

SYNTHESIS OF SELENIUM AND TELLURIUM

BASED CATION EXCHANGERS AND
THEIR SELECTED APPLICATIONS

BY

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DEDICATION -----	i
ACKNOWLEDGEMENTS -----	ii
ABSTRACT -----	iii
1. INTRODUCTION -----	1
1.2 Objectives of the Present Investigation	5
2. LITERATURE REVIEW -----	6
2.1. Synthesis and Ion-Exchange Properties of Zirconium and Thorium Based Inorganic Ion-Exchangers -----	6
3. EXPERIMENTAL -----	19
3.1. Synthesis -----	19
3.1.1. Zirconium Selenite -----	19
3.1.2. Thorium Tellurite -----	19
3.2. The Hydrogen Ion Liberation Capacity	20
3.3. p^H -Titration -----	21
3.4. Solubility of the Exchangers -----	21
3.5. Composition -----	22
3.5.1. Zirconium Selenite -----	22
3.5.2. Thorium Tellurite -----	22
3.6. Distribution Coefficient -----	22
3.7. Separations -----	23
4. RESULTS AND DISCUSSION -----	24
4.1. IR and Composition -----	24
4.2. Solubility of the Exchangers -----	27
4.3. Hydrogen Ion Liberation Capacity ---	29
4.4. p^H -Titration Curves -----	30
4.5. Distribution Coefficient -----	31
4.6. Chromatographic Separation -----	35
4.7. X-Ray Diffraction (XRD) -----	37
5. CONCLUSION-----	38
REFERENCES -----	39

APPENDIX: Table 5-12

Figure 4-22c

A C K N O W L E D G E M E N T S

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A B S T R A C T

The synthesis of zirconium selenite and thorium tellurite are reported. Zirconium selenite has been prepared by mixing 4 N HCl solution of zirconium oxychloride with 4 N HCl solution of sodium selenite, and by adjusting the acidity of the solution to about 1 M HCl. Thorium tellurite has been prepared by mixing 1 M HNO₃ solution of thorium nitrate with 4 N HCl solution of sodium tellurite, and by adjusting the acidity of the solution to about 1 M HCl. The chemical composition for both exchangers showed metal to anion Zr:Se and Th:Te ratio of 1:2. The IR spectrum of both exchangers revealed absorption bands in the region 3500-3000 cm⁻¹ due to water molecules and OH groups, and 1700-1600 cm⁻¹, which may be due to interstitial water. The hydrogen ion liberation capacity of zirconium selenite and thorium tellurite was found to be 1.2 meq/g and 1.12 meq/g respectively. Distribution coefficients of metal ions on both exchangers were determined at different p^H in the range 2-6.5. The distribution coefficients were higher for Pb, Co and Cu than for other metal ions. On the basis of distribution coefficients, separations of Pb²⁺ from Cu²⁺, Cd²⁺, Zn²⁺, Co²⁺, Mn²⁺, and Ni²⁺ have been achieved on both exchangers. A number of binary and ternary separations of metal ions have been achieved on the columns of both exchangers.

CHAPTER ONE

1. INTRODUCTION

1.1. History and Importance of Ion Exchangers

Ion-exchange processes were studied systematically only in the middle of the last century in connection with investigations of different soils.¹ The first commercially available ion-exchangers were amorphous aluminosilicate gels. These gels later was known as permutites but their instability toward acid solutions and variability of behaviour led chemists to seek alternatives.² This search eventually led to the synthesis of organic ion-exchange resins. These resins soon dominated the field because of their uniformity, chemical stability, and the ability to control resin properties by synthetic procedures.^{1,3} Ion-exchange is now a well established technique in many industrial process and is also widely employed in many chemical laboratories. However, the applications of ion-exchange to some important processes that occur at high temperatures or in the presence of ionizing radiation or highly oxidizing media are severely limited at present, because commercially available ion-exchange resins undergo degradation under such drastic conditions.^{4,5} Many inorganic substances exhibit ion-exchange properties, but the use of these substances is restricted because the exchange capacity is lower than that of ion-exchange resins and also such substances are useful only in a limited of pH.⁵ However, various inorganic ion-exchangers have a good resistance against both gamma-rays and charged

particles.^{6,7} The production of a chemically stable inorganic ion-exchanger would enable ion-exchange processes to be used in an intense radiation field. Thus, during the last two decades a large number of inorganic ion-exchangers have been synthesized and explored for their use.⁸⁻¹¹ These materials are classified into two groups (i) Insoluble acid salts of tetravalent metals¹²⁻¹⁸ having cation exchange properties and (ii) Hydrated oxides¹⁹⁻²³ having cation and anion exchange properties.

Amorphous insoluble acid salts of tetravalent metals have been known for long time. Since 1956 there has been increased interest in these compounds due to their good ion-exchange properties and their high resistance toward temperature and radiations. Thus, their practical applications in nuclear technology or ion-exchange occurring at high temperature were hoped for. They are, however, not very stable toward hydrolysis of their acid groups, and therefore their composition is often not well defined.²⁴ Many interesting properties of the insoluble acid salts of tetravalent metals depend on the crystalline structure of the material obtained rather than on the metal ion or polyvalent acid involved. Hence, starting from 1964 several insoluble acid salts of tetravalent metals were obtained as crystalline compounds, and these materials were found to be considerably more stable than the amorphous ones.^{25,26}

Insoluble acid salts can find practical applications on many fields. An important application is their use as ion-exchange materials. They have also better resistance to

temperature, oxidizing solutions, and acid media. Ion exchange in molten salts and applications in nuclear technology are therefore possible.^{27,28}

The discovery that large cations can be taken up by ionic forms with large inter-layer distance has opened new developments. The selectivity of zirconium phosphate for polyvalent cations is very high, and analytical separation as well as concentrating of these cations can be achieved.²⁶ Amorphous zirconium phosphate has been utilized in kidney machines for the removal of ammonium ions from blood.⁷ Polyhydrated zirconium phosphate can be used for the removal of both the ammonium ion and ammonia from blood or waste solutions.²⁹ Owing to the discontinuous phase transition during exchange, insoluble acid salts can also be employed as solid p^H buffers, while their salt forms could be used to maintain constant ionic fraction of a pair of cations, such as $Na^+ - K^+$, in solution.²⁶ Insoluble acid salts have also important applications in catalysis, Kalman et.al. has successfully employed the copper form of zirconium phosphate for the oxidation of CO to CO_2 and employed it as CO adsorbent in automobile exhaust pipe.³⁰ Recently zirconium phosphate has been loaded with several transition metal ions and used as potential catalyst.^{31,32} Zirconium phosphate has also been employed as a support for gas-solid chromatography^{33,34} and good separations have been obtained.

Inorganic ion-exchange membranes consisting of insoluble acid salts also have a wide practical applications e.g. lanthanum antimonate.³⁵ They represent a unique possibility for relating their electrochemical and osmotic properties to

the known reticular arrangement of the fixed charges and counter ions or steric factors. Owing to the selectivity and stability of inorganic exchangers, these membranes do find applications as selective electrodes in particular processes in which organic membranes cannot be employed because of their higher degradability.^{35,36} Some acid salts whose structures have not yet been defined possess interesting ion-sieve properties; e.g. thorium arsenate behaves as a very narrow ion-sieve and only H-Li exchange is therefore possible. This interesting property has already been exploited for the separation of Li^+ from other cations, and from natural waters. The very high selectivity of fibrous cerium phosphate for Pb^{2+} and certain other divalent cations has also a practical application in the removal of some heavy metal ions from industrial waters.³⁸ Impregnated papers or thin layers of insoluble acid salts have been successfully employed for several chromatographic separations of inorganic cations e.g. cerium arsenate.^{39,40}

The good ion-exchange properties of zirconium phosphate have recently stimulated the preparation of insoluble acid salts from selenites and tellurites acid groups.⁴¹⁻⁴⁴ Several materials exhibiting some ion-exchange properties have been obtained by Rawat and Singh.^{41,42} All these products are amorphous and very hydrolysable and their anion to metal ratios did not exceed more than 2. These materials were prepared by various methods and their properties, such as composition, exchange capacity, and chemical stability, were investigated in relation to the methods of synthesis. Exchange capacity

depends on the selenite and tellurite groups. The exchanger, which has maximum selenite and tellurite to metal ion ratios, has maximum exchange capacity. The ion-exchangers are characterized by the ratios of selenite to metal ion, tellurite to metal ion, and by their p^H titration curves. Tantalum selenite⁴¹ is industrially important for the separations of Fe^{3+} from Mn^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , VO^{2+} , and Al^{3+} and Ba^{3+} from Ca^{2+} , Sr^{2+} , and Mg^{2+} . This property has been used to separate and determine Fe^{3+} in nickel electroplating baths.

The H^+ ion liberation ion-exchange capacity of niobium selenite⁴² for ratios of Nb:Se (1:1, 1:2 and 2:3) by KNO_3 was found to be 0.95, 1.04 and 0.90 meq/g, respectively. Results of the ion-exchange capacity determinations suggest that the exchangeable protons in niobium selenite decreased with an increase in the niobium to selenite ratios. Separations of lanthanum-thorium, thorium-copper, lead-cadmium, zinc-lead, and lanthanum-cerium were achieved on small columns of niobium selenite. Thus due to their high selectivity, thermal stability and their use as a potential catalyst we intend to prepare other polymers based on selenium and tellurium such as zirconium(IV) selenite and thorium(IV) tellurite.

1.2. Objectives of the Present Investigation

- i) To synthesize zirconium(IV) selenite and thorium(IV) tellurite.
- ii) To explore their application, particularly chromatographic separations

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Synthesis and Ion-Exchange Properties of Zirconium and Thorium Based Inorganic Ion-Exchangers

Insoluble acid salts of zirconium(IV) and thorium(IV) are usually synthesized by direct mixing of salt solutions of these metals with an excess of polybasic acids or polybasic anions. The protons of the acid groups of the insoluble acid salts can be replaced by other cations which accounts for ion-exchange property of these compounds. Furthermore it was found that they have high selectivity for certain ions^{39,40} and this selectivity can be increased by thermal treatment.^{45,46} The insoluble acid salts of both metals zirconium and thorium are obtained as amorphous gels when prepared by rapid precipitation in the cold, but refluxing in solubilizing media slowly transforms them into crystals.^{25,47,48} Insoluble salts of polybasic metals, such as zirconium, and thorium phosphate or zirconium arsenates, antimonates, oxalates are generally amorphous or semicrystalline materials, which undergo extensive hydrolysis even in weakly alkaline or neutral solutions.⁴⁹⁻⁵³ However, these materials are found to have useful cation exchange properties including high uptakes of certain ions reasonable exchange rates, and interesting selectivities.⁵⁴⁻⁶⁰ Zirconium(IV) based ion-exchangers⁶³⁻⁷¹ where the exchanging ion groups are sulfides, oxalates, chromates, arsenates, and antimonates are generally synthesized by rapid precipitation of zirconium salts with an

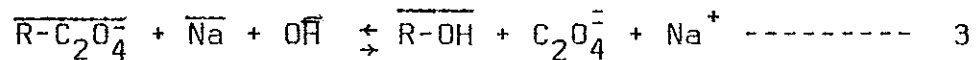
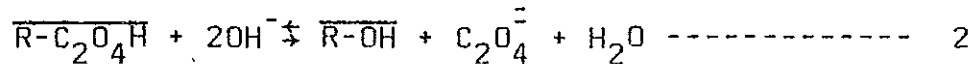
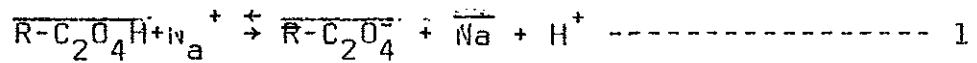
appropriate reagent at a definite p^H . Zirconium sulfide⁶⁵ is obtained by rapid mixing of Na_2S solution at $p^H 7.5$ with $ZrOCl_2$. It represents a white powder with $d=2.7$, easily exchanging Na^+ for Ca^{2+} and for ions forming insoluble sulfides and working well in frontal separation of $Cu(II)-Ca(II)$ and $Cu(II)-Fe(II)$; $Cu:Ca$ enrichment amounted to 5×10^4 .

Zirconium arsenate is synthesized by mixing $ZrOCl_2 \cdot 8H_2O$ in HNO_3 with $K_2HA_8O_4$ at $p^H 7.5$. The sorbent consists of a gray white particles (0.1-0.2 mm) with a bulk d of 1.7. It did not swell in water. The action of 3 N acids and 2 N bases had no effect on sorption properties. The capacity of zirconyl arsenate decreases with increasing p^H during mixing. At $p^H 7$ its capacity is equal to that of zirconium hydroxide. This material is well suited for frontal separation of $Ca(II)-Co(II)$ with $Co:Ca$ enrichment upto 10^4 . The exchange capacity does not vary with particle size. For all bivalent ions, the dependent of the capacity on the p^H is approximately equal. The sorption of C_s^+ at low p^H is relatively insensitive to the presence of bi- and trivalent ion. An enrichment factor of C_s^+ with respect to K or 2.5×10^4 is attained. The kinetics and mechanism of zirconium arsenate⁶⁷ ion-exchanger synthesis is studied in H_2O or 0.5-3 M HNO_3 . The composition ($A_8:Zr$ at ratio 1.6 to 2.0) and the structure (crystalline, amorphous, or weakly crystalline) of the products depend on HNO_3 concentration and aging time of the precipitate. Analogous to the formation in HNO_3 , when prepared in HCl or H_2SO_4

solutions, zirconium arsenate⁶⁸ transforms from gel to a crystalline structure. The chemical composition of the dry crystalline product prepared in the presence of excess As_2O_5 concentration is $\text{Zr}(\text{HAsO}_4)_2 \cdot \text{H}_2\text{O}$. On aging in HCl or H_2SO_4 the composition and the structure of the crystalline product is found to change. The ion uptake properties of zirconium arsenate exhibited the order of exchange affinities for alkali metals at p^{H} values lower than 2.6 as $\text{Cs}^+ > \text{K}^+ > \text{Na}^+$ between p^{H} 2.6 and 3.8 the order becomes $\text{K}^+ > \text{Cs}^+ > \text{Na}^+$ while between p^{H} 3.8 and 4.65 it changes to $\text{K}^+ > \text{Na}^+ > \text{Cs}^+$; finally above p^{H} 4.65 the order is completely reversed to $\text{Na}^+ > \text{K}^+ > \text{Cs}^+$. On refluxing amorphous zirconium arsenate with fairly concentrated arsenic acid, a crystalline product is obtained. The ion uptake curves of the crystalline zirconium arsenate showed that at the same counter ion content the equilibrium p^{H} 's below half conversion of the exchanger are in the order $\text{Cs}^+ > \text{Rb}^+ > \text{Li}^+ > \text{Na}^+ > \text{K}^+$, which is assumed to be due to the fact that Li^+ , Na^+ and K^+ are small enough to enter cavities according to their decreasing hydrated volume, while Rb^+ and Cs^+ are sufficiently large to undergo steric hindrance.⁶⁴

Another zirconium based sorbent is zirconyl oxalate^{65,69} which is precipitated from zirconium oxychloride and ammonium oxalate solutions at p^{H} 8. It is a white powder weak acid, separation enrichments of $\text{La}:\text{Ca}$ (1:1000) and $\text{Co}:\text{Ca}$ (1:10000) were 10^3 and 5×10^3 respectively. This exchanger is represented by the formula $\text{ZrO}(\text{OH}) \text{C}_2\text{O}_4\text{H}$, which accounts for the exchange

capacity as resulting from the ionization of the acid oxalate groups. Zirconyl oxalate undergo hydrolysis in alkaline media. The main reactions taking in neutralization of zirconyl oxalate with NaOH is represented as follows:



where the bar refers to the exchanger phase and R to the zirconium matrix.

Distribution coefficient determinations on the NH_4^+ -form of zirconyl oxalate, carried out in series alternating with conversion to the H^+ forms gave reproducible results in each series, but decreasing from series to series. On the other hand, batch experiments of tracer alkaline earths in HCl media, showed that they decrease when the acid concentration is raised upto 0.1 M, but increased thereafter. It is also found that higher acid concentrations tended to soften the exchanger grains and, eventually, to peptize them.

Zirconyl chromate^{65,70} is obtained in similar way by mixing Na_2CrO_4 with ZrOCl_2 at p^{H} 8, it is a yellow powder with ion-exchange p^{H} range 2-10. It has acidic properties working well in the separation of Ca(II)-Sr(II).

Zirconyl carbonate⁶⁵ is synthesized in analogous way by rapid precipitation of ammonium carbonate with ZrOCl_2 . This exchanger is not stable due to the liberation of CO_2 .

It is well suited for separation of Ca(II)-Mg(II). The ion exchange capacity is of the order 0.75-1 meq/g similar to that of ion-exchange resins.

Zirconium(IV) based antimonate sorbents^{56,57} are also found to behave as cation exchangers with relatively high capacity and showed unusual selectivities for the alkali metals, alkaline earth and rare earths compared to other zirconium based ion-exchangers. The alkali metals showed a unique order of atomic numbers, as is commonly observed, Na^+ is more strongly adsorbed than either K^+ or Rb^+ , while Rb^+ is more strongly adsorbed than K^+ . Differences in selectivity were large and separations were made for Na^+ , K^+ , Rb^+ with small columns of zirconium antimonate. This exchanger had an Sb(V)/Zr(IV) ratio of some what larger than 2 to 1. Zirconium antimonate⁵⁶ is reasonably stable in, concentrated and dilute HNO_3 and NH_3 , and it is not appreciably attacked by H_2SO_4 , HCl and NaOH upto concentration of about 2 M; Cs^+ uptake by the solid is 0.5 mole/kg at p^{H} 3, total Na^+ uptake by the exchanger originally in the H^+ -form is about 5 moles/kg.

Zirconium based polybasic mixed salts like zirconium molybdovanadate⁷² and zirconium phthalophosphate are also synthesized and their ion-exchange properties are investigated using monovalent and bivalent metal ions. These exchangers are presumed to be chemically more stable than their constituent counterparts. In this respect the chemical stability of the ion-exchanger zirconium molybdovanadate is studied in HCl , H_2SO_4 , and in chloride-sulfate solution. The ionic strength of the chloride-sulfate solutions is maintained at 0.20 while

p^H is 0.84-6.25. The stability is determined from the content of Zr, Mo(VI) and V(V) in the liquid phases and is better in HCl than in H_2SO_4 . The stability in the chloride-sulfate solutions increases with increasing p^H . Heat treatment of the exchanger at 300 °C improves its chemical stability but high temperature causes the degrading of the polymer.

Pertinent to this group of ion-exchangers is zirconium phthalophosphate⁷³ which is synthesized by mixing phthalic anhydride with $ZrO(NO_3)_2 \cdot 2H_2O$ in the presence of H_3PO_4 solution. The overall and strong groups ion-exchange capacity is determined as a function of p^H and temperature. The maximum ion-exchange capacity of the exchanger is 4.8 meq/g at p^H 10.8. Heating the exchanger at 100-700 °C showed that zirconium phthalophosphate retain its exchange properties even at high temperatures although its ion-exchange capacity decreases sharply with increasing temperature. Sorption experiments are carried out with a number of cations. Fe(II), Mn(II), Ni(II), Pb(II), Cu(II), and Ba(II) are sorbed by the dry exchanger; Al(III), Cr(III) and Co(II) are sorbed only by the swelled exchanger. The chemical stability of this material is examined by using 0.5-3 N solutions of HCl, HNO_3 , H_2SO_4 , NaOH and NH_4OH at room temperature and under heating. It is less stable in alkaline solutions setting free PO_4^{3-} , within the whole acidity interval investigated, no PO_4^{3-} is liberated although traces of Zr(IV) are observed in solid media at ≥ 1 N.

Among zirconium(IV) based ion-exchangers the detailed investigated acid salt is zirconium phosphate, and a considerable

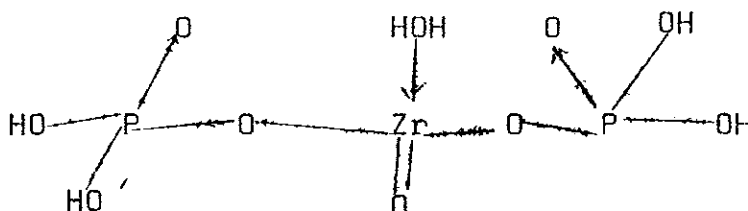
amount of information is now available, as to its mechanical and sorption properties.^{7,25,31} Zirconium phosphate is one of a stable class of synthetic inorganic ion-exchangers that can be prepared in granules. It is a typical polyfunctional weakly acid cation exchanger with capacities upto 5 meq/g in alkaline solutions. When the phosphate, zirconium ratio is low, anions in the original structure contribute anion exchange properties cations can be exchanged rapidly and reversibly on acid phosphate groups in the gels structure.⁷⁴

Normal zirconium phosphate ($\text{PO}_4^{-3}:\text{Zr}=2$) is obtained as a gelatinous precipitate when an excess of phosphoric acid or soluble phosphate is added to a soluble zirconium salt, and precipitation is very fast and leads to amorphous materials.^{26,63,75,76} This compound is represented as a monhydrogen phosphate $\text{Zr}(\text{HPO}_4)_2$ ⁷⁵. However, later on it is considered that a zirconium rather than a zirconyl salt would precipitate from aqueous solution, and hence represented the compound as $\text{ZrO}(\text{H}_2\text{PO}_4)_2$ ³⁰. Ahriand et.al.⁷⁶ has studied the hydrolysis of gelatinous zirconium phosphate and proposed a formula $\text{ZrO}_2 \cdot n\text{PO}_4 \cdot m\text{H}_2\text{O}$ in which $n=\text{PO}_4=\text{Zr}$ and m is the moles of water/mole of zirconium in the gel.

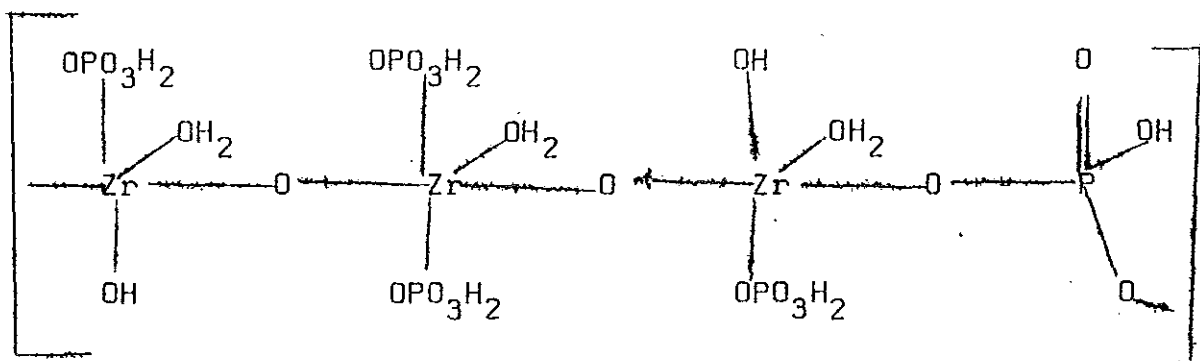
Turning to the more crystalline zirconium phosphate a suitable method is employed by Alberti and Torracca⁷⁷ to reduce the rate of precipitation in which crystalline materials are obtained. Alternatively, crystalline zirconium phosphate is obtained by Darfield²⁵ by refluxing the amorphous product in concentrated phosphoric acid. The formula of the crystalline product in the hydrogen form is $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$. Its

density is 2.72 g/cm^3 and its ion-exchange capacity 6.64 meq/g . It is now well established that zirconium phosphate prepared in different ways can have different $\text{PO}_4:\text{Zr}$ ratios. Moreover samples with the same $\text{PO}_4^{3-}:\text{Zr}$ ratio can show a diversity of ion-exchange properties.⁷⁸

Studies concerning this ion-exchanger were primarily directed towards elucidating ion-exchange properties and little attention was paid to the composition or structure of phosphate. However, the major difficulty attendant to the development of a quantitative theory of ion-exchange behaviour is precisely this lack of compositional or structural data. Blumental⁷⁵ proposed the following structural formula for zirconium phosphate to account for its behaviour as an acid.



However, Amphlet et.al.⁷⁴ and Grover⁷⁹ have supposed that zirconium phosphate consists of a Zr-O lattice with acid phosphate groups attached to a spare valency bonds. Based on the observed composition, X-ray and density data, Clearfield and Stynes²⁵ proposed that zirconium phosphate has the following structure.



Washing normal zirconium phosphate with water removes phosphate groups by hydrolysis. Larsen and Vissers⁸⁰ exhaustively washed the normal phosphate with conductivity water and obtained a product in which $\text{PO}_4^{3-}:\text{Zr}=1.72$. Baetsle' and Pelsmaekers precipitated zirconium phosphate from solutions containing PO_4^{3-} to Zr(IV) ratios of 3,2,1.75. The precipitates had different compositions but on washing, products of constant composition in which $\text{PO}_4^{3-}:\text{Zr}$, 1.66-1.68 were obtained.

The capacity and sorption studies on a number of zirconium phosphate samples ranging from amorphous to very good crystalline materials were also undertaken by many workers in this field.^{23,25,78,82} Some investigations concerning the ion-exchange property of zirconium phosphate have shown that the order of selectivity of zirconium phosphate for the alkali metal ions is the same as that of the strong acid organic ion-exchange resins, namely $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$.⁸² Clearfield and Stynes have determined the amount of replaceable hydrogen ion present in the zirconium phosphate by NaCl+NaOH titrations. The crystalline samples gave a sharp,

15

permanent end-point which correspond to the replacement of two hydrogen ions permolecule of zirconium phosphate. In contrast the gelatinous samples gave an initial end-point which faded on standing for 1-2 hr. It was proposed that the fading of the end-point appears to result from hydrolysis of phosphate groups. Similar phosphate release was shown by Nancollas and Pekarek⁷⁸ to be accompanied by an uptake of chloride ion which was readily replaced by water. Potassium and lithium ion titration curves were similar to the sodium ion curves. They also exhibited two hydrogen ions. However, the Cs⁺ pick up was negligible, which is in marked contrast to that of the gels which strongly absorb cesium ion. Crystalline zirconium phosphate is interesting in that it consists of a layered structure which is capable of some degree of lattice expansion to accomodate small unhydrated ions (e.g. Li⁺, Na⁺ and K⁺) while larger ions e.g. Cs⁺ are sterically excluded.^{7,30} However it was found that if sufficient energy for the exchange is supplied, i.e. by increasing the p^H value of the external solution, the layers can spread apart and large cations such as Rb⁺ or Cs⁺ can enter inside the crystals.⁸³ The titration curves for Ca²⁺ on crystalline zirconium phosphate have only a single inflexion point and all the exchange sites are available at low p^H.⁸⁴ A similar result was obtained by Clearfield and Smith in their studies of Sr²⁺ ion-exchange.⁶³ Results of equilibration studies of the crystalline metal ion-forms^{84,85} showed that the potassium form almost completely excluded both Li⁺ and Na⁺ and total replacement is only observed for Na⁺ exchange on the lithium form. It appears

that a certain fraction of the sites on the sodium form are not available to K^+ and Li^+ . In addition, Li^+ cannot be completely removed from the lithium form by K^+ .

Determinations of the electrical conductivity of zirconium phosphate of different degrees of crystallinity and in several ionic forms are also in progress. Preliminary results seem to indicate that the conductivity of $Zr(HPO_4)_2 \cdot H_2O$ increases with increasing degree of disorder in the crystal structure.²⁶

Paralleling the progress in the systematic study of zirconium phosphate type ion-exchangers, rapid developments were taking place in the chemistry of thorium phosphate. Insoluble acid salts of thorium(IV) have generally been obtained as amorphous, fibrous, and semi-crystalline materials. Alberti and Constantino⁵¹ prepared both amorphous and fibrous thorium phosphate at room temperature with $PO_4:Th$ ratio from 1.5 to 2.1. They showed that the composition of thorium phosphate is $ThO_2 \cdot P_2O_5 \cdot 4H_2O$ and the ion-exchange capacity for Na^+ was reported to be 3.7 meq/g. It was found that the formation of fibrous phosphate was favored by a high PO_4/Th ratio, high temperature and a long digestion time. A low yield or no precipitate was obtained when the phosphoric acid concentration is higher than 2 M. The chemical composition of solid fibrous thorium phosphate was found to have a PO_4/Th ratio of about 2. From the sodium uptake the ion-exchange capacity was found to be 3.85 meq/g. Anil and Kailas⁵² synthesize thorium phosphate with slight modification by changing the temperature to 80 °C. The products so obtained are in the

form of both amorphous and fibrous, hard white materials, suitable for use as support free ion-exchange sheets. No change in the form or colour was observed when it was heated in boiling water, dilute mineral acids and dilute alkalies, but when the product was refluxed with 5 M phosphoric acid for 12 hr it changed to semi-transparent beads. When the exchanger was immersed in 1 M nitric acid at room temperature for 24 hr, the $\text{PO}_4:\text{Th}$ ratio decreased from its original value. The exchanger remained unaffected in concentrated nitric acid, sulphuric acid, perchloric acid, (60%). In concentrated hydrochloric acid, the sample became yellow after a few hours. The IR spectrum of thorium phosphate reveal two well defined peaks at $980\text{-}1140\text{ cm}^{-1}$ and 1640 cm^{-1} . The first peak $980\text{-}1140\text{ cm}^{-1}$ is considered to be due to ionic phosphate which is observed as one sharp peak in normal phosphate but as an assembly of three peaks in the polymer samples. The second peak at 1640 cm^{-1} was suggested to be due to interstitial water present in the polymer molecules.

The exchanger was found to comprise monofunctional acids. The titration curves with Li^+ , Na^+ and K^+ lie on the same line at low p^{H} values, but at higher p^{H} , the curve for Na^+ lies between those for Li^+ and K^+ . On titration with alkali alone, there is a more rapid increase in p^{H} than in the presence of salt e.g. sodium chloride. The ion-exchange selectivity at p^{H} 6-6.5 for univalent ions follow the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ and for bivalent ions $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$. As the hydrated ionic radius decreases, the ion-exchange

capacity increase. Anil and Kailas⁵³ have undertaken a study in the measurement of distribution coefficients, separations of Pb^{2+} from Cu^{2+} , Cd^{2+} , Zn^{2+} , Ca^{2+} , Mg^{2+} , Co^{2+} , Mn^{2+} and Hg^{2+} , and of Bi^{3+} from Zn^{2+} , Cu^{2+} , Co^{2+} , Cd^{2+} and Hg^{2+} have been achieved with thorium phosphate.

CHAPTER THREE

3. EXPERIMENTAL

3.1. Synthesis

3.1.1. Zirconium Selenite

Solution of zirconium oxychloride, 0.25 M, was prepared by dissolving $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in HCl (4 M). Solution of sodium selenite, 0.5 M, was prepared by dissolving Na_2SeO_3 in 4 M HCl. The exchanger where the zirconium to selenite molar ratio is 0.50 was obtained by adding 0.5 M sodium selenite (50 ml) drop wise from a buret into a beaker containing 50 ml of HCl solution of 0.25 M zirconium oxychloride with constant stirring and at room temperature. The acidity of the solution was adjusted to about 1 M HCl. The precipitate so obtained was kept for 24 hr, filtered and washed with distilled water until it is free of chloride ion, dried at 40°C for 4 days. Three different samples were prepared by changing the mixing ratio of Zr:Se as 1:2, 1:1 and 1;5:1 to give sample Nos. 1,2 and 3 respectively. The materials were ground and sieved to 90-180 mesh, soaked in 2 M HNO_3 overnight, washed with distilled water and dried again at 40°C . The molar mixing ratio of the synthesis is shown in Table 1.

3.1.2. Thorium Tellurite

Solution of thorium nitrate, 0.1 M, was prepared by dissolving $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ in 1 M HNO_3 . Solution of sodium tellurite, 0.2 M, was prepared by dissolving Na_2TeO_3 in 4 M

HCl. The exchanger where the thorium to tellurite molar ratio is 0.50 was obtained by adding 0.2 M sodium tellurite (50 ml) dropwise from a buret into a beaker containing 50 ml of HNO_3 solution of 0.1 M thorium nitrate with constant stirring and at room temperature. The acidity of the solution was adjusted to about 1 M HCl. The precipitate so obtained was kept for 24 hr, filtered and washed with distilled water until it is free of chloride ion, dried at 40°C for 4 days. Three different samples were prepared by changing the mixing ratio of Th:Te as 1:2, 1:1 and 1.5:1 to give sample Nos. 4, 5 and 6 respectively. The materials were ground and sieved to 90-180 mesh, soaked in 2 M HNO_3 overnight, washed with distilled water and dried again at 40°C . All the reagents and chemicals used in the synthesis were BDH reagents of AR grade. The molar mixing ratio of the synthesis is shown in Table 1.

3.2. The Hydrogen Ion Liberation Capacity

The hydrogen ion liberation capacities of the three samples for both exchangers were determined by batch operation as follows⁵². A 50 ml volume of different concentrations of sodium chloride solutions were mixed with 0.25 g of the exchanger and shaken intermittently for 12 hr. A 50 ml of the aliquot was taken and titrated with standard 0.1 N NaOH solution using methylorange as indicator. The effect of the concentration of neutral salt solution on the exchange capacity in batch operation is shown in figs 1 and 2. The results obtained with the use of 2 M sodium chloride solution are reported in Table 1.

3.3. p^H-Titration

A 25 ml volume of solution containing different amounts of MOH (M=Li, Na or K) was added to 0.1 g of the exchanger. After intermittent shaking for 6 hr at 30 °C, the p^H was recorded. The experiment was repeated in the presence of salts keeping the-metal ions concentrations constant at 0.1 MCl + MOH (M=Li, Na or K).

3.4. Solubility of the Exchangers

The solubility of both exchangers (molar ratio 0.5) was determined in several solvents at room temperature. A 0.1 g of the material was equilibrated with 50 ml volume of the solvent and kept for 12 hr with intermittent shaking. Zirconium(IV) was determined by standard spectrophotometric method using alizarin red-S at 525 nm, and p^H 0.7⁸⁶. Selenium was determined titrimetrically as follows.⁸⁷ To the sample solution containing selenium was added 5 ml of 1 % KI, the liberated iodine was then titrated with standard 0.1 N Na₂S₂O₃ solution. Thorium was determined by standard spectrophotometric method with carmine red at 560 nm, at p^H 2.5.⁸⁸ Tellurium was determined titrimetrically as follows.⁸⁹ To the sample solution containing tellurium was added 20 ml of concentrated HCl, 15 ml of concentrated H₂SO₄, and 3 g MnSO₄. The titration was carried out by addition, first 25 ml of standard 0.1 N K₂Cr₂O₇ solution. The solution was then permitted to stand for 15 minutes and back titrated with standard 0.1 N ferrous ammonium sulphate. Ferrous penanthroline being used as indicator. The results are given in Table 2.

3.5. Composition

3.5.1. Zirconium Selenite

For determination of chemical composition of zirconium(IV) selenite 2 mg of the sample (molar ratio 0.5) was boiled with 50 ml of concentrated NaOH, for 12 hr to precipitate zirconium, which was dissolved in concentrated HCl.⁷¹ The same procedures employed for chemical stability determination were adopted to estimate zirconium⁸⁶ and selenium⁸⁷ in the supernatant obtained from the synthesis experiment. The absolute amount of Zr:Se was found to be 1:2.11.

3.5.2 Thorium Tellurite

Similarly the chemical composition of thorium(IV) tellurite 2 mg of the sample (molar ratio 0.5) was boiled with 50 ml of concentrated HCl, for 1 hr.⁵² The solution was cooled and then filtered. The amount of thorium⁸⁸ and tellurium⁸⁹ released in the solution were then determined by the methods previously described in the solubility studies procedure. The absolute amount of Th:Te was found to be 1:2.17.

3.6. Distribution Coefficients (K_d)

The values of the distribution coefficients (K_d) of Pb^{2+} , Mn^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} and Co^{2+} were determined as follows.⁵⁵ 0.1 g of the exchanger (molar ratio 0.5) was equilibrated with 10 ml of solution containing 7×10^{-3} M metal ions at pH_2 , pH_3 , pH_4 , pH_6 , $pH_{6.5}$ with intermittent shaking

at 30 °C. The concentration of metal ions in the solid and the liquid phase was deduced from the concentration relative to the initial concentration in the solution. The K_d values were calculated using the following equation.

$$K_d = \frac{\text{amount of metal ion on the exchanger} \times \text{volume(ml)}}{\text{amount of metal ion in the solution} \times \text{exchanger(g)}}$$

Amount of metal ions were determined by using a Varian Techtron 1100 atomic absorption spectrometer. The results are given in Table 4.

3.7. Separations

For separation studies 2 g of the exchanger (molar ratio 0.5) in the H^+ -form was taken in a glass column packed to 3.5 cm in height and of inner diameter 0.69 cm. Mixture of metal ions was then applied and allowed to pass through the column.^{42,55} The metal ions adsorbed on the exchanger were then eluted with suitable eluting reagent. The rate of flow was 0.5 ml/min and 5 ml fraction of effluent were collected for metal ion determination. The results are summarized in Tables 5-12.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1. IR and Composition

The products obtained are in the form of amorphous hard white materials. The molar ratio of Zr^{4+}/SeO_3^{2-} and Th^{4+}/TeO_3^{2-} of the exchangers prepared are present in Table 1. The external appearance of the material did not change with the difference in the mixing ratio. From the chemical analysis the molar composition of zirconium(IV) selenite shows that zirconium(IV) and selenium are present in the ratio of 1:2. A similar result was also found for the molar composition of thorium(IV) tellurite where thorium(IV) and tellurium are present in the ratio of 1:2. The IR spectrum of sample Nos. 1 and 4 dried at 40 °C was obtained by KBr disc method (Figs 17 and 18).

IR spectrum of zirconium selenite in H^+ -form exhibits strong absorption bands in the regions $3500-300\text{ cm}^{-1}$, $1700-1600\text{ cm}^{-1}$, $800-650\text{ cm}^{-1}$, and $400-500\text{ cm}^{-1}$. The broad peak in the region $3500-300\text{ cm}^{-1}$ may be due to presence of water molecules and OH groups. The second peak in the region $1700-1600\text{ cm}^{-1}$ with a maximum about 1640 cm^{-1} can be possibly assigned as characteristics of interstitial water molecules. The third peak in the region $800-650\text{ cm}^{-1}$ may be $400-500\text{ cm}^{-1}$ may be ascribed to $Zr-O$.⁹¹ The IR spectrum of thorium tellurite in H^+ -form revealed absorption bands in the region $3500-3000\text{ cm}^{-1}$, $1700-1600\text{ cm}^{-1}$, $800-600\text{ cm}^{-1}$, $400-350\text{ cm}^{-1}$.

The broad peak in the region $3500-3000\text{cm}^{-1}$ may be due to the presence of water molecules and OH groups. The second peak in the region $1700-1600\text{cm}^{-1}$ with a maximum 1630cm^{-1} may be due to interstitial water present in the polymer molecules. The third peak in the region $800-600\text{cm}^{-1}$ may be due to ionic tellurite TeO_3^{2-} .⁹⁰ The fourth peak in the region $400-350\text{cm}^{-1}$ may be ascribed to Th-O.⁹¹

The IR spectrum of the gelatinous precipitates obtained by addition of hydroxyl ions to solutions of zirconium oxychloride and thorium nitrate,⁹² was also run by KBr disc method (Figs 19 and 20), to compare with the IR spectrum of zirconium selenite and thorium tellurite. The absorption bands in the region $1700-1600\text{cm}^{-1}$ which is due to interstitial water present in the exchanger is not revealed in the IR spectrum of both hydroxides. The absorption band in the region $800-650\text{cm}^{-1}$ which is due to the ionic selenite (SeO_3^{2-}) is not exhibited in the IR spectrum of zirconium hydroxide. Similarly the absorption band in the region $800-600\text{cm}^{-1}$ which is due to TeO_3^{2-} is absent in the IR spectrum of thorium hydroxide where as the broad peak in the region $3500-3000\text{cm}^{-1}$ which is due to the presence of water molecules and OH groups is revealed in the IR spectrum of both hydroxides.

Table 1: Synthesis and Ion Exchange Properties of
the Exchangers

A. Zirconium Selenite

Sample No.	ZrOCl ₂ ·8H ₂ O Molarity (mole/liter)	Na ₂ SeO ₃ Molarity (mole/liter)	Mixing ratio	Hydrogen ion liberation capacity meq/g
1	0.25	0.50	0.50	1.20
2	0.10	0.10	1	0.96
3	0.081	0.054	1.50	0.76

B. Thorium Tellurite

	Th(NO ₃) ₄ ·6H ₂ O Molarity (mole/liter)	Na ₂ TeO ₃ Molarity (mole/liter)	Mixing ratio	Hydrogen ion liberation capacity meq/g
4	0.10	0.20	0.50	1.12
5	0.10	0.10	1	0.88
6	0.20	0.133	1.50	0.30

4.2. Solubility of the Exchangers

Both exchangers (molar ratio 0.50) dissolved completely in concentrated nitric acid, sulphuric acid, perchloric acid (60%) and hydrochloric acid after 12 hr at room temperature. Detailed studies on the solubility of the exchangers were carried out in different solvents at room temperature (Table 2). No change in the form or colour was observed when immersed in dilute mineral acids. Table 2 shows the solubility of both exchangers in various mineral acids at different concentrations. The exchangers are stable in dilute nitric acid, sulphuric acid, hydrochloric acid, (less than 1 N) but they are fairly unstable in basic solution, that is, they dissolve or peptize even in 0.1 N sodium hydroxide solution. The solubility studies indicate that both exchangers are not very stable in alkaline medium in which a loss of selenite and tellurite groups occur. The differing solubility in the various acids can be related to the different complexing power of these acids towards thorium and zirconium.^{37,38} Very low solubility values in dilute and weakly complexing acids can be noted. The exchangers are relatively stable in nitric acid compared to other mineral acids. Thus dilute HNO_3 solution can be employed to regenerate salt forms of these exchangers without appreciable dissolution of the material. From the solubility studies it seems that zirconium selenite is chemically more stable than thorium tellurite. The stability of both exchangers decreases remarkably when the concentrations of the respective solvents increase.

Table 2: Solubility of Zirconium Selenite and Thorium Tellurite

Molar ratio = 0.50

Equilibration time = 12 hr

Quantity of exchanger = 0.10 g

Volume of solvent = 50 ml

Ser No	Solvent	Zirconium dissolved (mg/50 ml)	Selenite dissolved (mg/50 ml)	Thorium dissolved (mg/50 ml)	Tellurite dissolved (mg/50 ml)
1	1 M HCl	0.150	8.29	0.22	12.76
2	0.5 M HCl	0.074	2.76	0.120	6.38
3	1 M HNO ₃	0.135	4.73	0.190	8.93
4	0.5 M HNO ₃	0.038	1.97	0.107	5.10
5	1 M H ₂ SO ₄	0.210	23.68	0.30	56.7
6	0.5 M H ₂ SO ₄	0.118	6.97	0.131	30.6
7	0.1 N NaOH	0.174	29.2	0.202	66.4
8	0.01 N NaOH	0.063	22.8	0.141	51.04
9	4 M acetic acid	0.042	3.94	0.061	28
10	8 M acetic acid	0.089	5.92	0.100	42.1
11	4 N NH ₃	0.162	34.6	0.26	44.6
12	01 N NH ₃	0.124	24.8	0.150	25.5

Average deviation = 0.1 - 0.30

Number of analysis = 3

4.3. Hydrogen Ion Liberation Capacity

Generally, the exchange capacity of a weakly acidic cation exchanger must be determined with an alkaline solution.^{54,55} Zirconium selenite and thorium tellurite exchangers however are unstable in alkaline solution. Therefore, a measure of exchange capacity was taken as the amount of hydrogen ion liberated by a neutral salt, such as sodium chloride. The hydrogen ion liberation capacity also depends on the concentration of the neutral salt solution.^{5,37,53} The effect of the concentration of neutral salt solution on the hydrogen ion liberation capacity of the exchangers is shown in Figs 1 and 2. For both exchangers a constant exchange capacity was obtained for sodium chloride solution of concentration greater than 2 M. The hydrogen ion liberation capacity was found to be strikingly dependent upon the ratio of anion to metal in the products, namely the greater the ratio, the higher the capacity. Table 1 shows that sample No. 1 with lower ratio of Zr^{4+}/SeO_3^{2-} (molar ratio=0.5) has high hydrogen ion liberation capacity of 1.2 meq/g. The result suggests that the exchangeable protons in zirconium selenite decreases with an increase in the Zr:Se ratio, which indicates that the exchangeable protons originate from the selenite group.

Similar behaviour was also observed for thorium tellurite hydrogen ion liberation capacity where sample No. 4 with lower ratio of thorium to tellurite (molar ratio=0.50) has high hydrogen ion liberation capacity of 1.12 meq/g indicating

that the active sites are on the tellurite group. This result is in agreement with other works concerning hydrogen ion liberation capacity determinations where the exchange capacity decreases as the ratio of anion to metal decreases.^{5,41,42.}

4.4. p^H- Titration Curves

As there is only one break in the titration curves (Figs 3,4,5 and 6) the exchangers should comprise weak mono-functional acids. On titration with alkali alone, there is a more rapid increase in p^H than in the presence of salt (e.g sodium chloride) as can be seen from Figs 4 and 6. The addition of sodium chloride releases some of the H⁺ from the exchangers and thus lowers the p^H. Figs 3-5 show that the titration curve with K⁺ lies below those with Na⁺ and Li⁺ at low p^H values, while the opposite is found at higher p^H's. From the titration curves it can be seen that at p^H values lower than 10 K⁺ is more strongly absorbed than Na⁺ and Li⁺, the order of exchange affinity being K⁺>Na⁺>Li⁺, while above p^H 10 the order becomes Li⁺>Na⁺>K⁺. This reversal in selectivity observed for amorphous zirconium selenite and thorium tellurite as the conversion to the salt form proceeds may be due to the same steric effect that have been found to reverse the mobility sequence of the alkali metal ions in amorphous zirconium arsenate⁶⁴ and zirconium phosphate²⁵. Therefore the same explanation given for zirconium arsenate and zirconium phosphate ion-exchange properties can be applied to the

present result. Representing both exchangers with the same model, we suppose that these amorphous exchangers, due to their disordered structure, exchange hydrogen with other counter ions through channels or cavities widely differing in size. Larger cavities may have enough room for ions to be hydrated, but more and more dehydrated ions must be exchanged with hydrogen as the size of the cavities decreases. In the course of the titration, larger cavities are involved first and the exchangers will prefer the counter ion with the smallest hydrated volume, since smaller and smaller cavities have to be involved as the conversion proceeds, the affinity order will gradually change and the exchangers will finally prefer the ion with the smallest crystalline radius.

4.5. Distribution Coefficients (K_d)

Distribution coefficients of metal ions on zirconium selenite and thorium tellurite were determined in the p^H range from 2 to 6.5 (Table 4). At $p^H 2$ the adsorption of metal ions on zirconium selenite show the following selectivity series $Pb > Co > Mn > Ni > Cu > Zn > Cd$, between $p^H 3$ to 6 the order becomes $Pb > Co > Mn > Ni > Cu > Cd > Zn$, while at $p^H 6.5$ it changes to $Pb > Zn > Mn > Cu > Cd > Co > Ni$. The selectivity series of metal ions on thorium tellurite at $p^H 2$ was found to follow the order $Pb > Cu > Zn > Mn > Co > Ni > Cd$, between $p^H 3-6$ the order is the same as $p^H 2$ except for some selectivity difference of Cd and Ni, i.e. $Pb > Cu > Zn > Mn > Co > Cd > Ni$, while at $p^H 6.5$ the order is $Pb > Cu > Mn > Ni > Co > Cd > Zn$. Table 3 shows that zirconium selenite has higher affinity for Pb and Co while thorium

tellurite has higher affinity for Pb and Cu. The results suggest that distribution coefficients are highly depend on the p^H of the initial solution. The order of the K_d values with different metal ions indicates differential selectivity. At all p^H conditions distribution coefficients were higher for lead than for other metals for both exchangers, and it is therefore possible to separate this metal from other metals that have much lower distribution coefficients.

In general the prder of affinity of metal ions depends on the hydrated ionic radius. For univalent and bivalent ions the following selectivity order, $Li^+ < Na^+ < K^+$, and $Mg^{2+} < Ca^{2+} < Ba^{2+}$ was observed on thorium phosphate.⁵² As the hydrated ionic radius decreases the adsorption of metal ions on the exchanger increases. The data which shows the relationship of adsorption and hydrated ionic radius is given below.

Table 3: Ion-Exchange Capacity of Thorium Phosphate for Bivalent and Univalent Cations

Metal Ion	Hydrated Ionic Radius (A°)	Ion-Exchange Capacity meq/g
Li^+	3.4	0.38
Na^+	2.76	0.74
K^+	2.32	1.12
Mg^{2+}	7.00	0.54
Ca^{2+}	6.30	0.89
Ba^{2+}	5.90	1.50

Some inorganic ion-exchanger such as C-SBA or MnO_2 ⁵⁵ show size preference selectivity for ions having specific ionic radii, but no such correlation was found between the K_d values and effective ionic radii of metal ion studied on zirconium selenite and thorium tellurite. It is shown that most ion exchangers exhibit a general selectivity sequence between members of four groups of ions, i.e. polyvalent metals > divalent transition metals > alkaline earth metals > alkali metals.

This behaviour is not shown by the insoluble salt of inorganic acids, e.g., zirconium and tin phosphate gels,^{5,7} which exhibit considerable overlap in the selectivity between three groups of the ions. The selectivity of zirconium phosphate⁹³ for transition metal ions have been reported to be in the order $\text{Ni} < \text{Co} < \text{Mn} < \text{Zn} < \text{Cu}$. Where as the selectivities of thorium phosphate⁵³ for transition metal ions and lead at p^{H} 5.5-6.5 have been reported to be in the order $\text{Pb} > \text{Cu} > \text{Zn} > \text{Mn} > \text{Cd} > \text{Co} > \text{Ni}$.

A slightly different selectivity order was observed on zirconium selenite and thorium tellurite at molar ratio of metal to anion (0.5)). This marked difference in behaviour towards transition metal ions is very difficult to explain without the knowledge of the structure of the exchangers. Unfortunately at this moment it is not possible to work out the structure of these exchangers, since these materials are obtained as amorphous powder. However, like zirconium selenite and thorium tellurite, some inorganic ion-exchangers,

Table 4: Distribution Coefficient of Metal Ions on the Exchangers (Molar ratio = 0.50)

Equilibration time = 14 hr

Quantity of exchanger = 0.10 g

Volume of solution = 10 ml

Concentration of metal ions = 7×10^{-3} M

Metal Ion	K_d values at $p^H = 2$		K_d values at $p^H = 3$		K_d values at $p^H = 4$		K_d values at $p^H = 6$		K_d values at $p^H = 6.5$	
	A	B	A	B	A	B	A	B	A	B
C_d^{2+}	5298	6072.83	219.46	257.40	277.17	386.50	372.84	512.120	5298	3498.97
Mn^{2+}	35075.87	717487.93	521.69	415.16	714.74	607.12	912.61	825.16	17474.60	5054.63
Zn^{2+}	8650	25931.98	186.31	625.31	238.20	815.20	315.63	1020.8	34.725	7086.85
Cu^{2+}	8660.95	53498.77	267.11	809.146	309.150	1021.30	435.21	1596.120	13083.20	9283.37
Ni^{2+}	18418.5	10194.11	317.211	191.25	429.301	275.33	526.16	414.60	2445.42	4142.42
Co^{2+}	40597.67	13492.23	942.315	332.53	1012.47	468.36	1678.11	556.27	3474.16	4066.45
Pb^{2+}	165776.70	56810.56	8356.23	5221.30	11431.11	8341.42	13501.20	9346.20	63536.36	14544.35

A - Exchanger Zirconium Selenite

B - Exchanger Thorium Tellurite

Average deviation = ± 8

Number of analysis = 3

e.g. thorium phosphate⁵³ and cerium phosphate,⁵⁰ showed high selectivity for lead.

4.6. Chromatographic Separation

In order to ascertain that zirconium selenite and thorium tellurite could be used as typical ion-exchangers and to investigate their properties of selectivity, an attempt was made to separate a mixture of lead and some other transition metal ions. It is evident that separations of metal ions are achieved on the basis of differences in K_d values.^{53,55}

On the basis of distribution studies some representative separations of analytical interest have been achieved. As zirconium selenite and thorium tellurite showed extremely high selectivity for Pb(II), the separation of Pb(II) from divalent transition metal ions was carried out:

Typical plots of the elution curves of the metal ions from Pb(II) in Fig. 7 and 8 for both exchangers show the separation of Pb(II) from other metal ions is complete. As shown in figs. 7 and 8, the separation of Pb(II) by the use of 2 M NaNO₃+0.15 M HNO₃ as an eluent is very sharp except for a slight failing of some transition metals. This failing is, perhaps, due to slow rate of exchange corresponding to the prolonged elution of hydrogen.⁵ Improved recovery for these metal ions was observed with a yield higher than 99% Table 5 and 6. An attempt was made to separate Cu(II) from Zn(II), and Mn(II) from Ni(II) on zirconium selenite column and Co(II) from Cd(II) and Mn(II) from Ni(II) on thorium

tellurite column by increasing the concentration of nitric acid which is used as eluent figs 9 and 10. The elution peaks were sharp and the yields were quantitative between 80-99% Tables 7 and 8, with complete separation. From the elution curves, it seems possible to separate micro-amounts of Cu(II), Mn(II), and Co(II) from macro-amounts of Zn(II), Ni(II) and Cd(II).

Ternary separations were also carried out on both exchangers. Separations of Mn(II) from Co(II) and Pb(II) on zirconium selenite Fig. 11, and separation of Zn(II) from Cu(II) and Pb(II) on thorium tellurite Fig 12 were achieved and recoveries were in the range of 95-99% for all metal ions tested Tables 9 and 10. Separation of lead from a mixture of six transition metal ions was also attempted on the columns of both exchangers. In both cases lead was separated from the multisystem figs 13 and 14. The overlapping of the elution curves of the transition metal ions indicated that separation of a mixture of these metal ions by chromatographic development on columns of both exchangers is not complete, eventhough they may show relatively large differences in their K_d . This might be due to that different metal ions may have different equilibration time in order to be adsorbed on the active sites, as the result the active sites will be fully occupied by the metal ions with low equilibration time, so during elution metal ions which are not adsorbed may come out leading to overlapping of elution curves.¹⁰

4.7. X-Ray Diffraction (XRD)

X-ray powder diffraction was taken using

CuK_α radiation. The X-ray diffractogram indicates that both ion-exchangers are amorphous. (Figs 21 and 22).

5. CONCLUSION

From studies of the fundamental properties of zirconium selenite and thorium tellurite, these materials were found to be promising cation exchangers. The high selectivity of zirconium selenite and thorium tellurite for Pb(II) can be compared with fibrous cerium phosphate⁵⁰, thorium phosphate,⁵³ lead and tin antimonates⁵⁵ which exhibited high selectivity for Pb(II). In summary, zirconium selenite and thorium tellurite can be utilized for the separation of trace amounts of lead in a wide variety of minerals and materials.

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APPENDIX

Table 6: Separation of Lead from Other Metals on Thorium Tellurite Column

(Molar ratio = 0.50)

Flow rate = 0.5 ml/min

Packed height = 3.5 cm

Diameter = 0.69 cm

Mixture Separated	Eluent	Effluent Collected (ml)	Taken (mg)	Found (mg)	Recovery (%)
1 Pb(II) and Cd(II)	0.01 M HNO ₃	25	2.60	2.55	98 (Cd)
	2 M NaNO ₃ +0.15 M HNO ₃	40	2.65	2.61	98.4 (Pb)
2 Pb(II) and Zn(II)	0.01 M HNO ₃	25	1.50	1.49	99.3 (Zn)
	2 M NaNO ₃ +0.15 M HNO ₃	40	2.65	2.60	98 (Pb)
3 Pb(II) and Cu(II)	0.01 M HNO ₃	25	1.49	1.45	97.3 (Cu)
	2 M NaNO ₃ +0.15 M HNO ₃	40	2.65	2.63	99.2 (Pb)
4 Pb(II) and Mn(II)	0.01 M HNO ₃	25	1.00	1.00	100 (Mn)
	2 M NaNO ₃ + 0.15 M HNO ₃	40	2.65	2.64	99.6 (Pb)
5 Pb(II) and Co(II)	0.01 M HNO ₃	25	0.65	0.61	93.8 (Co)
	2 M NaNO ₃ +0.15 M HNO ₃	40	2.65	2.64	99.6 (Pb)
6 Pb(II) and Ni(II)	0.01 M HNO ₃	25	1.50	1.48	98.6 (Ni)
	2 M NaNO ₃ +0.15 M HNO ₃	40	2.65	2.61	98.4 (Pb)

Average deviation = 0.2-0.5

Number of analysis = 3

Table 7: Other Binary Separation on Zirconium Selenite Column (Molar ratio = 0.50

Flow rate = 0.5 ml/min

Packed height = 3.5 cm

Diameter = 0.69 cm

Mixture Separated	Eluent	Effluent Collected (ml)	Taken (mg)	Found (mg)	Recovery (%)
1 Cu(II) and Zn(II)	0.2 M HNO ₃	30	1.52	1.50	99.3 (Zn)
	3 M HNO ₃	30	2.10	2.00	97 (Cu)
2 Mn(II) and Ni(II)	0.2 M HNO ₃	30	1.60	1.50	93.7 (Ni)
	3 M HNO ₃	30	1.65	1.62	98 (Mn)

Average deviation = 0.3-0.5

Number of Analysis = 3

Table 8 Other Binary Separations on Thorium Tellurite Column (Molar ratio = 0.50)

Flow rate = 0.5 ml/min

Packed height = 3.5 cm

Diameter = 0.69 cm

Mixture Separated	Eluent	Effluent Collected (ml)	Taken (mg)	Found (mg)	Recovery (%)
1. Co(II) and Cd(II)	0.2 M HNO ₃	30	2.50	2.00	80 (Cd)
	3 M HNO ₃	30	1.60	1.50	93.7 (Co)
2. Mn(II) and Ni(II)	0.2 M HNO ₃	30	2.20	2.00	91 (Ni)
	3 M HNO ₃	30	1.52	1.50	98.6 (Mn)

Average deviation = 0.1-0.2

Number of analysis = 3

Table 9: Ternary Separation on Zirconium Selenite Column (Molar ratio = 0.50)

Flow rate = 0.5 ml/min

Packed height = 3.5 cm

Diameter = 0.69 cm

Mixture Separated	Eluent	Effluent Collected (ml)	Taken (mg)	Found (mg)	Recovery (%)
Mn(II), Co(II) and Pb(II)	0.5 M HNO ₃	30	2.50	2.43	97.2 (Mn)
	2 M HNO ₃	30	2.10	2.00	95.2 (Co)
	4 M HNO ₃	40	1.70	1.67	98.8 (Pb)

Average deviation = 0.2-0.4

Number of analysis = 3

Table 10. Ternary Separation on Thorium Tellurite Column (Molar ratio = 0.50)

Flow rate = 0.5 ml/min

Packed height = 3.5 cm

Diameter = 0.69 cm

Mixture Separated	Eluent	Effluent Collected (ml)	Taken (mg)	Found (mg)	Recovery (%)
Zn(II), Cu(II) and Pb(II)	0.5 M HNO ₃	30	1.60	1.58	98.7 (Zn)
	2 M HNO ₃	30	1.00	0.98	98 (Cu)
	4 M HNO ₃	40	2.60	2.59	99.2 (Pb)

Average deviation = 0.1-0.4

Number of analysis = 3

47

Table 11: Separation of Mixture of Seven Metal Ions on Zirconium Selenite Column
(Molar ratio = 0.50)

Flow rate = 0.5 ml/min

Packed height = 3.5 cm

Diameter = 0.69 cm

Mixture Separated	Eluent	Effluene Collected (ml)	Taken (mg)	Found (mg)	Recovery (%)
Zn(II), Cd(II), Cu(II), Ni(II)	0.04 M HNO ₃	40	1.00	0.87	87 (Zn)
Mn(II), Co(II), and Pb(II)	0.1 M HNO ₃	40	1.55	1.50	96.7 (Cd)
	0.5 M HNO ₃	40	1.70	1.50	88.20 (Cu)
	1 M HNO ₃	40	1.40	1.31	93.50 (Ni)
	2 M HNO ₃	40	2.40	2.38	99.2 (Mn)
	4 M HNO ₃	40	1.40	1.37	97.8 (Co)
	5 M HNO ₃	40	2.60	2.49	95.7 (Pb)

Average deviation = 0.1-0.3

Number of analysis = 3

48

Table 12: Separation of Mixtures of Seven Metal Ions on Thorium Tellurite Column

(Molar ratio = 0.50)

Flow rate = 0.5 ml/min

Packed height = 3.5 cm

Diameter = 0.69 cm

Mixture Separated	Eluent	Effluent Collected (ml)	Taken (mg)	Found (mg)	Recovery (%)
Ni(II), Cd(II), Cd(II),	0.04 M HNO ₃	40	1.40	1.30	92.8 (Ni)
Mn(II), Zn(II), Cu(II), & Pb(II)	0.1 M HNO ₃	40	1.55	1.51	97.4 (Cd)
	0.5 M HNO ₃	40	1.40	1.30	92.8 (Cu)
	1 M HNO ₃	40	2.40	2.31	96.3 (Mn)
	2 M HNO ₃	40	1.00	0.91	91 (Zn)
	4 M HNO ₃	40	1.70	1.52	89.4 (Cu)
	5 M HNO ₃	40	2.60	2.50	96.2 (Pb)

Average deviation = 0.2-0.4

Number of analysis = 3

674

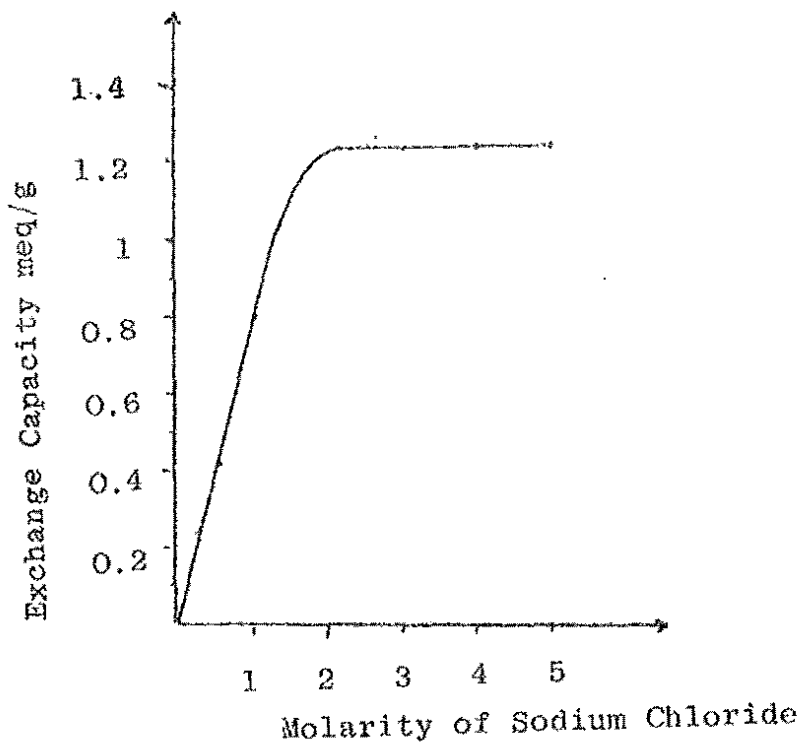


Fig. 1: Exchange Capacity of Zirconium Selenite as a Function of Concentration for Na^+ ions.

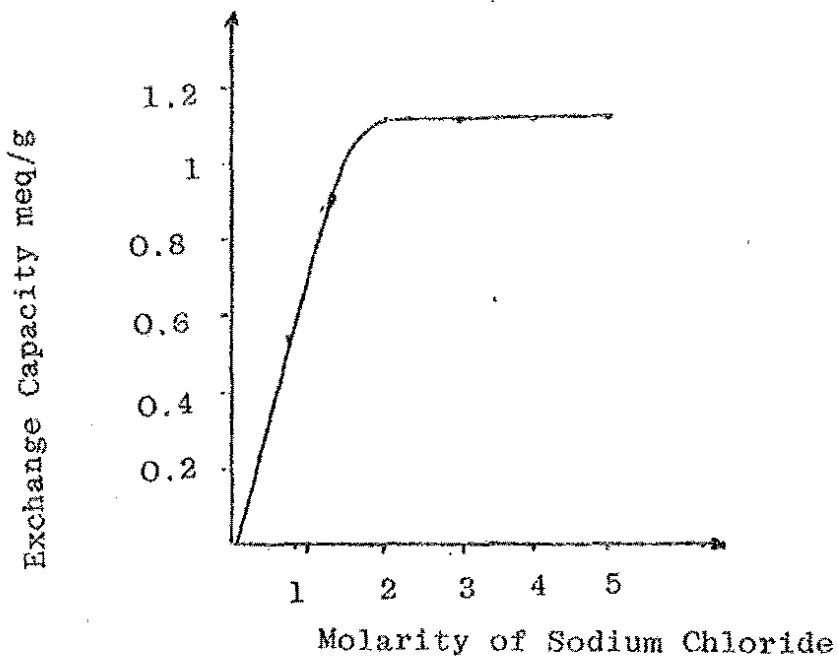
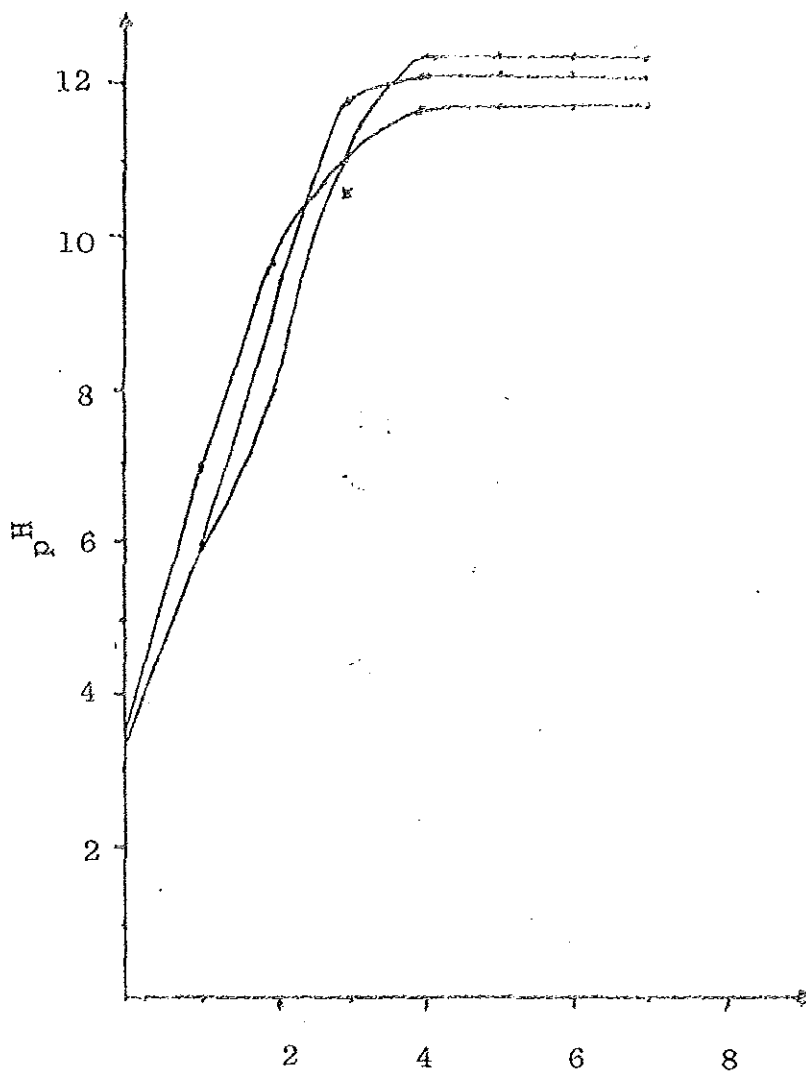
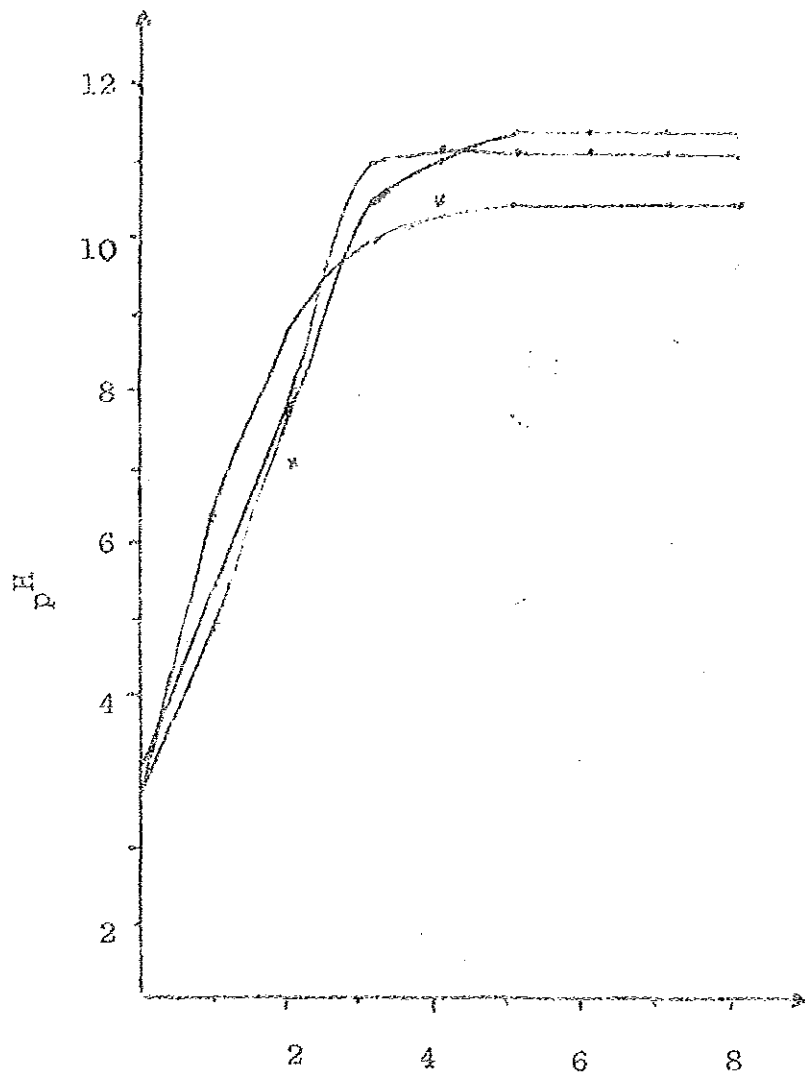


Fig. 2: Exchange Capacity of Thorium Tellurite as a Function of Concentration for Na^+ ions.



OH^- Ions Added in meq/0.1 g Exchanger

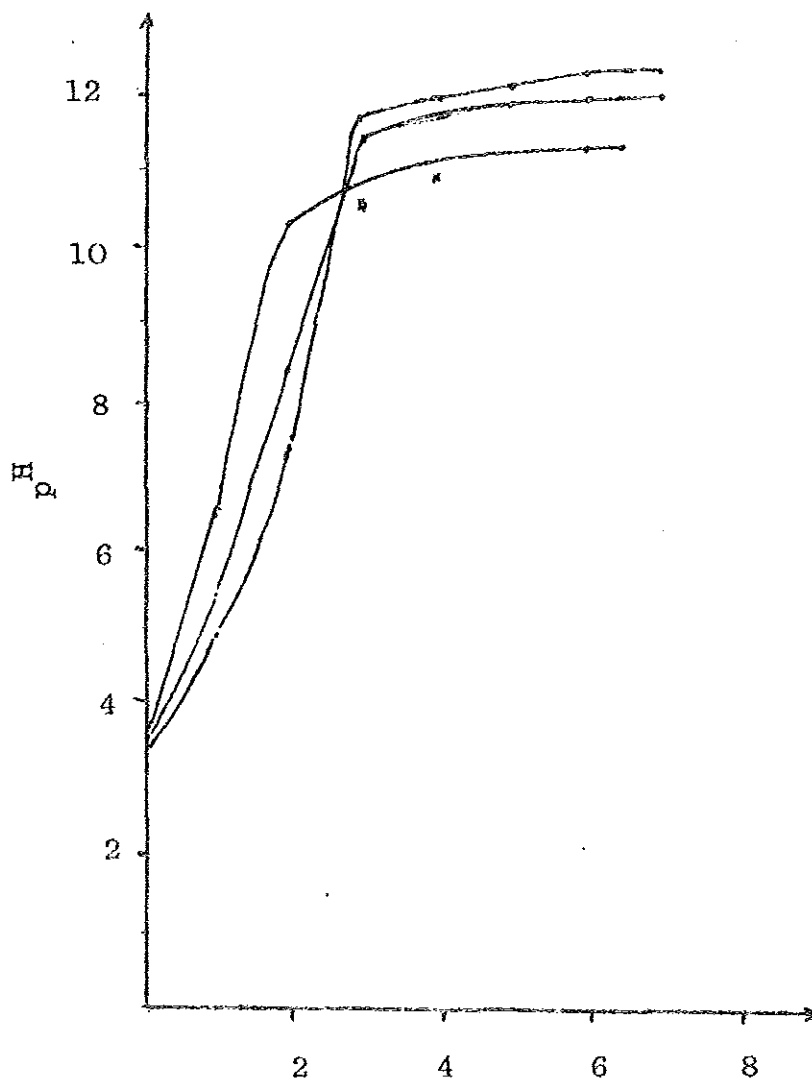
Fig. 3 pH titration curve for zirconium selenite sample No. 1 in the absence of salt.
Titrant: LiOH, NaOH, and KOH



[OH⁻] Ions Added in meq/0.1 g of the Exchanger

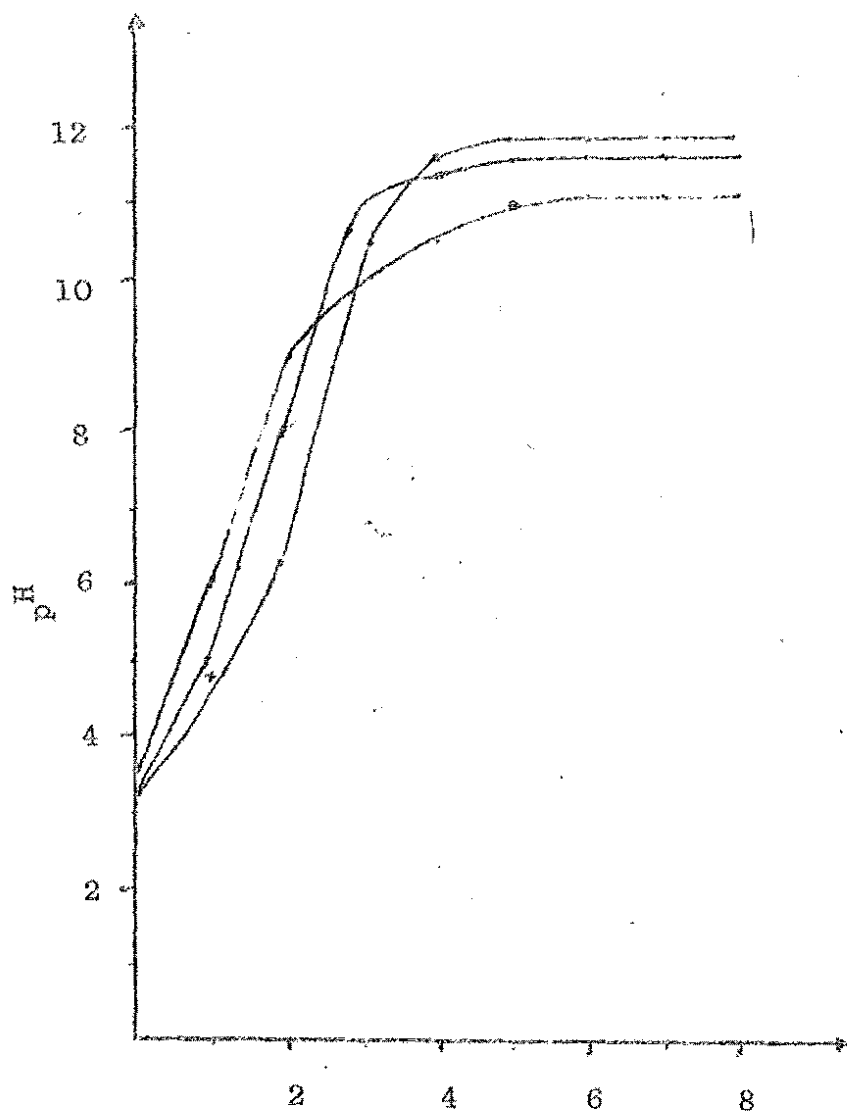
Fig. 4. p^H titration curve for zirconium selenite sample No. 1 in the present of salt.

Titration: LiOH+LiCl, NaOH+NaCl, and KOH+KCl.



(OH⁻) ions added meq/0.1 g of the exchanger

Fig. 5: p^H Titration Curve for Thorium Tellurite Sample No. 4 in the Absence of Salt Titrant: LiOH, NaOH and KOH.

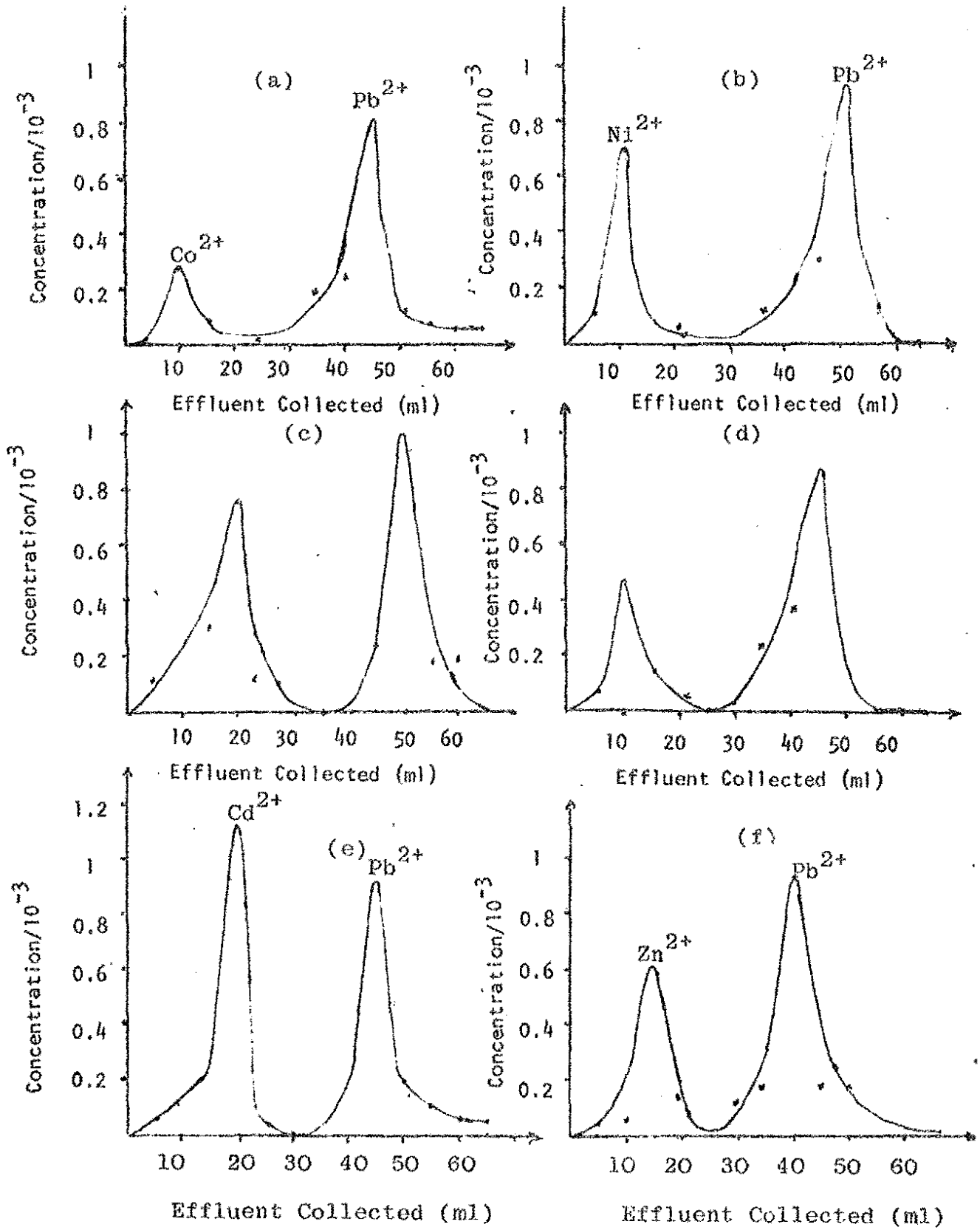


[OH⁻] ions added meq/0.1 g of the exchanger.

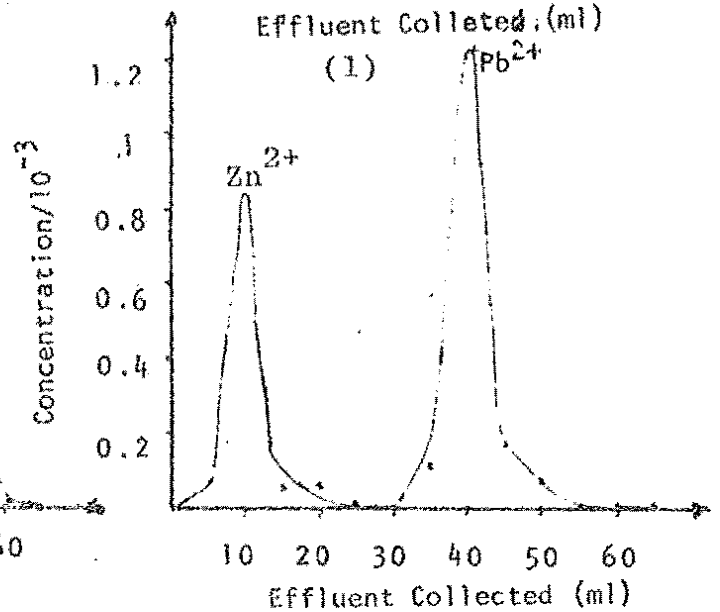
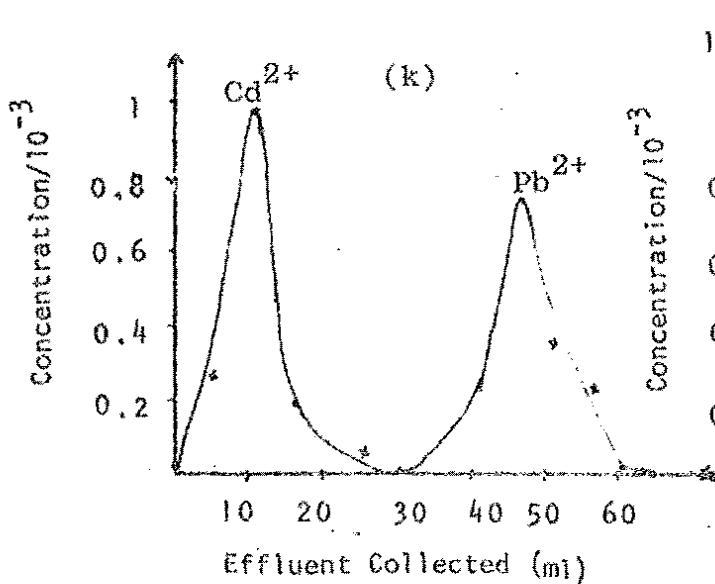
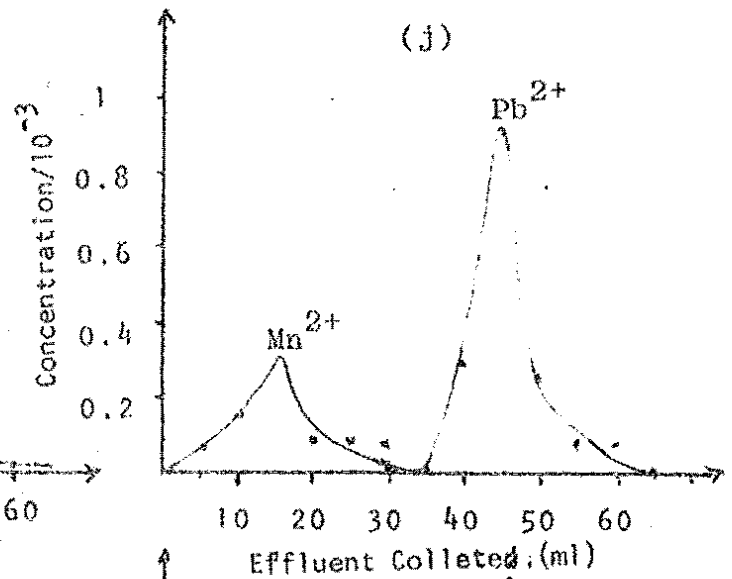
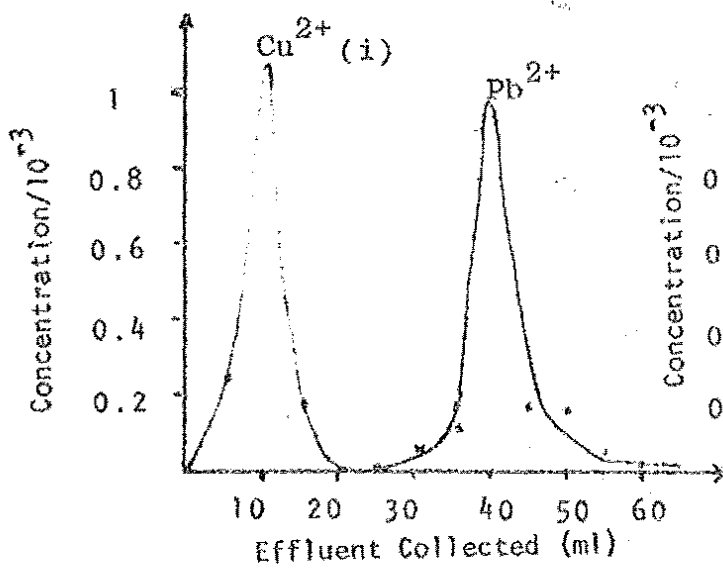
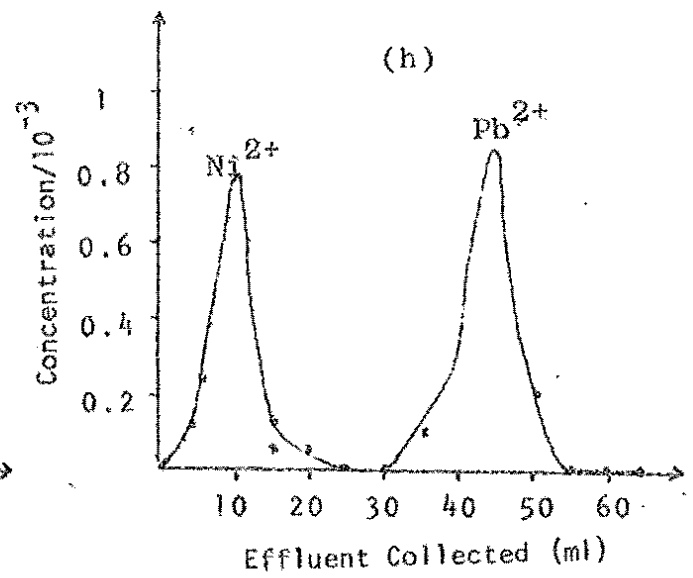
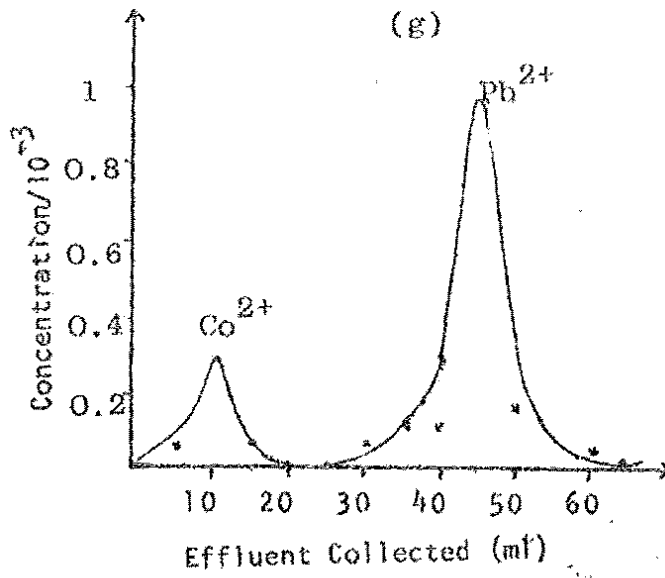
Fig. 6: p^H Titration Curve for Thorium Tellurite Sample No. 4 in the Presence of Salt,

Titrant: LiOH+LiCl, NaOH+NaCl, and KOH+KCl

Fig. 7: Separation of (a) Co(II), (b) Ni(II), (c) Cu(II), (d) Mn(II), (e) Cd(II) and (f) Zn(II) from Pb(II) on Zirconium Selenite Exchanger.



Separation of (g) Co(II) , (h) Ni(II) , (i) Cu(II) ,
 (j) Mn(II) , (k) Cd(II) and (l) Zn(II) from Pb(II)
 on Thorium Tellurite Exchanger.



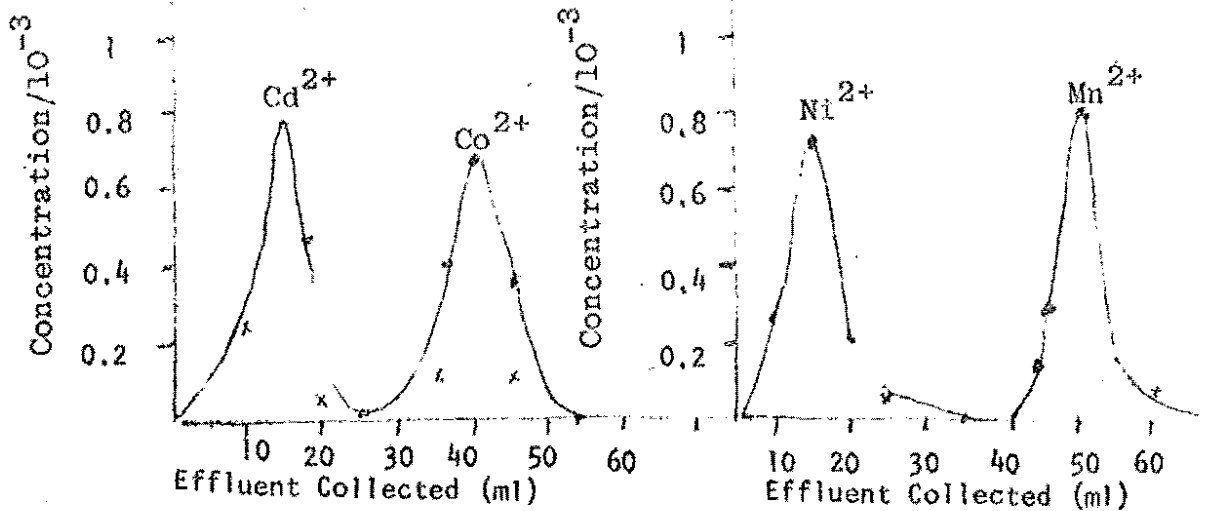


Fig. 10 Separation of Cd(II) from Co(II) and Ni(II) from Mn(II) on Thorium Tellurite Exchanger.

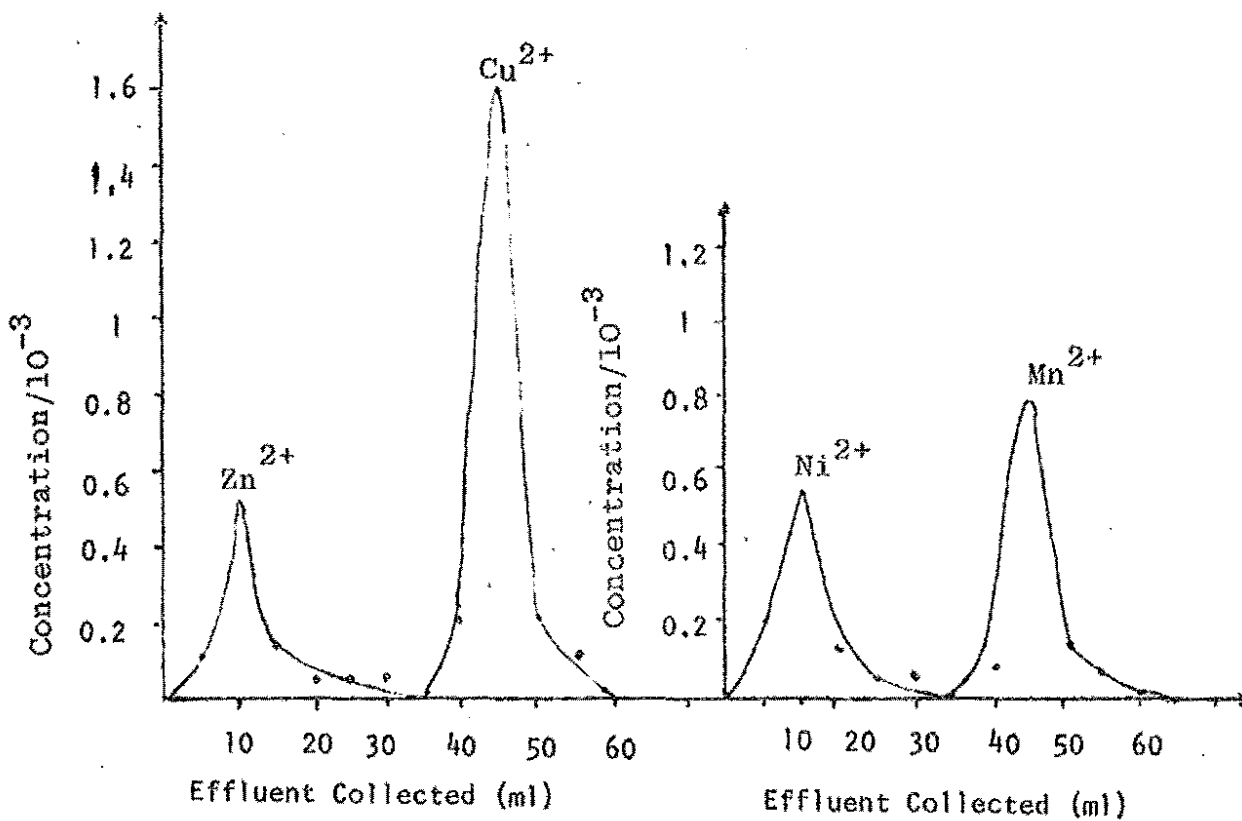


Fig. 9 Separation of Zn(II) from Cd(II) and Ni(II) from Mn(II) on Zirconium Selenite Exchanger.

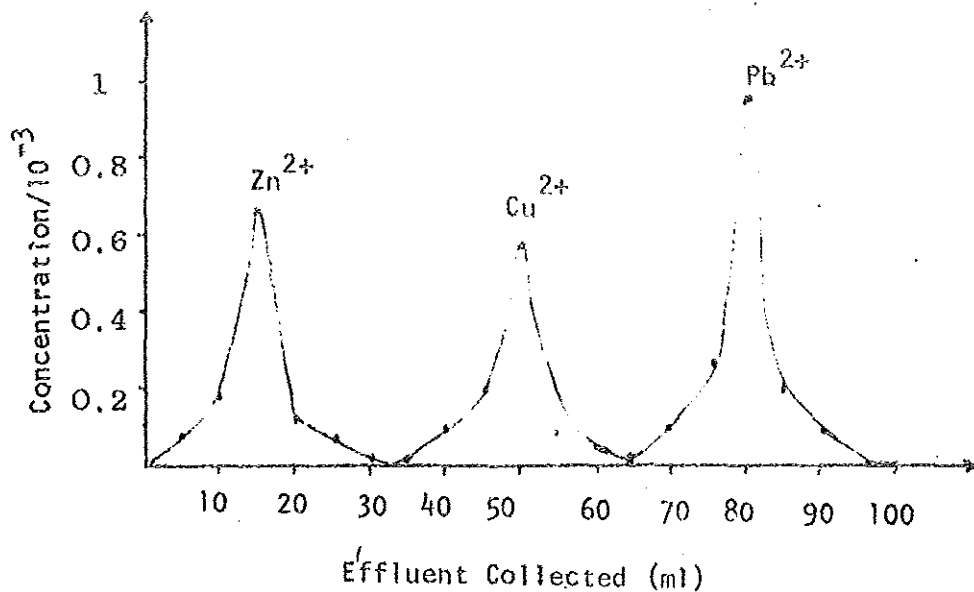


Fig. 12: Separation of Zn(II), Cu(II) and Pb(II) on Thorium Tellurite Exchanger

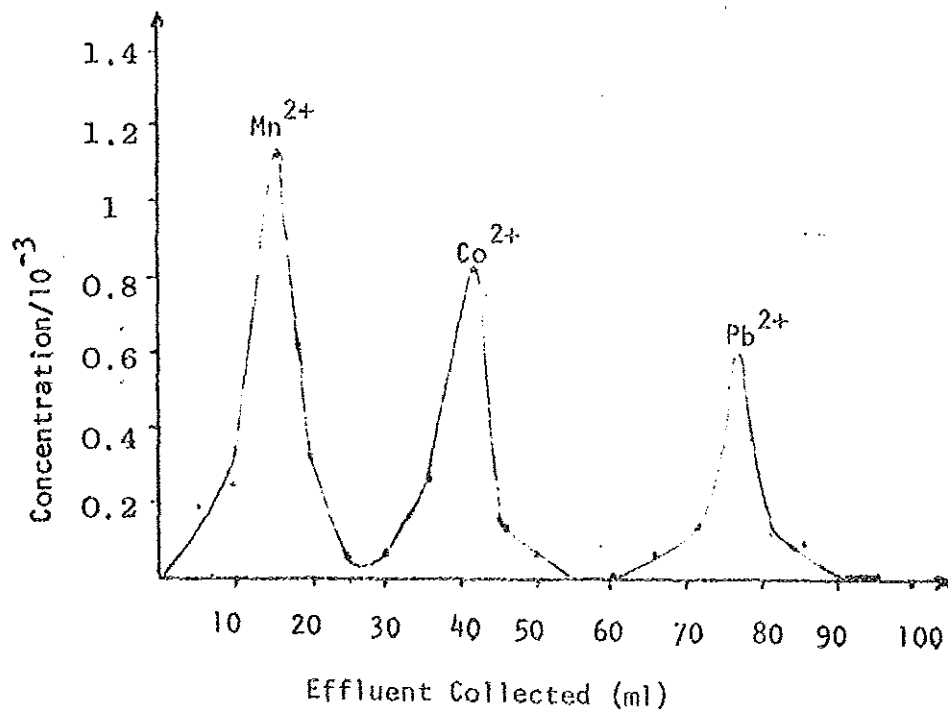


Fig. 11: Separation of Mn(II), Co(II) and Pb(II) on Zirconium Selenite Exchanger.

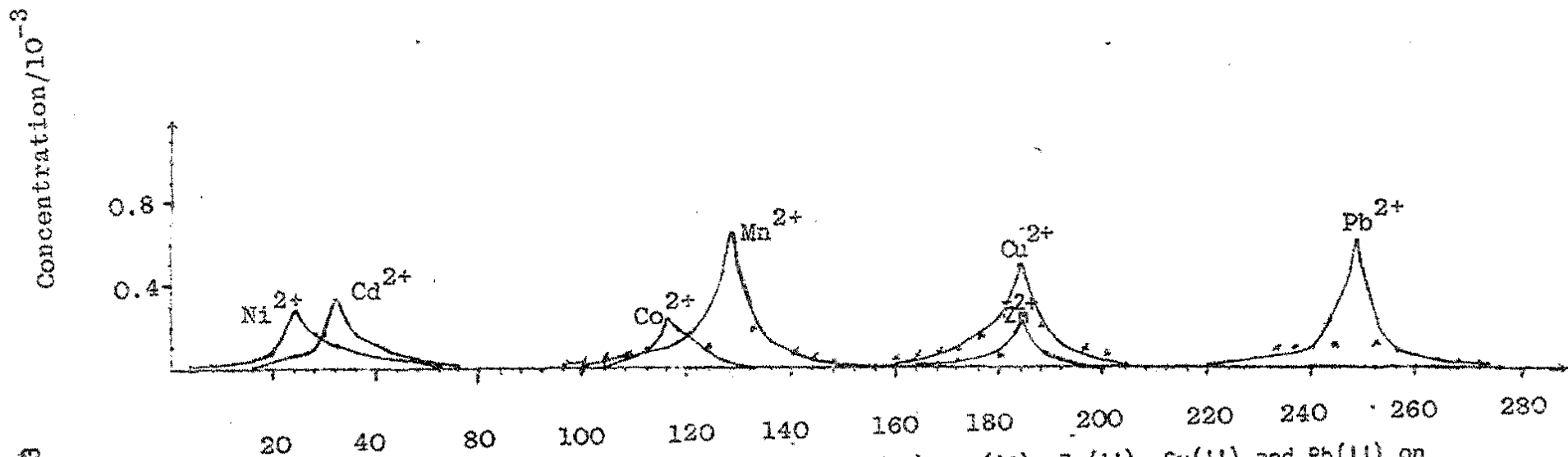


Fig. 14 Separation of Ni(II), Cd(II), Co(II), Mn(II), Zn(II), Zn(II), Cu(II) and Pb(II) on Thorium Tellurite Exchanger.

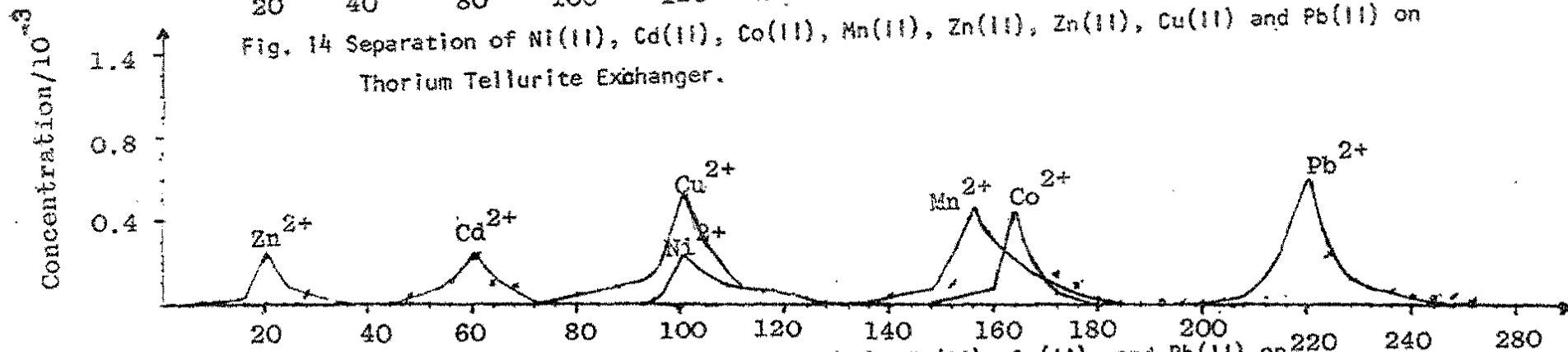


Fig. 15 Separation of Ni(II), Cd(II), Co(II), Mn(II), Zn(II), Cu(II), and Pb(II) on Zirconium Selenite Exchanger.

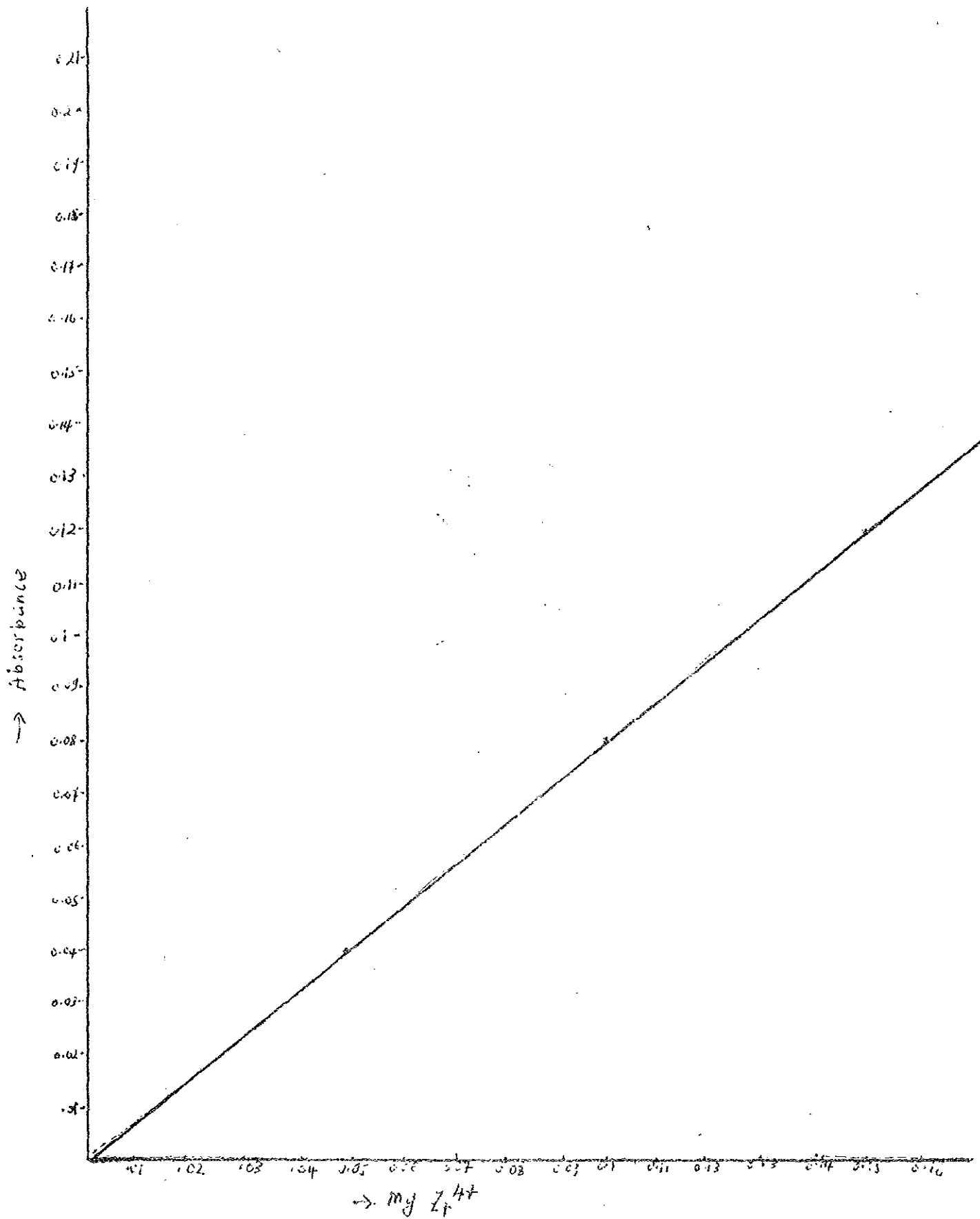


Fig. 15. Calibration Curve for Zirconium Determination

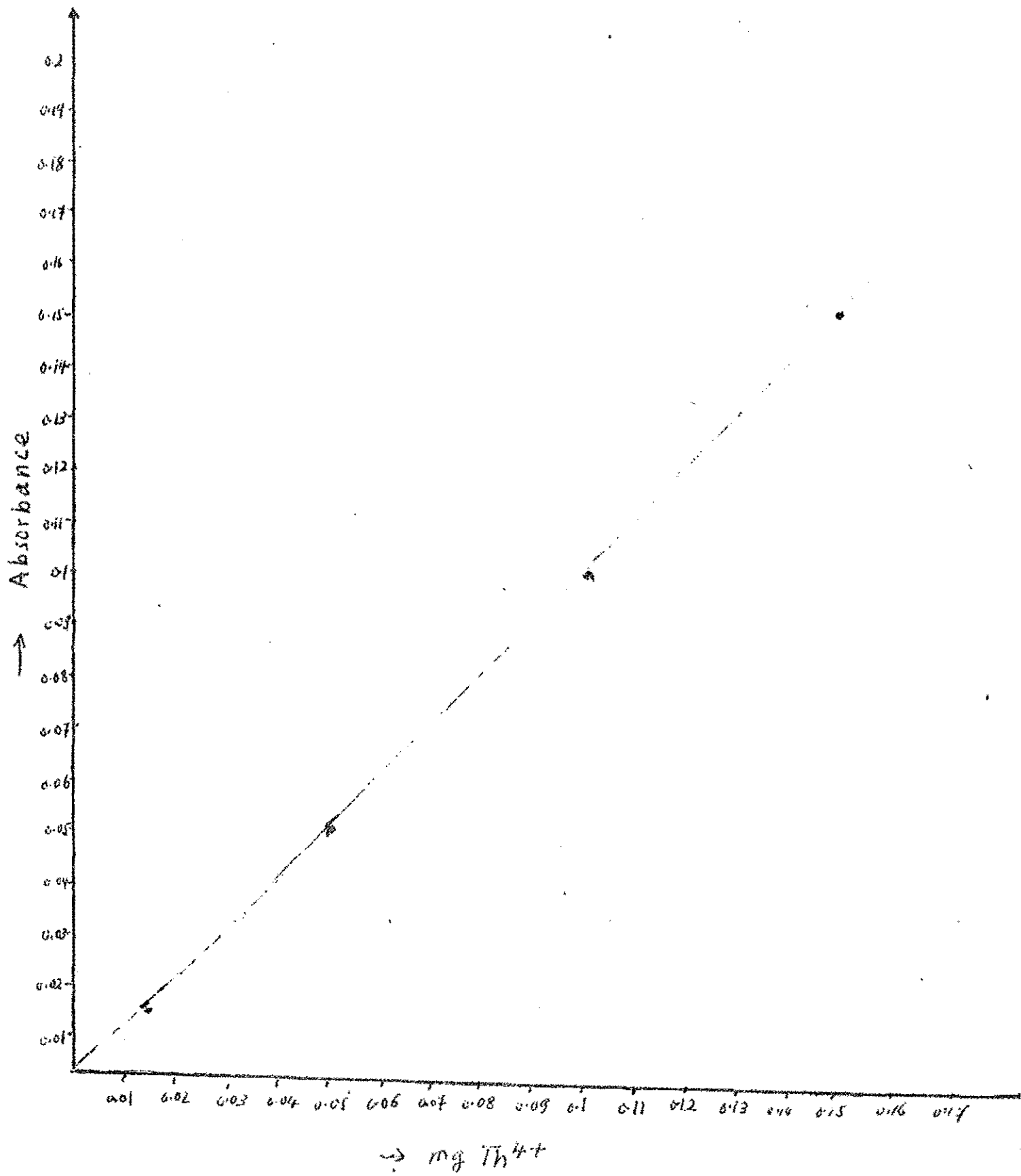


Fig. 16 Calibration Curve for Thorium Determination.

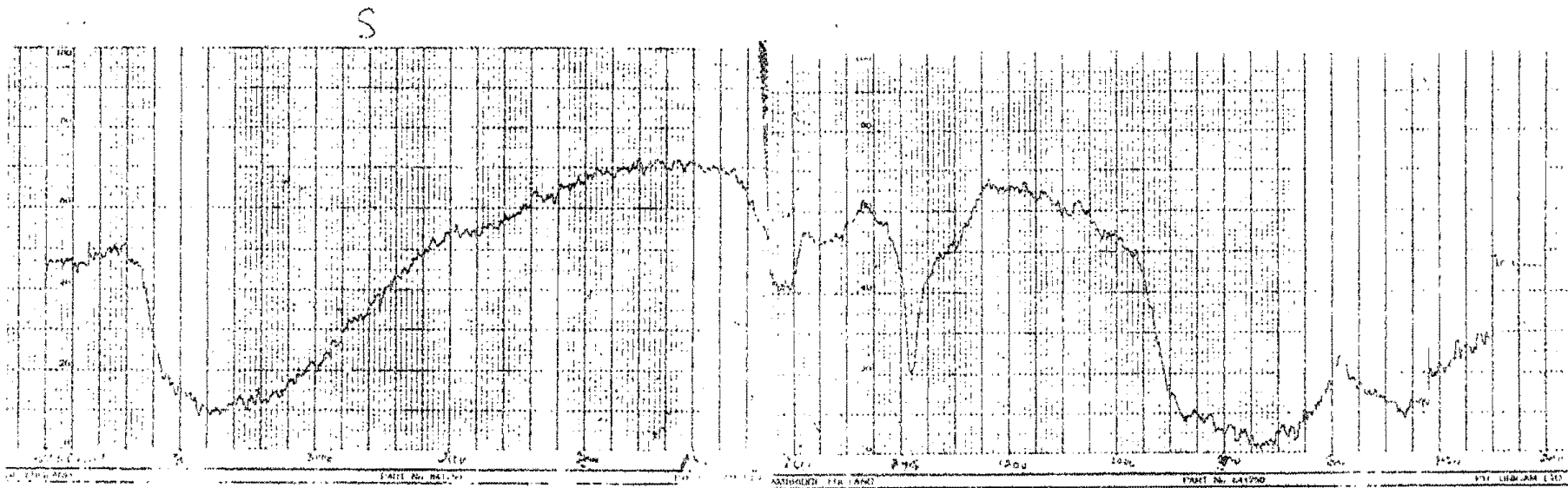


Fig. 17 Infrared Spectra of Zirconium Selenite (Sample No. 1)

Zr:Se = 0.50

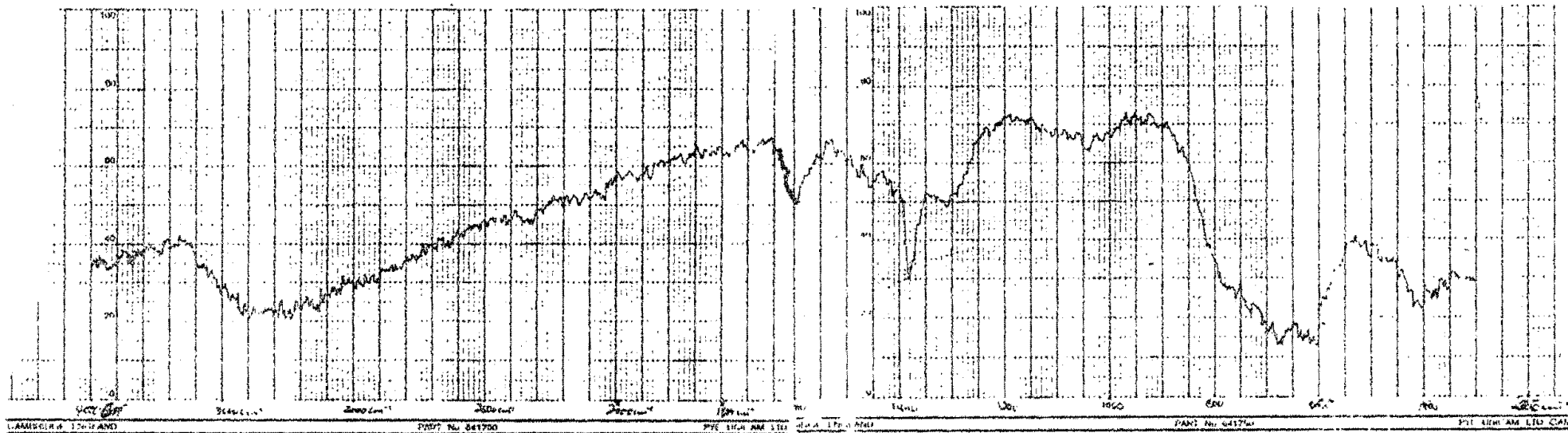


Fig. 18 Infrared Spectra of Thorium Tellurite (Sample No. 4)

Th: Te = 0.50

140H

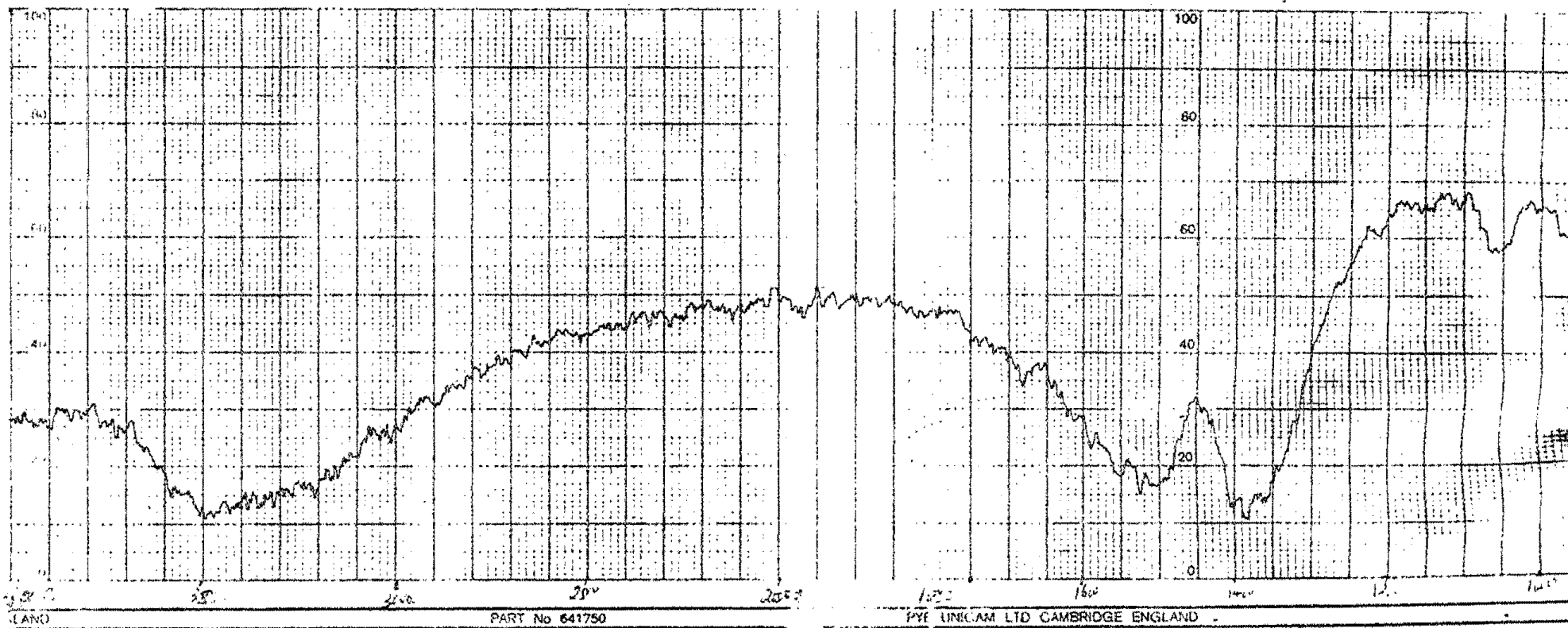


Fig. 20 Infrared Spectra of the Hydrolysis Product of Thorium.

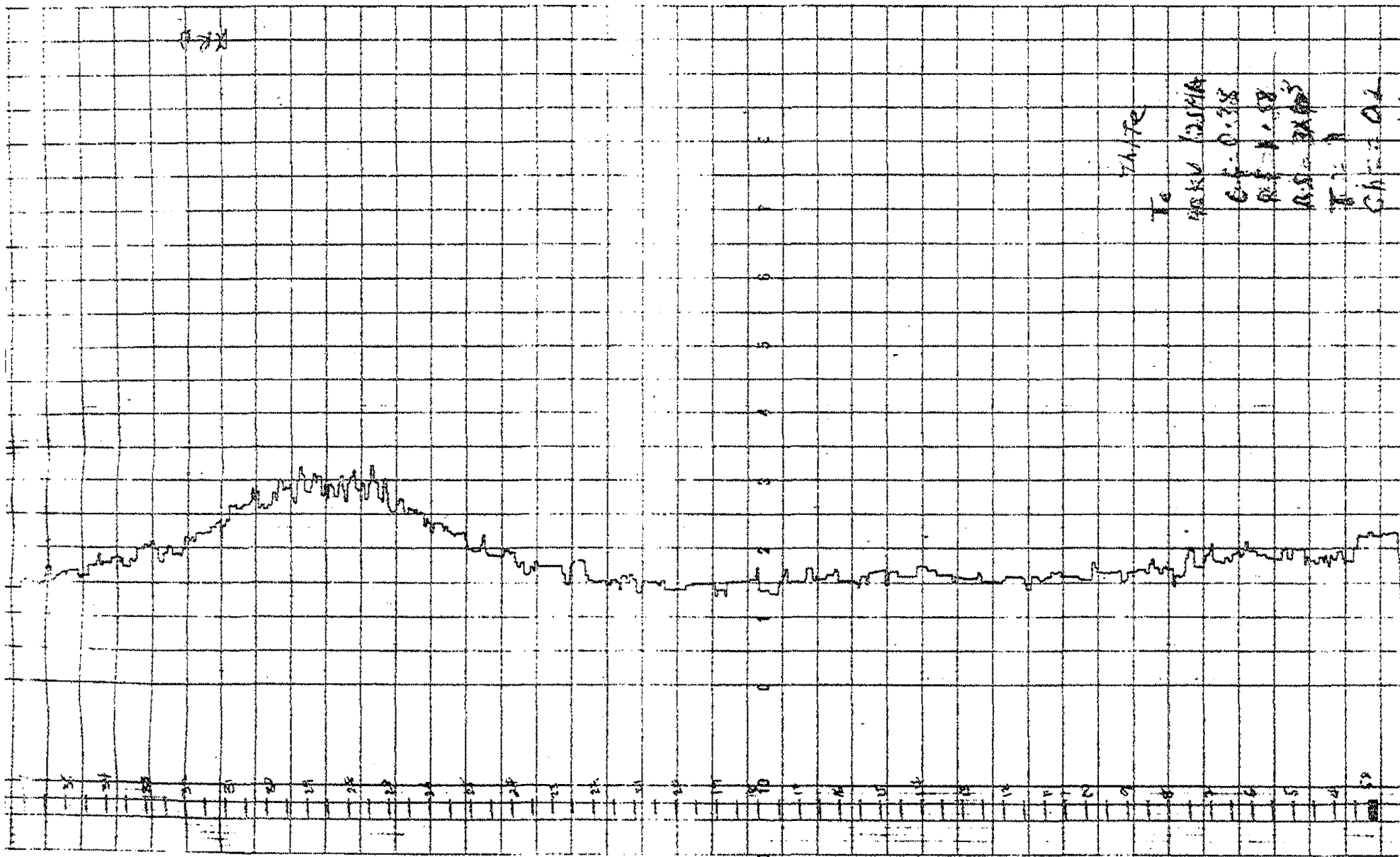


Fig. 22 X-Ray Diffractogram of Thorium Tellurite.