

EFFECT OF HEAT ON THE EXCHANGER

Temperature (°C)	Colour of the beads	Capacity (mequiv./g)
Room temp.	Blue black	2.02
100	Blue black	2.02
200	Dirty black	0.60
300	Brownish black	0.02
400	Brown	0.01

X-ray diffraction studies

X-ray diffraction studies showed that tin(IV) hexacyanoferrate(II) is slightly crystalline at room temperature. The crystalline character increases as the temperature is raised, and at 400° a good X-ray pattern is observed.

DISCUSSION

From Tables I and II it is clear that in highly acidic solutions (pH 1) the molar ratio of tin and iron in the gel depends upon the volume ratio of mixing. At higher pH values (pH 4–7) the amount of tin present is always greater than the iron content of the sample. It is probably due to the formation of some tin hydroxide at the higher pH values. This inference is supported by the fact that the precipitates formed at pH 6.9 show Sn:Fe ratio as 100:1. Moreover the samples prepared at pH 10 and at pH 13 dissolve easily in acid solutions. On drying, all the gels turn blue black or prussian blue. This is perhaps due to a redox phenomenon taking place in the system which is indicated by the positive tests obtained for ferro- and ferricyanides in an alkaline solution of the exchanger. When the exchanger is, however, dissolved in a sulphuric acid–hydrochloric acid mixture the solution does not give a positive test for these radicals. This may be due to the decomposition of ferrocyanide and the subsequent oxidation of Fe(II) to Fe(III) by oxygen dissolved in the solution. Such a solution, therefore, gives the test for iron in the trivalent state only. Furthermore, in acidic solutions potassium ferrocyanide forms ferrocyanic acid $[H_4Fe(CN)_6]$. Some of the iron in the bivalent state is oxidized to Fe(III), which with ferrocyanic acid, forms prussian blue $Fe_4[Fe(CN)_6]_3$ in the system, thus resulting in the blue coloured material.

On the basis of chemical and thermogravimetric analysis of the sample and the formula given for titanium(IV) ferrocyanide[21], the following formula for tin(IV) hexacyanoferrate(II) is proposed:

$$[(SnO)_3 \cdot (OH)_3 \cdot HFe(CN)_6 \cdot 3H_2O]_n$$

As shown by the above formula there is only one replaceable hydrogen atom per molecule which is attached to the $Fe(CN)_6^{4-}$ group. This is suggested by one inflection point observed in the titration curve of the exchanger (Fig. 1). The pyrolysis curve for stannic ferrocyanide (Fig. 2) confirms other aspects of the proposed formula. Thus, if this formula is considered to be correct and the percentage weight losses

which are indicated at each break of the curve, are correlated with certain chemical transformations taking place on heating, the following inferences are possible:

(a) Three water molecules per mole of the exchanger are present as water of crystallization. They are lost on heating it up to 125° giving a weight loss of 7.6% (theoretical weight loss of 7.5% due to the removal of 3 H_2O).

(b) Above 125° condensation of the molecule takes place which is indicated by a further loss of 4% in weight of the exchanger at 230°. This loss corresponds to two water molecules which are removed from the structure (theoretical total weight loss of 12.4% at 230° due to the loss of 5 H_2O).

(c) Cyanogen begins to be evolved[22] at 237°, the steeper portion between 230° and 355° therefore corresponds to the decomposition of ferrocyanide and the loss of cyanide as cyanogen. At 355° the total weight loss is 23.4% which closely resembles the theoretical weight loss (23.3%) if three cyanide radicals are assumed to be lost at this temperature.

The portion between 355° and 525° corresponds to one cyanide radical only. It seems therefore that there are only four cyanide radicals available in one molecule of stannic ferrocyanide. Two cyanide radicals must therefore be lost at lower temperatures. This is supported by the fact that a smell of HCN is observed on drying the product.

The titration curve (Fig. 1) shows that when only NaCl is used it releases hydrogen ions and hence a sharp decrease of pH occurs. On the addition of NaOH the pH increases rapidly and above pH 7 the exchanger begins to dissolve. On gradually increasing the volume of NaOH the rate of dissolution and hydrolysis of the exchanger increases and there is a corresponding increase in the pH of the solution. This is perhaps due to the fact that the partial exchange of H^+ with Na^+ slows down the rate of exchange and the release of H^+ ions. No appreciable change in pH is recorded above pH 12.1.

The observed K_d values of metal ions (Table VI) show that this exchanger has a great affinity for Pb, Cd, Cu, Al, Ga, Ni, Co, Mn, Zn, Ba, Sr, Ca, Mg, Y, Bi, Sm, Nd, and Pr in aqueous solutions. Sodium, potassium and indium have low K_d values, and therefore it is possible to separate them from other metal ions. The adsorption of metal ions was also studied in 0.1 M HNO_3 which showed that the K_d value decreased as the hydrogen ion concentration increased. This fact can be predicted if the ion-exchange reaction is defined by the equation:

$$M_{aq.}^{n+} + nHR \rightleftharpoons MR + nH^+$$
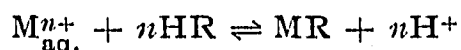
and

$$K_d = \frac{[M_R]}{[M_{aq.}^{n+}]}$$

where

$[M_{aq.}^{n+}]$ = concn. of metal ion in the solution;

$[M_R]$ = concn. of metal ion in the exchanger.

If the hydrogen ion concentration is increased the reaction will tend to proceed in the reverse direction and therefore the adsorption of the metal ion on the exchanger

is decreased. Thus rare earths (Sm, Nd, Pr) which show high adsorption in aqueous medium, have very low K_d values in 0.1 M HNO$_3$. Similarly, Ba, Sr, Ca, and Mg lose their affinity for the exchanger in acid solutions. On the basis of the distribution studies the following separations are possible:

Alkali metals and alkaline earths from Pb(II), Cd(II), Cu(II), Al(III), Ga(III), Ni(II), Co(II), Mn(II), Zn(II).

Arsenic(III), which is taken as arsenite, is not adsorbed on the exchanger beads, obviously due to the cation-exchange behaviour of the material, which completely elutes the arsenite ion. This fact has successfully been utilized for the quantitative separation of arsenic from the metal ions which commonly interfere with this ion such as Pb(II), Cd(II), Cu(II), Ni(II), Co(II), Mn(II) and Zn(II).

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