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Ion exchange separation and determination of Iron in some appetizers and biological materials

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ABSTRACT

The distribution coefficient (K_d) of some metal ions have been determined at various pH values on stannic (IV) arsenate cation exchanger. Based on this study, the separation of some important pairs of metal ions has been achieved. The separation of Fe(III) from Ni(II), Co(II), Mn(II), Ca(II) and Al(III) have been achieved quantitatively in some synthetic mixtures. The quantitative separation of Fe(III) from some appetizers and from biological material has also been achieved. The method is simple, rapid and highly selective with good accuracy and precision within the experimental error range (±2%).

Keywords: Ion exchange separations/ stannic arsenate/ column chromatography/ion separation/ appetizers/ biological materials

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INTRODUCTION

Synthetic inorganic ion exchangers (SIIE) have growing interest in field of separation science [1, 3]. A large number of studies have been made for their preparation, properties and applications to the simple binary and ternary separation of metals ions by different chromatographic technologies [3-18]. Although a variety of stationary and mobile phases have been developed to achieve the selective, analytically difficult, environmentally important, binary, ternary and multinary separation of metal ions in planar chromatography [19-22]. On the contrary, every SIIE has specific selectively towards one or two metallic species. They are also highly stable to a wide range of pH and up to high temperature. I have successfully utilized the stannic (IV) antimonate columns for the analysis of Mg(II) and Al(III) in some antacid formulations[23]. However their real analytical applications in the field biological and pharmaceutical sciences are still lacking.

Iron is an important constituent of biological systems and appetizers. Excess intake of iron causes siderosis and may be harmful due to deposition of unused iron in various organs of the body[24] and deficiency causes anemia due to malnutrition, parasite and helminthes diseases, infections and several other factors[25]. Excess intake of iron also causes gastrointestinal irritation, nausea, vomiting, diarrhea or constipation, ulceration in the intestine. Thus determination of iron becomes important. The determination of iron is difficult due to the interference of certain ions and organic species. To encounter this problem Korkisch and Huebner[26] used the organic resins to separate metallic species from multivitamin preparations prior to their determination by atomic absorption spectrophotometry (AAS).

The stannic (IV) arsenate has outstanding thermal and chemical stability, a high uptake for cations[27] and high selectivity towards iron, which give us impetus to extend our studies for the analysis of iron in pharmaceutical and biological materials using stannic (IV) arsenate columns. This paper reports the analysis of iron in some commercially available appetizers and in some biological materials using stannic (IV) arsenate columns. The method can be successfully applied in the field of medical and pharmaceutical sciences for diagnosis and determination of iron in formulations respectively.

MATERIALS AND METHODS

Reagents

Stannic chloride (Trizma) and sodium arsenate (E. Merck) were used. All the other reagents were of Analar grade.

Preparation of the ion exchange material

60 ml of a 1:1 mixture of H_2SO_4 and HCl (v/v) were added to the mixture of aqueous solutions of $SnCl_4.5H_2O$ (90 g) and Na_2HAsO_3 (90 g) in a three necked flask. Concentrated HNO_3 (45 ml) was now added and the contents diluted to 3.6 L with water, then evaporated to 3L with continuous stirring. A white precipitate was obtained, dried at 40^o C, cracked by the addition of water, washed and converted into H^+ form by treatment with 2M HNO_3.

Distribution coefficients (K_d)

200 mg of the exchanger bead (100 – 200 mesh) in the H^+ from was equilibrated with 25 ml of the solution whose metal ion concentration was adjusted to 3% of the total ion exchange capacity of the material. The equilibrium was obtained by keeping the solution overnight with constant shaking and the metal ions left in the solution was determined with EDTA as titrant. The K_d values as summarized in Table 1 were obtained by the equation [23].

$$K_d = \frac{I - F}{F} \times \frac{V}{A} \quad (ml/g)$$

Where,
I = Initial amount of the metal ions in the solution phase
F = Final amount of the metal ion in the solution phase
V = Volume of the solution
A = Amount of the exchanger (g)

Separation of metal ions

Quantitative separation of the metal ions was achieved on a glass column (height 50 cm, i.d. 0.6 cm, packed with 2 g (100-200 mesh) exchanger in H^+ form. A metal ion mixture was transferred into the exchanger column. The flow rate of the effluent was maintained 1 ml/min throughout the elution process.

Analysis of samples

Stock solution of the drug formulations were prepared as follows -15 ml of the formulation were taken in a beaker and heated with a minimum amount of an oxidizing mixture (conc. HNO_3 + $HClO_4$ 1:2 v/v) to destroy the organic matter. The clean solution thus obtained was reduced to a volume 1-2 ml to remove the excess acid and make up to 100 ml with DMW in a standard flask.

1 ml of the stock solution was loaded on the column containing 2 g of the exchanger and the separations were achieved by the same procedure as described above for synthetic mixtures. 80 ml of 0.01 M HNO_3 was sufficient to elute out all the metal ions quantitatively except iron which remains on the column it was then eluted by 100 ml of 1M HNO_3. After destroying the acid by evaporation, Iron was determined in the effluent by the EDTA titration using Cu-Pan as an indicator [28].

Analysis of iron in biological samples

The sample such as Kidney, spleen, lever preserved in formalin were collected from different hospitals. The samples were dried in an air oven at 110^o C for 3-4 hours so as to obtain a constant weight. These samples of lever (4g) kidney (3g) were digested in 45 ml of perchloric acid and nitric acid mixture (1:1) while spleen (2g) were digested in 10 ml concentrated nitric acid and 49 ml perchloric acid and nitric acid mixture (1:8), respectively until a white

residue was obtained. The residue was taken up in water, filtered and diluted to 50 ml. A 1.0 ml aliquot of the sample solution was used for the column operation.

Table 1 – Distribution coefficient (K_d) of metal ions at different pH values on stannic (IV) arsenate.

Cations	pH			
	2	5	8	9
Mg^{2+}	32.80	41.20	760	468.50
Ca^{2+}	56.80	247.20	2486	1140
Sr^{2+}	74.20	394.00	3100	4140
Ba^{2+}	144.50	1360	7560	5110.0
Zn^{2+}	141.00	258	2535	956.20
Cd^{2+}	151.83	635.80	3700	1945.00
Hg^{2+}	40.00	11.80	108.60	135.00
Bi^{2+}	10600	16000	5200	21400.00
Al^{3+}	610	48	2490	695.00
Ga^{2+}	2050	10.80	8000	2234.00
In^{2+}	1514	30.20	10070	3320.00
Mn^{2+}	28.40	100.00	1900	1120
Fe^{3+}	1200	78.00	TA*	TA*
Ni^{2+}	23.00	35.00	1310	655.00
Co^{2+}	360	372.70	1134.00	690.00
Cu^{2+}	815	655.20	3050.00	2515.00

* TA = Total Adsorption

Table 2 - Quantitative separation of metal ions from synthetic mixtures achieved on stannic (IV) arsenate columns.

S.N.	Separation achieved M_1 — M_2	Amount taken (µg) M_1	Amount taken (µg) M_2	Amount found (µg) M_1	Amount found (µg) M_2	Error (%) M_1	Error (%) M_2	Eluent and if volume used for different metals
1.	Sr^{2+} — Ba^{2+}	123.0	112.0	124.2	113.6	+0.97	+1.43	A – 0.8% NH_4Cl, 60 ml B – 1% NH_4NO_3 in 2% HNO_3, 35 ml
2.	Mg^{2+} — Ba^{2+}	64.0	112.0	62.8	110.2	-1.87	-1.60	A – 0.8% NH_4Cl, 45 ml B – 1% NH_4NO_3 in 2% HNO_3, 40 ml
3.	Ca^{2+} — Ba^{2+}	64.0	112.0	64.8	113.2	+1.25	+1.07	A – 0.8% NH_4Cl, 65 ml B – 1% NH_4NO_3 in 2% HNO_3, 40 ml
4.	Co^{2+} — Fe^{3+}	147.3	140.0	146.8	138.2	-0.33	-1.28	A – 2% HNO_3, 40 ml B – 5% NH_4NO_3 in 5% HNO_3, 85 ml
5.	Al^{3+} — Fe^{3+}	67.5	140.0	67.2	142.4	-0.44	+1.71	A – 2.5% HNO_3, 80 ml B – 5% NH_4NO_3 in 5% HNO_3, 100 ml
6.	Mn^{2+} — Fe^{3+}	71.0	140.0	71.2	140.8	+0.28	+0.57	A – 1% HNO_3, 60 ml B – 5% NH_4NO_3 in 5% HNO_3, 105 ml
7.	Ca^{2+} — Fe^{3+}	64.0	140.0	63.5	141.5	0.78	+1.07	A – 1% NH_4NO_3, 80 ml B – 5% NH_4NO_3 in 5% HNO_3, 95 ml
8.	Ni^{2+} — Fe^{3+}	180.0	140.0	179.6	138.8	0.22	0.85	A – 2% HNO_3, 35 ml B – 5% NH_4NO_3 in 5% HNO_3, 85 ml
9.	Al^{3+} — In^{3+}	67.5	140.0	68.0	141.2	+0.73	+0.85	A – 2% NH_4NO_3 in 5% HNO_3, 110 ml B – 5% NH_4NO_3 in 5% HNO_3, 75 ml
10.	Mg^{2+} — Al^{3+}	64.0	67.5	66.0	66.5	+3.13	-1.47	A – 8% NH_4Cl, 50 ml B – 2.5% HNO_3, 100 ml
11.	Synthetic mixture containing Co^{2+}, Al^{3+}, Mn^{2+}, Ca^{2+}, Ni^{2+}, Mg^{2+} and Fe^{3+}	147.3 Co^{2+} 67.5 Al^{3+} 71.0 Mn^{2+} 64.0 Ca^{2+} 180.0 Ni^{2+} 67.5 Mg^{2+} 140.0 Fe^{3+}		139.9 Fe^{3+}		-0.71 Fe^{3+}		5% NH_4NO_3 in 5% HNO_3, 110 ml
12.	Synthetic mixture containing Co^{2+}, Al^{3+}, Mn^{2+}, Ca^{2+}, Ni^{2+}, Mg^{2+} and Fe^{3+}	147.3 Co^{2+} 67.5 Al^{3+} 71.0 Mn^{2+} 64.0 Ca^{2+} 180.0 Ni^{2+} 67.5 Mg^{2+} 280.0 Fe^{3+}		277.8 Fe^{3+}		-0.78 Fe^{3+}		5% NH_4NO_3 in 5% HNO_3, 110 ml

Table 3 – Separation of Iron from other metal ions in various appetizers and Iron preparations on stannic (IV) arsenate columns.

S. No.	Trade name of drug	Labelled metallic composition (per 15 ml) of the formulation	Iron content obtained (mg)	% Deviation from labelled composition	Coefficient of Variance
1.	CALRON (East India)	Ferric ammonium citrate 555 mg (equivalent to Fe 125 mg), Sodium glycero phosphate 420 mg, Calcium glycerophosphate 60 mg, Vit A 1200 iu, Vit D 540 iu, Vit B_1 18.0 mcg, Nicotinamide 15.0 mg, Ethyl alcohol 14.25 ng	126	+0.88	1.33
2.	MAXIM Hp (Dabur)	Protein hydrate 1.2 g, Carbohydrate 10 g, Vit B_1 0.6 mg, Vit B_2 1 mg, Vit B_5 5 mg, Niacinamide 8 mg, Vit B_{12} 3 mcg, D-Panthenol 1.5 mg, Ferric ammonium citrate 100 mg (equivalent to Fe – 22.5 mg), Manganese sulphate 1 mg, Magnesium chloride 10 mg, Zinc sulphate 8 mg	22.4	-0.44	1.12
3.	DEXORANGE PLUS (Franco Indian)	Haemoglobin 2.095 gm. Ferric ammonium citrate 125 mg. (equivalent to Fe 28.9 mg), Vit B_{12} 7.5 mg, Folic acid 0.5 g, Alcohol 0.87 ml (5.5% v/v)	28.2	-0.35	1.10
4.	FERROCHELATE (Albert David)	Elemental Iron (Ferric ammonium citrate) 180 mg (Fe – 40.5 mg), Vit B_{12} 15 mcg, Folic acid 3 mg, L-Lysin hydrochloride 210 mg	40.86	+0.88	1.66
5.	HAEM UP (Cadila)	Ferric ammonium citrate 100 mg (equivalent to Fe 28.9 mg), Glycenarated haemoglobin 1 g, Cupric sulphate 30 mcg, Manganese sulphate 30 mcg, Zinc sulphate 30 mcg, Alcohol 0.87 ml (5.5% v/v)	29.2	+1.03	2.84

Table 4 – Analysis of Iron in some biological materials by ion exchange column chromatography using stannic (IV) arsenate.

Sample	Amount applied** (µg/g)	Amount found by i.e. separation (µg/g)	% Recovery	Standard deviation	Coefficient of Variance
Human liver	900	897.2	99.68	0.09	0.10
Kidney	500	498.4	99.68	0.10	0.16
Splean	1120	1116.0	99.64	0.36	0.46

* An average of five replicats.

** Amount applied standardized by I.C.P. method.

The adsorption and separation of iron were carried out as in case of synthetic mixture. The 1 ml of the aliquot solution was loaded on column maintaining a flow rate of 2-3 drops/minute. The Fe(III) ions present in the solution are thus retained on the column due to the high selectivity of the material for these ions. They were then leached out with 1 M NH_4NO_3 as eluent and the effluent was analyzed for the presence of Fe(III) ions by EDTA titration using Cu-PAN as indicator. The result have been summarized in Table 3 while the separation of Fe(III) from synthetic mixture has been given in Table 2.

RESULTS AND DISCUSSION

The distribution coefficient (K_d) for various metal ions (Table 1) show that the exchange has high selectivity towards transitional metals. Table 1 shows that the sequence of adsorption for the alkaline earths and for Al(III), Ga(III) and In(III) is as follow Ba>Sr>Ca>Mg; In>Ga>Al. Table 1 shows that stannic arsenate has a higher uptake of metal ion in comparison to the other ion exchange materials prepared earlier[27]. The high uptake, good ion exchange capacity, the differential selectivity and good stability of the stannic arsenate make it promising for different analytical separations. Several binary separations achieved actually on stannic arsenate columns have been given in Table 2.

On the basis of the separation achieved on stannic arsenate columns, the quantitative separation of Fe(III) from appetizers and from biological materials have been made possible. The results of these studies are summarized in Table 3 & 4. The results of the analysis of Fe(III) in biological materials were found to be more than 99% and are in agreement with the induction coupled plasma mass spectrophotometric analysis (ICP). Analysis of synthetic mixture (Table 2) and the coefficient of variance (Table 3 & 4) confirm the validity and consistency of the procedure as indicated by the degree of accuracy obtained. The ion exchanger columns can be repeatedly regenerated by passing 100 ml of 2M HNO_3, through the column and the eluents are easily available and are inexpensive.

CONCLUSION

The proposed method is simple, highly selective to separate Fe(III) quantitatively from appetizers and from biological materials. The method can be conveniently used in comparison to the presently available methods. The ammonium chloride and nitric acid used as eluent are of naturally occurring substances in biological process as waste and decaying materials has great analytical importance for the separation of Fe(III) in appetizers and biological materials.

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REFERENCES

[1] W. Schmidt, "*Synthetic Inorganic Ion Exchange Materials*" in , *Ion Exchange Technology : Theory, Materials and Applications*. (Eds.) Inamuddin, M. Luqman, Springer, **2012**, p.277-298
[2] M. Qureshi, K. G. Varshney (Eds) *Inorganic Ion Exchangers in Chemical Analysis*, CRC Press, Boca Raton, Florida, USA, **1991**
[3] A. Khan, A. M. Asisi, A. R. Malik, N. Ajum, A. A. P. Khan, I. Khan, P. K. Mondol, *Int. J. Electrochem. Sci.*, **2012**, 7, 3854
[4] T. Fujiwara, *JAET- Testing*, **2012**, 004, 1-13
[5] M. A. Tretyak, L. M. Rozhdest Venskeya , V. M. Belyakov, *Ukrain Khim Zhurnal*, **2013**, 79,15
[6] L. Xiong, M. Gu, K. Lu, Y. Luo, *Hejishu*, **2013**, 36,10301-5; *Colloids and Surfaces (A) Physiochemical Aspect*, **2013**, 417, 243
[7] H. K. Sharma, N.Sharma, *Res. J. Chem. and Environ.* , **2013,** 17,34-39
[8] B. Tylar, K. M. L. Pashow, T. C. Shachic, D. T. Hobbs, *Solv. Ext. and Ion Exch.*, **2013,** 31,122
[9] R. Chakraborty, S. Dhara, B. Sarkar, S. Bose, P. Chattopadhyay, Rediochem. (Moscow), **2011,** 53,534
[10] G. M. Ibrahim, B. El-Gammal, I. M. El-Naggar, *Sep. Sci. Tech.* , **2011,** 46,664
[11] P. Sharma, Neetu, *Desalination*, **2011,** 267,277
[12] N. K. Misra, *J. Ind. Chem. Soc.* , **2003,** 80,714
[13] H. K. Sharma, N. Sharma, *Der Chemica Sinica*, **2013**,4,182-188
[14] A. K. Misra, *J. Planar Chromatogr. Mod. TLC*, **1993**,6,274-277
[15] R. P. S. Rajput, A. K. Misra, S. Agrawal, *J. Ind. Chem. Soc.*,**1988**,65,744-745
[16] A. K. Misra, R. P. S. Rajput, *J. Planar Chromatogr. Mod. TLC*,**1990**,3,83-85
[17] A. K. Misra, R. P. S. Rajput, *J. Liq. Chromatogr*., **1990**,13,1435-1445
[18] S. S. Dhote, L. Desmukh, L. M. J. Paliwal, *Der Chemica Sinica*, **2012,**3,225-230
[19] A. K. Misra, S. Pachauri, *Ind. J. Chem. Technol*.,**2002**,9,239-241
[20] A. K. Misra, *Ind. J. Chem. Technol*.,**2003**,10,367
[21] S. M. Wanjari, L. Desmukh, L. M. J. Paliwal, *Der Chemica Sinica*,**2011**,2,222-227
[22] V. S. Nagpurkar, L. Desmukh, L. M. J. Paliwal, *Der Chemica Sinica*,**2012**,3,824-829
[23] A. K. Misra, *Ind. J. Chem. Tech.* , **2000,** 7,132
[24] A. G. Gilman, L. S. Gookman, T. W. Rall, F. Murad, *The Pharmaceutical basis of Therapeutic, 7th Edition,McMillan Publishing House*, **1985,** p.1317
[25] S. B. Vohora, *Medical Elemetology*, IHMMR Printing Press, Hamdard Nagar, New Delhi, **1983,** p.89
[26] J. Korkisch, H. Huebner, *Micro. Chem. Acta*, **1976,** 11,311
[27] M. Qureshi, H. S. Ralhose, R. Kumar, *J. Chem. Soc.(A)*, **1970,** 2,1986
[28] C. N. Reilley, R. W. Schmid, Fawzys, *J. Chem. Edu.* , **1959,** 36,555.