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Some Properties of Iron(III) Selenite and Its Applications for the Determination of Thorium

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A new inorganic ion exchanger, iron(III) selenite has been synthesized having an Fe:Se ratio of 2:3 and cation exchange capacity of 0.40 meq g^{-1}. It is fairly stable in water and dilute solutions of acids, bases, and salts. Ion distribution studies on twenty one metal ions have been done in water. Iron(III) selenite granules in H$^+$-form have also been used as indicators in the determination of thorium in presence of some rare earth cations using hexacyanoferrate(II) as titrant. On the basis of chemical analysis, pH titrations, thermal and infrared analyses the following scheme for the decomposition of iron(III) selenite has been proposed:

$$2Fe_2O_3\cdot 3H_2SeO_3\cdot 2H_2O \xrightarrow{140\,°C} 2Fe_2O_3\cdot 3H_2SeO_3 \xrightarrow{500\,°C} 2Fe_2O_3\,.$$

The analytical importance of synthetic inorganic ion exchangers is now firmly established due to their high selectivity, thermal stability and resistance to radiations. There are, however, two fundamental problems which still lack a solution: The ion exchangers, unless crystalline, do not have reproducible properties and they are not chemically stable. It was found that phosphate,[1] arsenate,[2] antimonate,[3] tungstate,[4] and molybdate[5] of iron(III) show interesting properties. Selenites of zirconium,[6] tin,[7] and titanium[8] have been synthesized and used for various separations. A search of literature showed that no such studies have so far been reported on iron(III) selenite. Therefore, a new inorganic ion exchanger, iron(III) selenite has been investigated. The present work describes the synthesis, ion-exchange properties, and analytical applications of iron(III) selenite.

Experimental

Reagents. Sodium selenite (Loba Chemie) and iron(III) nitrate (BDH) were used for the synthesis. All other chemicals used were of AnalaR grade.

Potassium hexacyanoferrate(II): Standard solution of potassium hexacyanoferrate(II) solution (0.025 M)[†] was prepared by exact weighing and 1.0 g of sodium carbonate was added per liter.

Nitrates of thorium and other metal ions standardized with EDTA were used.

Synthesis of Iron(III) Selenite. The conditions of synthesis are given in Table 1. The iron(III) nitrate solution (0.05 M) was added to a solution of sodium selenite (0.05 M) with constant stirring. The pH of the mother liquor was adjusted to 1.5 (Table 1) by adding either 0.1 M HNO_3 or 0.1 M NaOH. The precipitate so obtained was heated at 60 °C for half an hour and it was allowed to settle for 24 h. Then it was filtered and washed with distilled water till free from nitrate ion. It was heat-treated at 40 °C, converted to H$^+$-form using 0.1 M HNO_3 and finally washed with demineralized water to remove excess of the acid. Finally it was heat-treated at 40 °C in an electric oven.

Analysis of Metals. Analysis of iron(III) has been done volumetrically using iodometric technique[9] and selenium has been precipitated as selenium metal[10] by passing sulfur dioxide through acidic solution of the material. The red selenium metal separates out. It is then filtered and weighed after heat-treating at 120 °C in an oven to constant weight.

The various cations used for the distribution coefficients determination have been determined by volumetric methods using metal indicators such as Eriochrome Black-T, Xylenol Orange, and PAN and titrating them against standard EDTA solution.

Table 1. Conditions of Synthesis and Properties of Iron(III) Selenites (H$^+$-form)

Sample No.	Conditions of synthesis				Properties	
	Molarity of reagents(M)		Mixing volume ratio		Color in H$^+$-form	Ion-exchange capacity/ meq g^{-1}
	Fe	Se	Fe	Se		
I	0.05	0.05	1	3	Brown	0.30
II	0.05	0.05	1	2	Brown	0.40
III	0.05	0.05	1	3	Brown	0.35
IV	0.05	0.05	2	1	No exchanger formed	—
V	0.075	0.075	1	2	Brown	0.41
VI	0.025	0.025	1	2	Brown (poor yield)	—
VII	0.10	0.10	1	2	Brown	0.40

[†] 1 M=1 mol dm^{-3}.

Instrumentation. The solubility of the meterial has been determined colorimetrically using spectrophoto-colorimeter (DDR). The pH of the solutions during potentiometric titrations was measured using a Toshniwal pH meter (CL-46, India). X-Ray diffractograms were obtained by using a PW 1720 X-ray generator with a Debye-Scherrer camera. Infrared studies were made using a Pye Unicam, SP 300 Philips (England) spectrophotometer.

Adsorption Studies. Adsorption studies were carried out by keeping cation solution in contact with the exchanger. Two hundred mg of the exchanger is added in each container containing cation solution and the volume is made to 20 ml by using the demineralized water. After 24 h cation solution is separated from the exchanger and cation is estimated using standard EDTA solution.

Chemical Composition. One hundred mg of iron(III) selenite sample was dissolved in 10 ml of hydrochloric acid. Iron was determined volumetrically[9] while selenium was determined by reducing it to red metal with sulfur dioxide.[10]

Ion-Exchange Capacity. The ion exchange capacity of the different samples of iron(III) selenite was determined by the column method. One g sample of the exchanger in the H^+-form was placed in the column with glass wool support. Alkali or alkaline earth metal nitrate solution (1.0 M) was used as the eluent. The effluent collected in each case, at the rate of 5—10 drops per min, was about 400 ml. The H^+-ions thus eluted from the column were titrimetrically determined against a 0.1 M standard solution of sodium hydroxide.

Distribution Coefficients. Distribution coefficients (K_d) for some inorganic ions have been determined in water. The K_d values were calculated using the equation

$$K_d = \frac{C_0 - C}{C} \cdot \frac{L}{m} (\text{ml g}^{-1}) ,$$

where C_0 and C are initial and residual concentrations of metal ion solution respectively. L is a solution volume (ml) and m is the amount of ion-exchanger sample taken (g). The cation solution was kept in contact with the exchanger for 24 h.

Effect of Temperature on Ion Exchange Capacity. Sample II in the H^+-form was dried at different temperatures in a muffle furnace for 2 h and the ion exchange capacity for Na^+ (1.0 M) was determined by the column method.

Chemical Stability. Fifty mg of the sample II was shaken with 20 ml of different solvents for 24 h. The supernatant liquid was analysed colorimetrically for selenium[11] and iron.[12]

Potentiometric Titrations. The pH titrations of iron(III) selenite sample II were performed using 0.1 M standard solution of different bases like lithium, sodium, and potassium hydroxide by the method of Topp and Pepper.[13] Five hundred mg of the exchanger was added in each flask and the total volume of the solution was made 50 ml (MOH+MCl).

X-Ray Studies. X-Ray diffraction studies were made on iron(III) selenite by the powder method. The powdered sample was filled in a quartz capillary of 0.5 mm diameter. It was then exposed to X-rays for few hours and its pattern was recorded.

Thermal Analysis and Infrared Studies. Thermal studies were performed on a Paulik Erdey MCM derivatograph (Hungary). The infrared spectra of iron(III) selenite (H^+-form) were obtained in KBr pellet.

Determination of Thorium. To the thorium nitrate solution (3 to 12 mg as thorium) were added 5 ml of 0.1 M HNO_3 so that the pH of the solution becomes 2—3. To this 3—4 granules (<0.1 mg) of iron(III) selenite in H^+-form were added and the titration was conducted by adding potassium hexacyanoferrate(II) (0.025 M) dropwise with vigorous shaking till the granules turn blue in color.

Results and Discussion

The results of the study of synthesis and ion exchange capacity of different samples of iron(III) selenite in H^+-form are presented in Table 1. These results show that ion-exchange capacity is independent of the concentration of reactants. Out of the seven samples prepared, one prepared by mixing 0.05 M solution of iron(III) nitrate and sodium selenite in the volume ratio of 1:2 at pH 1.5 (Table 1) was found to be quite chemically stable and having reasonable ion-exchange capacity. Therefore sample II was selected for detailed studies. Five batches of sample II were prepared under similar conditions and the material was found to be reproducible. A typical analysis for the product heat-treated at 40 °C shows 43% Fe_2O_3, 44.9% SeO_2, and 12.1% H_2O, indicating an empirical fomula $2Fe_2O_3 \cdot 3H_2SeO_3 \cdot 5H_2O$, $2Fe_2O_3 \cdot 3SeO_2 \cdot 5H_2O$. The distribution coefficients of Ce^{3+}, Ba^{2+}, Sr^{2+}, and Pb^{2+} were determined with each sample so as to check its reproducibility.

In order to determine the working capacity of

Table 2. Ion-Exchange Capacity of Iron(III) Selenite (Sample II) for Some Uni- and Bivalent Cations

Metal ion	Salt solution used	Concentration of salt/M	Ion-exchange capacity/meq g^{-1}	Hybrated ionic radii/Å
Li^+	$LiNO_3$	1.0	0.32	3.40
Na^+	$NaNO_3$	1.0	0.32	2.76
K^+	KNO_3	1.0	0.42	2.32
Mg^{2+}	$Mg(NO_3)_2$	0.5	0.25	7.00
Ca^{2+}	$Ca(NO_3)_2$	0.5	0.27	6.30
Sr^{2+}	$Sr(NO_3)_2$	0.5	0.29	—
Ba^{2+}	$Ba(NO_3)_2$	0.5	0.40	5.90

iron(III) selenite (H^+-form) as an ion-exchanger, the ion exchange capacity for sample II was determined for some uni- and bivalent cations (Table 2). The order of exchange capacities for alkali and alkaline earth metal ions respectively is: $K^+ > Na^+ = Li^+$ and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. These results suggest that the ion exchange capacity decreases from 0.42 to 0.32 and 0.40 to 0.25 meq g^{-1} on going from K^+ to Li^+ and Ba^{2+} to Mg^{2+} respectively. On the basis of the radii of the hydrated ions one would expect the same order.

The analytical significance of iron(III) selenite (H^+-form) can be evaluated from the results of K_d values given in Table 3. These results show that this material has high selectivity to Pb^{2+} in water. This makes it possible to separate Pb^{2+} from a large number of other cations. Sample II was heat-treated at different temperatures for 2 h and the ion exchange capacity for Na^+ was determined (Table 4). These results indicate that as temperature is raised from 40 to 200 °C, a slow decrease in ion exchange capacity is observed. On further raising the temperature there is abrupt decrease in the exchange capacity due to loss of selenium. The results of chemical stability of iron(III) selenite in H^+-form showed that the material was considerably stable in water, acids, bases, and organic solvents (Table 5).

The pH-titration curves of lithium, sodium, and potassium hydroxide for air-dried iron(III) selenite in H^+-form (Fig. 1) show two plateaux each one at pH 7 and the other at pH 9. This bifunctional behavior is similar to both crystalline zirconium phosphate[14] and arsenate[15,16] which also exhibit two pH titration plateaux. All the three curves are very much similar. The initial cation exchange selectivity sequence was $Na^+ > K^+ > Li^+$. At the first pH plateau, the selectivity was $Na^+ > Li^+ > K^+$. As exchange progressed the position of Li^+ shifted to give the sequence $Li^+ > Na^+ > K^+$. The exchange capacity for K^+ changes on heat treatment and it is reduced to about half when heated to 300 °C. When iron(III) selenite in H^+-form is treated at 500 °C to constant weight, the cation exchange capacity is completely lost. The titration

Table 3. Distribution Coefficients (ml g^{-1}) of Some Metal Ions on Iron(III) Selenite Sample II in Water

Metal ion	K_d	Metal ion	K_d
La^{3+}	8	Zn^{2+}	0
Dy^{3+}	5	Mn^{2+}	0
Nd^{3+}	20	Cu^{2+}	17
Gd^{3+}	16	Ni^{2+}	4
Pr^{3+}	10	Mg^{2+}	0
Er^{3+}	2	Cd^{2+}	5
Sm^{3+}	20	Ca^{2+}	0
Ce^{3+}	13	Ba^{2+}	5
Y^{3+}	19	Sr^{2+}	0
Th^{4+}	45	Fe^{3+}	80
Pb^{2+}	132		
Co^{2+}	3		

Amount of ion-exchanger used=200 mg, volume of equilibrated solution=20 ml, initial concentration of metal ion in solution=0.0025 M, concentration of EDTA standard solution=0.025 M

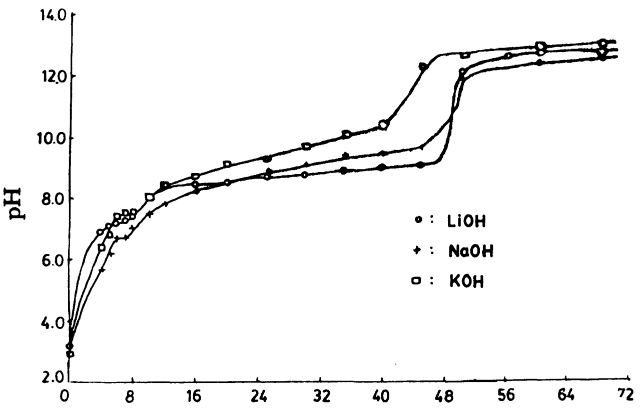
Table 5. Solubility of Iron(III) Selenite in Various Solvents

Solvent	Solubility iron(III)	Se(μg/50 ml)
$NaNO_3$ (1.0 M)	0	81
NH_4NO_3 (1.0 M)	0	155
NaOH (0.1 M)	0	158
HNO_3 (0.1 M)	50	125
HNO_3 (0.075 M)	42	100
HNO_3 (0.05 M)	32	80
HCl (0.075 M)	50	200
H_2SO_4 (0.05 M)	105	275
CH_3COOH (0.1 M)	0	227
Dioxan	0	0
DMF	0	0
DMSO	0	92
C_2H_5OH	0	0

Table 4. Change of Properties of Iron(III) Selenite with Heating Temperature

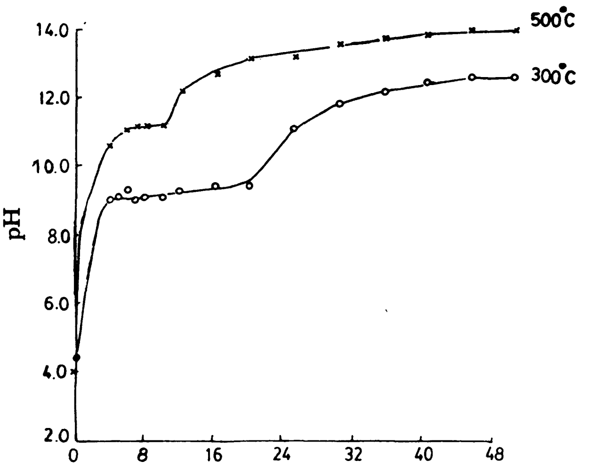
Drying temp °C	Composition $Fe_2O_3:SeO_2$	Ion-exchange capacity/meq g^{-1}	Colour	IR bands/cm^{-1}
40	1:1.5	0.40	Brown	3360, 1625, 1390, 710, 500
100	1:1.5	0.32	Brown	3400, 1625, 1390, 715, 490
200	1:1.5	0.27	Brown	3400, 1625, 1390, 710, 410
300	1:1.14	0.13	Dark brown	3400, 1625, 710, 475
400	1:0.75	0.10	Dark brown	710, 460
500	1:0.03	0.09	Black	535, 460, 310
600	1:0.00	0.08	Black	525, 455, 310
500[a)]	—	—		525, 450, 300

a) $Fe(OH)_3$ dried at 500 °C.



Vol. of 0.1 M standard base added (ml/0.5 g)

Fig. 1. pH-Titrations of iron(III) selenite (H$^+$-form).



Vol. of 0.1 M standard base added (ml/0.5 g)

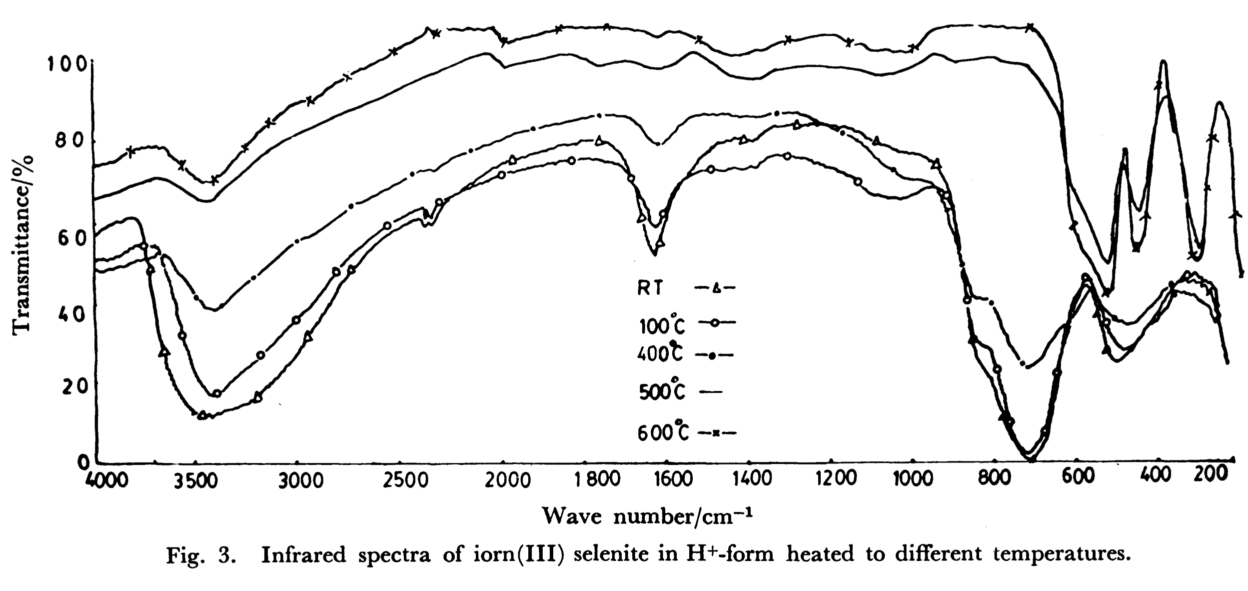
Fig. 2. pH-Titrations of iron(III) selenite (H$^+$-form) heat-treated at different temperatures.

curves obtained for the materials dried at 300 and 500 °C give support to this observation. That is to say, of the most acidic exchange group, the titration curve of iron(III) selenite in H$^+$-form heat-treated at 300 °C shows a considerable decrease in cation-exchange capacity. At 500 °C, the inflection point originating from the most acidic hydrogen ions completely disappears (Fig. 2).

X-Ray powder diffraction pattern shows that as the drying temperature is increased to 40, 300, and 600 °C, a number of d lines appear. This clearly shows that the material is crystalline at 40 °C as well as at 500 °C.

The infrared studies of iron(III) selenite (Fig. 3) show five absorption peaks with maxima at 3360, 1625, 1390, 710, and 500 cm^{-1}. The band at 3360 cm^{-1} is due to OH stretch of interstitial water, and the band at 1625 cm^{-1} is due to its bending mode. The bands at 1390 and 710 cm^{-1} are due to Se–OH stretching vibrations. The stretching vibration of Fe–O appears at 500 cm^{-1}.

The DTA curve of iron(III) selenite in H$^+$-form (Fig. 4) shows that there are three endothermic effects (140, 470, and 500 °C). The first endothermic effect (at 140 °C) may be due to the loss of two molecules of water and this is confirmed by analysis and the thermogravimetric analysis. The second endothermic effect (at 470 °C) is accompanied by simultaneous loss of three molecules of water and selenium dioxide (SeO_2). The composition of the product after this endothermic effect at 500 °C corresponds to the formula Fe_2O_3. The infrared spectra show no bands corresponding to stretching or deformation vibration of $-OH$ or $-OH_2$ groups or Se–O groups. A weak band at 3360 cm^{-1} is evidently due to the absorption of moisture on the specimen at the time of recording infrared spectrum. The infrared spectrum of iron(III) selenite dried at 500 °C is very much similar to the



Wave number/cm^{-1}

Fig. 3. Infrared spectra of iorn(III) selenite in H$^+$-form heated to different temperatures.

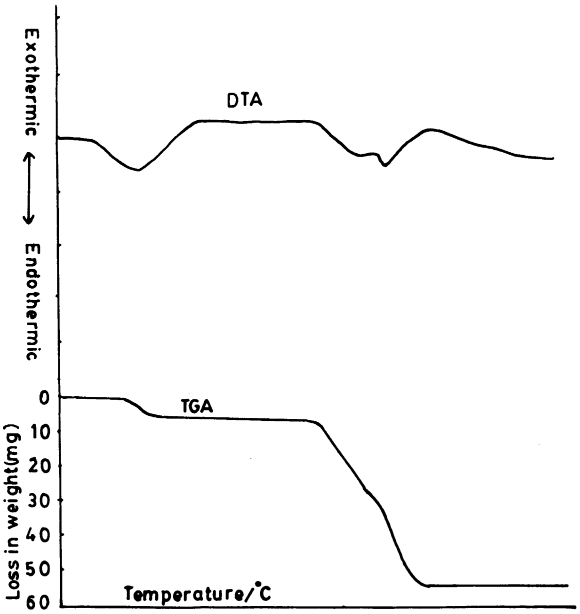


Fig. 4. Simultaneous TGA and DTA of 100 mg of iron(III) selenite in H$^+$-form.
Heating rate : 6° min^{-1}.

spectra of iron(III) oxide at 500 °C, indicating that at this temperature the dominant species present is Fe_2O_3.

The following scheme was obtained for the decomposition of iron(III) selenite in H$^+$-form when it is heated under the conditions for recording DTA curve:

$$\begin{array}{c} 2Fe_2O_3\cdot 3H_2SeO_3\cdot 2H_2O \\ \downarrow {\scriptstyle 140\,°C} \\ 2Fe_2O_3\cdot 3H_2SeO_3 \\ \downarrow {\scriptstyle 500\,°C} \\ 2Fe_2O_3 \end{array}$$

Iron(III) selenite granules in H$^+$-form can also be used as an indicator for the determination of thorium using hexacyanoferrate(II) as titrant. By proposed method 3.02 to 12.06 mg of thorium without and with rare earths can be determined within the conventional error (0.5—1%) for single observation. The amount of the rare earths added as impurities varies from 4.35 to 15.37 mg. This method is superior to other methods involving Th–EDTA. The method is based on the fact that when all the Th(IV) ions are precipitated as $ThFe(CN)_6$ a slight excess of hexacyanoferrate(II) gives a sharp color change to the granules from brown to blue due to the formation of Prussian Blue. As the rare earths used do not form insoluble ferrocyanides under these conditions, they do not interfere.

The method is particularly useful in dilute solution, where the precipitates are not so dense and the color change on the granules can easily be detected at the equivalence point. In more concentrated solutions, the granules are not visible through the thick precipitate, but the color on the solid phase can be seen by raising the beaker above eye level and viewing the granules at the bottom. The titrant solution should not come into direct contact with the indicator granules.

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