SYNTHESIS OF PYROPHOSPHATE AND SELENOPYROPHOSPHATE BASED CATION EXCHANGERS AND THEIR SELECTED APPLICATIONS

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Synthesis of Pyrophosphate and Selenopyrophosphate Based Cation Exchangers and their Selected Applications

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DEDICATION

To my father, Ato Kassa Ayane
To my mother,W/o Tsige Asfaw

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ABSTRACT

The synthesis of cerium(IV) pyrophosphate and cerium(IV) selenopyroposphate by mixing aqueous solution of tetrasodium pyrophosphate with cerium(IV) sulfate in 1 M sulfuric acid and tetrasodium pyrophosphate, sodium selenite with cerium(IV) sulfate, respectively, are reported. Elemental analyses showed that Ce: PO_4^{3-} ratio is 1:2 for cerium(IV) pyrophosphate and 0.47:1:0.03, Ce : PO_4^{3-} : SeO_3^{2-} for cerium(IV) selenopyrophosphate. IR spectra of both exchangers showed five peaks at frequencies Ca. 3400, 1600,1200,980,200-300 cm^{-1}, which are due to water and hydroxyl group, lattice water, phosphate group, P-O-P and Ce-O stretching vibrations, respectively. The hydrogen ion liberation capacities of cerium(IV) pyrophosphate and cerium(IV) selenopyrophosphate were found to be 1.40 and 1.15 meq/g respectively in neutral salt, and about 3 meq/g at pH 8 with ion uptake measurement. The chemical stability, pH titration, X-ray diffraction, and ion uptake have been studied. On the basis of distribution coefficient obtained at different pH for some metals column separation of this same metal ions was performed. The solid electrical conductivity of the exchangers was also determined.

1. INTRODUCTION

1.1. Importance Of Ion Exchangers

Ion exchange is now a well established separation technique. It has found application not only in water purification, the original major application, but also in analytical chemistry in such areas as in separation and isolation of new elements, in hydrometallurgy, and in many specialized fields related to the utilization of atomic energy (1).

Ion exchange was originally discovered to take place in soils by Thompson (2) and by Way and Roy (3). The active compounds were latter identified by Lamberg and Wiengner (4) to be clays, glauconite, zeolite, and humic acids. The first commercially available ion exchangers were amorphous aluminosilicate gels (permutites) (5,6). The instability toward acid solutions and variability of behaviour led chemists to seek alternatives. This search eventually led to the synthesis of organic ion exchange resins(7). Although resins have excellent ion exchange capacity, their chemical stability, uniformity, ease of controllability during synthesis, etc. (8), are severly limited when they are applied at high temperature, highly oxidizing media, or in the presence of ionising radiation.

Starting from 1956 (9) there has been increased interest in the production of chemically stable inorganic ion exchangers, which has advantage over ion exchange resins. The first known inorganic substances (zeolites) is useful in a limited range of pH (10). Inorganic ion exchangers would enable ion exchange to take place in an intense radiation. Besides, it is conceivable that in some cases a special peculiarity in comparison with the properties of organic resins may lead to improvements even under normal operating conditions. Thus, much attention has been given to the development of synthetic inorganic ion exchangers during the last decades. These materials are classified in to two groups; first, insoluble acid salts of tetravalent metals (11-17), and secondly, hydrated oxides having cation and anion exchange properties (18-22). Hydrous oxides are precipitate products of metals, which are soluble in common mineral acids (e.g. Zr(IV), Sn(IV), etc.), after treatment with base until precipitation is complete.

Insoluble acid salts in addition to their use as ion exchange materials in molten salts (23-26) and nuclear technology, have important practical applicaitons. The discovery that large cations can be taken up by ionic forms with large interlayer distance has opened new development. Analytical separation or concentration of these cation can be performed (33). Amorphous zirconium phosphate has been utilized in kidney machines for the removal of ammonium ions from blood (27). Owing

to the discontinuous phase transition during exchange, insoluble acid salts can also be employed as solid pH buffers, while their acid salt forms could be used to maintain constant ionic fraction of a pair of cations, such as Na^+ - K^+, in solution (33).

Furthermore, it is known that layered insoluble acid salts have catalytic activity. To date, only a few applicaitons of the catalytic activity of these are known. Kalman et al. (28) have successfully employed the copper form of the zirconium phosphate for the oxidation of CO to CO_2 and this has found wide application in the control of automobile pollution. Recently zirconium phosphate has been loaded with several transition metal ions, and these materials were found promising as catalysts (29,30). Zirconium phosphate has also been employed as a support for gas solid chromatography (31,32). Interesting separtions have been obtained by Allulli et al. (32) with the potassium form of zirconium phosphate.

Inorganic membranes consisting of insoluble acid salts are interesting from both a fundamental and a potential point of view (34,35). Owing to their stability, these membranes have found applications in particular processes in which organic membranes can not be employed because of their high degradability (36). Some of the promising applications could be in fuel cells at high temprature or in the concentration of wastes containing fission products. Some acid salts with crystalline structures possess

interesting ion-sieve properties, e.g. thorium arsenate behaves as a very narrow ion sieve: its protons being exchanged only by anhydrous Li^+,: This interesting property has already been employed for the separation of Li^+ from other cations (37).

A crystalline form of cerium(IV) phosphate exhibiting a fibrous structure and a high ion exchange capacity has been obtained. The fibrous structure permits the preparation of sheets similar to cellulose paper (38). Such sheets have not been prepared with other inorganic exchangers up to now. Inorganic ion exchange sheets (cerium phosphate paper) have a number of features such as porosity, good mechanical and chemical stability, high ion exchange capacity and selectivity, which make them very attractive for chromatographic or electrophoretic studies of inorganic ions. This paper is selective for K^+, Cs^+ ,Rb^+, Ag^+, Tl^+, Fe^{2+}, Pb^{2+}. Furthermore, because of their stability up to 200°C, cerium phosphate papers can also be used for chromatographic studies in some fused salt systems. Many impregnated papers or thin layers of insoluble acid salts have been successuflly employed for several chromatographic separations of inorganic ions (39 - 42).

The need to obtain inorganic ion exchangers with good ion exchange property stimulated the preparation of pyrohosphate and selenopyrophosphate based cation exchangers, Ming, et al.(43), prepared stannic pyrophosphate, with ion exchange capacity of

2.69 meq/g, which is 2-3 times higher than that of other stannic based and phosphorus containing inorganic ion exchangers and ten times than that of stannic phosphate. The effect of ion exchange kinetics is good, and it is more thermally and chemically stable than stannic phosphate. The same authors (44) have prepared stannic selenopyrophosphate with exchange capacity of 2.29 (K^+ meq/g) . It was selective for Ag^+, Pb^{2+}, Sr^{2+}, Zr^{+4} and Bi^{3+}. Thus, due to their good character of pyrophosphate and selenopyrophosphate containing exchangers, we intended to prepare insoluble acid salts based on cerium(IV), selenite and pyrophosphate.

1.2. Objective Of The Present Work

i) To synthesize cerium(IV) pyrophosphate and cerium(IV) selenopyrophosphate.

ii) To explore their ion exchange behaviour and their application as cation exchangers.

2. LITERATURE REVIEW

2.1. Synthesis and Ion Exchange Properties of Cerium Based Ion Exchangers

Insoluble acid salts of tetravalent metals, which have ion exchange character, are prepared by direct mixing of the salt solution of given polyvalent metal ion with a polybasic acid. Elements of groups IV ,V, and VI of the periodic table, plus other ions of high charge, like Ce(IV) and U(VI) , that do not properly fall into these groups produce insoluble acid salts. The polybasic acids are derived from phosphoric acid (H_3PO_4), tellurites (TeO_3^{2-}), tungstates (WO_4^{2-}), arsenates (AsO_4^{3-}), arsenites, selenites (SeO_3^{2-}), molybdates (MoO_4^{2-}), vanadates (VO_3^-), etc. Insoulble acid salts of tetravalent metals have been known in the form of amorphous, crystalline semicrystalline, and fibrous material. Though amorphous salts are known for long and they were first to be synthesized, they are easily hydrolyzed. Therefore, starting from 1964 several insoluble acid salts of tetravatent metals were obtaind as crystalline compounds, which are found to be considerably more stable than the amorphous ones (33).

When a solution of the polybasic acid is mixed with a solution containing tetravalent metal a precipitate of the insoluble acid salt is formed, the compostion , degree of

crystallinity and structure of which is strongly dependent on experimental conditions (45) such as temperature, digestion time, polybasic acid/ tetravalent metal ratio in solution, rate and order of mixing, stirring, etc. Studies (46,47) indicate how widely the properties of an amorphous inorganic ion exchanger may change when the conditions of preparations are varied. The method of preparation has considerable effect on their composition and the degree of hydration. These two factors are responsible for the size and shape of the cavities inside the exchangers and its chemical stability (48).

Advantages and disadvantages of amorphous and crystalline exchangers are compared by Alberti (49) as follows. Crystalline materials, besides having a more definte compostion compare favourably with the corresponding amorphous ones as regards to thermal degradation and stability towards hydrolysis. Moreover, several crystalline exchangers exhibit good ion sieve properties and therefore they can be employed to carry out very good separations of inorganic ions of different crystalline radius. However, ion exchange studies with crystalline materials are complicated by the formation of new crystal phases and by hysteresis phenomena and therefore amorphous exchangers may be preferred for some particular uses.

The synthesis, effect of temprature, selectivity to different ions, preparation of different forms of ion-exchangers,

etc. of cerium(IV) ion containing insoluble acid salt with different polybasic acids will be presented, which were reported by various workers.

It's well known that many polybasic acid salts of cerium precipitate exhibit ion exchange properties. However, most of the work has been restricted to cerium(IV) phosphate and little experimental work has been reported on selenite, tellurite, arsenite, arsenate, etc. cerium(IV) phosphate compounds are amorphous, crystalline or fibrous, the amorphous having a greater tendency towards hydrolysis (45).

The effects of temperature digestion time PO_4/Ce ratio in solution and the order of mixing of the reactants on the composition and degree of crystallinity of cerium(IV) phosphate are reported (45). Four different cerium phosphate materials have been obtained : (1) amorphous cerium(IV) phosphate with PO_4/Ce = 1.7 (2) microcrystalline cerium(IV) phosphate with PO_4/Ce = 1.15, (3) microcrystallie cerium (IV) phosphate with PO_4/Ce = 1.55, and (4) fibrous crystalline cerium(IV) phosphate with PO_4/Ce =2. Preparative procedures and some ion exchange properties of these materials are reported and discussed. Fibrous cerium(IV) phosphate has been employed for the preparation of inorganic ion exchange papers or membranes containing no binder.

Rocco (50) investigated the ion exchange properties of cerium(IV) phosphate including rates of reaction, distribution coefficients of alkali metals, capacity and column behaviour of some elements . The compound has properties analogous to ,but not identical with zirconium phosphate. Cesium and barium were successfully separated on short column of cerium(IV) phosphate at room temprature. Rocco et al., (51) described the preparation of the H^+ and NH_4^+ forms of cerium(IV) phosphate. pH titration curves were determined for these ion exchange absorbents. The sodium capacity measured over pH range of 0.10 -11.7 increased over this range. The rate of realease of H^+ from cerium(IV) phosphate by NaCl, CsCl, $BaCl_2$, and $SrCl_2$ was determined; bivalent ions were more effective than monovalent. The distribution coefficients of Li^+, Na^+, K^+, Rb^+, and Cs^+ in HCl, $HClO_4$, and NH_4Cl were determined. The elution of sodium and cesium by increasing concentration of hydrochloric acid enabled a separation to be achieved, NH_4Cl elution from the NH_4^+ form of cerium(IV) phosphate was not effective. The elution of cesium and barium using NH_4Cl,HCl, and $HClO_4$ were also studied; good separation was achieved. Koening, et al., (52) prepared amorphous products with different composition by combining mineral acid solutions of Ce(IV) compounds and phosphoric acid. It display almost the sorption sequence for macro and tracer amounts ($Na^+ < Ag^+ < Cs^+$) (53).

When we see crystalline products of cerium(IV) phosphate, Koening, et al., (52) were able to produce crystalline precipitate $(Ce\text{-}O\text{-}Ce)(HPO_4)_8.H_2O$ by diluting hot Ce(IV) solutions in concentrated H_3PO_4. Where as crystalline phosphate sulfate will be produced in a sulfuric acid solution of Ce(IV) phosphate. Ion exchange properties of monovalent cations of crystalline forms of cerium phosphate were studied (53). In weak mineral acid solutions cerium(IV) phosphates of different origin exhibit variable sequence of sorption depending on structure. This is valid for Na, Cs, and Ag in traces as in macroamounts. Such crystalline cerium(IV) phophstes that are produced in a sulfuric acid medium are efficient cation exchangers. Towards macroamounts of the quoted elements they show the sequence $Cs^+ < Na^+ < Ag^+$, and towards trace amounts the sequence $Na^+ < Ag^+ < Cs^+$.

A microcrystalline cerium(IV) phosphate with formula $CeH_2P_2O_8$ 1.33 H_2O has been synthesized (54). The sodium uptake curve of amorphous and fibrous cerium(IV) phosphate shows that at pH 3 all three forms of CeP have about the same capacity for Na^+ ions, while in the pH range 3-7 microcrystalline cerium(IV) phosphate possesses a capacity which is higher than the amorphous but lower than the fibrous product. It has been characterized by its X-ray diffraction pattern that dehydration is accompained by a remarkable change in the structure of the exchanger. The chemical stability of microcrystalline cerium(IV) phosphate was evaluated by equilibrating 1.00g. of the samples with 200 ml of

soulutions of various mineral acids and in $HClO_4$. The stability of cerium in phosphate is very good.

Investigations were also carried out on crystal cerium(IV) phosphate in the Na^+, K^+, Li^+ and Cs^+ forms (55). The various salt forms were prepared according to the result obtained in ion uptake measurements. The water loss up to 150°C is about one mole of water of crystallization. The bands belonging to structural water decrease with increase in the alkali metal content. The stretching frequencies are characteristic of PO_4^{3-} groups , changing according to the ionic radii; i.e., samples with different alkali metal contents have different structures. Bhattacharyya (56) has prepared cerium(IV) phosphate by mixing cerium(IV) sulfate in hot H_3PO_4 at 80°C. It was hard granular variety which is suitable for column use (with Ce(IV) : PO_4^{3-} = 1:2).

Ion exchange behaviour of fibrous cerium(IV) phosphate, titration curves with alkali and alkali earth metal ions show that the ion exchange processes occur without phase transition (57). The exchanger displays a wide range of acidities like an amorphous or semicrystalline material. About 30 % of exchangeable protons are much more acidic than the others. In these sites, the exchanger prefers counter ions that have a large ionic radius, while several inversion occur at high metal loadings. Furthermore, the shapes of the Na^+/K^+ and Na^+/Cs^+ isotherms also

indicate that there are about 30 % of sites where the counter ion that have the largest ionic radius are preferred. Separation factors and distribution coefficient values for various cations at different concentrations were determined and a marked selectivity for Pb^{2+}, Ag^{+}, Ba^{2+} and Tl^{+} was found. The selectivity for Pb^{2+} was investigated for the full range of composition of the exchanger and the H^{+}/Pb^{2+} isotherm was obtained. The batch analytical separtion of Ca^{2+} /Pb^{2+} at low pH values showed that Pb^{2+} is selectively exchanged even in the presence of large amounts of Ca^{2+}.

A crystalline form of cerium(IV) phosphate exhibiting a fibrous structure and a high ion exchange capacity has been obtained (41). Cerium phosphate paper was prepared from the slurry . The paper can be solubilized by some strong complexing agents of cerium(IV) such as concentrated H_2SO_4 and Ce(IV) phosphate can be reduced to Ce(III) phosphate by strong reducing agents and $HClO_4$ has been employed as eluent. It was concluded that cellulose - CeP paper, R_F values are generally higher than on pure CeP paper. Cellulose - CeP paper can be employed if fast separations are required. However, in some cases long tails are obtained. This can be understood taking into account that when the rate of the ion exchange processes is slow with regard to the rate of the chromatographic development a state of equilibrium can not be reached. Thus in cellulose - CeP paper the longer tails are due to the higher rate of the chromatographic process.

The high selectivity of CeP paper for K^+, Cs^+, Rb^+, Ag^+, Tl^+, Fe^{2+} and Pb^{2+} must be emphasized the considerable differences in some Rf values indicate that it is possible to carry out several separation of inorganic ions.

Besides, cerium(IV) phosphate applicaiton as a chromatographic paper and Inorganic ion exchange membranes were carried out using $Ce(HPO_4)_2$, $Ce(HAsO_4)_2$; amorphous, fibrous and crystalline exchangers and poly (vinylidene fluoride) as a binder (34).

The inorganic cation exchange are constituted by acid phosphates or arsenates of tetravalent metals in solid solutions with each other or with part of the phosphate or arsenate groups substituted by phosphite groups (58). The cation exchangers containing phosphite groups are prepared by reacting a compound of tetravalent metal and with one of the following pairs of acids: phosphoric-phosphorous and arsenic-phosphorous in aqueous phase crystallization was obtained by boiling under reflux or by heating in an autoclave at < 300°C, and also by conducting the reaction in the presence of a complexing agent for the tetravalent metal.

Inorganic exchangers other than phosphoric acid containing Ce(IV) have been reported. $Ce(HAsO_4)_2.2H_2O$ is obtained as a yellow microcrystalline powder and is very stable to hydrolysis

(59) . Its ion exchange capacity for Li^+ and Na^+ is 4.35 meq/g, while larger ions such as K^+ and Cs^+ are partially excluded. Ion exchange properties and structure modificaiton during dehydration and salt conversion processes are also examined, and discussed. The salt forms of the exchanger do not loose water between 120°C and 500°C. X-ray diffraction patterns of the samples dried at various tempratures show that the first interplanar distance of cerium arsenate dihydrate (10.1A) is reduced to 9.1 and 7.7 A respectively for the monohydrate and the anhydrous product.

Investigations on crystalline cerium arsenate and its alkali metal forms was also studied by Kornyei et al. (60). The ion exchanger properties of ceric arsenate hydrate $Ce(HAsO_4)_2.2H_2O$ with interlayer distance of 1.015 nm, and its exchanged alkali forms were studied by using dead point titration. The ceric arsenate can be fully saturated to total exchange capacity with lithium and sodium ions and partly with potassium, radon and cesium ions. The mechanism of water loss in the exchange process was studied. Investigations were carried out on crystal arsenate (55) in the Li, Na, K and Cs forms. The various salt forms were prepared according to the results obtained in ion uptake measurements. The water loss upto 150°C is ~1 mole of water of crystallization. Because of the water loss, the lattices shrunk, which can be followed by comparing the first interplaner distances. When the samples are heated, the band width decreases, giving a more definite band separation which in accordance with

x-ray data, indicates a higher degree of crystallinity. The change in crystalline structure was ascribed to the decrease in water content of the sample. The bands belonging to structural water decrease with increase in the alkali metal content. The stretching frequencies are characteristics of $HAsO_4^{2-}$ group ,which are changing according to the ionic radii,i.e.,samples with different alkali metals have different structures.

Studies on the synthesis and ion exchange properties, and composition of cerium arsenite (61) have been carried out. This exchanger is stable in water, ethanol, acetic acid, sulfuric acid (2 M) and nitric acid (1 M) and in solutions of lithium chloride, magnesium chloride, calcium chloride, and barium chloride. It retains about 50% of its exchange value after drying at 100°C . It can be regenerated twice with out any appreciable decrease in exchange capacity. The empirical formula proposed is the $CeO_2As_2O_3.5H_2O$, Ce: arsenite ratio was calulated from titrimetric and gravimetric analyses. Ce(IV) arsenite shows high affinity for Pb^{2+}, Hg^{2+}, Sn^{2+}, Bi^{3+}, Ca^{2+}, Th^{4+}. The binary separations ranging from 98 to 100% have been achieved on cerium(IV) arsenite columns. The uptake of these ions is not a simple exchange but rather a process involving the introduction of ions into the matrix of the sorbent. And it was assumed that adsorption and ion-sieve besides ion exchange are responsible for the high uptake of these elements.

A cloumn of ceric tungstate (62) was prepared by mixing cerium(IV) sulfate in 2 N sulfuric acid and aqueous solution of sodium tungstate in 1:1 molar ratio.The uptake of a few polyvalent ions such as Ca^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, UO^{2+}, Cr^{3+}, Y^{3+}, Nd^{3+}, Sm^{3+}, Tb^{3+},Tm^{3+}, Yb^{3+}, Lu^{3+}, Zr^{4+}, Hf^{4+} ,Sn^{4+}, Nb^{5+}, Se^{6+}, Mo^{6+}, and W^{6+} at a very small concentrations was studied.

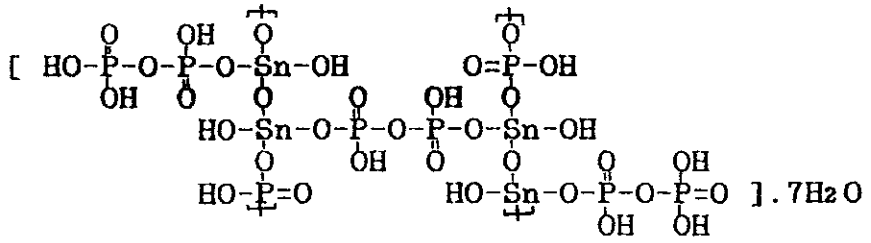
Amorphous (non crystalline or glassy) samples of a new inorganic ion exchanger, Ce(IV) selenite (48), have been prepared under varying conditions. The material prepared in a 1:1 ratio was studied in detail, because it shows good ion exchange capacity and is stable in water and in dilute mineral acids. It has been studied for its IR, thermogravimetry, and distribution coefficient values in water. On the basis of Kd values, binary separations of Cu^{2+} from Zn^{2+} and Mn^{2+}; Co^{2+} from Mn^{2+}, and that of Th^{4+} from Cr^{3+}, have been achieved. Cerium(IV) selenite may prove more useful when used in different solvent media, where the presence of these solvent media for various cations will be pronounced due to enhanced selectivity. Cerium(IV) tellurite(s) (63) have been prepared as a new inorganic cation exchanger by mixing solutions of Ce(IV) ammonium sulfate and tellurous acid of different concentration at different pH values.The ion exchange capacity of the sample at pH 6 is 0.90 meq/g (dry) for Na^{+} ions. The chemical composition, thermal and chemical stability, pH titration, infrared spectroscopy, thermogravimetry, DTA were also

performed. It was also found that cerium(IV) tellurite is chemically more stable than chromium tellurite.

In addition hydrous oxides of cerium was also obtained as ion exchangers. Rocco (50) concluded that ceric oxide possesses anion exchange properties in acidic solution and cation exchange properties in basic solution. The compound has properties analogous to, but not identical with, zirconium oxide. it was also described (51) that the preparation of the H^+ forms of ceric oxide. pH titration curves were determined for this ion exchange adsorbent. De, et al. (64) prepared ion exchangers of $CeO_2.2.58H_2O$ (cryst.) to $CeO_2.3.OH_2O$ (amorphous) and pH titration curves obtained by using alkali. Ion exchange capacities follow the sequence: $Li^+ < Na^+ < K^+ < NH_4^+$, and capacity increases with pH. Distribution coeffcients were determined at pH 6-8.

Concerning compounds containing pyrophosphate, two inorganic ion exchangers, (44) stannic pyrophosphate(I) and stannic selenopyrophosphate(II) were prepared. The mixing ratio of stannic and pyrophosphate was 1:2 and the mixing ratio of stannic, selenium and pyrophosphate was 1:1:1; the pH of the mixtures were 1.5 and 1.0 respectively. The ion exchange capacities of I and II were 2.69 and 2.29 (K^+ meq/g), respectively. I was very stable in HNO_3, H_2SO_4, $HClO_4$, HCOOH tartaric acid, citric acid, and some salt solutions. I had very

high affinity for Zr^{4+}, Th^{4+}, La^{3+} , Y^{3+}, Bi^{3+} and II was selective for Ag^{+}, Pb^{2+}, Sr^{2+} , Zr^{4+} ,and Bi^{3+} .The separations **of binary systems, Th^{4+}- Sc^{3+}, La^{3+} - Sc^{3+}, Zr^{4+} - trivalent** rare earth elements were achieved by using I column. Recoveries were upto 97.3% for Zr (1 mg) and 92.7% for rare earth elements (1-10 ug), respectively, structures and chemical formulas were given for I and II respectively.



(I)

$$[(15\ SnO.8\ OH).10\ H_2P_2O_7.2\ HSeO_3]_n.5n\ H_2O \qquad \text{(II)}$$

3. EXPERIMENTAL

3.1. General

3.1.1. Apparatus

IR Spectra in the region of 4000-200cm^{-1} were recorded on a Pye Unicam and Perkin-Elmer 727B IR-Spectrophotometer as KBr disc. UV - Vis spectra were recorded on a Beckman DU-65 spectrophotometer. The concentration of alkali and heavy metals were measured by using a Varian Specter AA20 Atomic Absorption Spectrophotmeter. Resonance lines 553.5, 223.1, 422.7, 228.8, 240.7, 324.8, 766.5, 670.8, 285.2, 589.0, 232.0, 217.0, 213.9 nms were used for Ba^{2+}, Bi^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, K^{+}, Li^{+}, Mg^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Zn^{2+} respectively with acetylene flame. pH measurments were made with WTW Bedienumgsanleitung pH 523. A GFL mbH D 3006 Burgwedel Type 3020 orbital shaker was used for the whole shaking purpose. Heating at 110°C was made with TS 110 oven (GDR)and Electro-Type-LM-112-10 furnance was used in the range 110 to 600°C. X-ray measurments were made with Rigakugeiger Flex (Japan) Difractometer using CuK_{α} radiation.

3.1.2.Reagents

Sodium selenite (Sigma), tetrasodium pyrophosphate of Analar grade (BDH, Poole, GB) and cerium(IV) sulfate (Hopkins and

Williams) were used for the synthesis of the exchangers $Bi(NO_3)_3.5H_2O$, $BaCl_2.2H_2O$, $Zn(NO_3)_2$, $(NH_4)_6Mo_7O_{24}.4H_2O$, NH_4VO_3, $Ni(NO_3)_2.6H_2O$, NaOH, $Pb(NO_3)_2$, $Cd(NO_3)_2.4H_2O$, $Cu(NO_3)_2.3H_2O$, Mohr's salt AR, acetic acid, sulfuric acid (BDH Poole, GB); $Co(NO_3)_2.6H_2O$, $MgCl_2.6H_2O$ (Hopkins); $NaNO_3$ (George Meker), HCl, HNO_3 (Riedel de Haen) NH_3 AR reagent (BioLab); $HClO_4$ (Merk) were also used.

Cerium(IV)sulfate, 0.1 M, was prepared by dissolving in 1 M H_2SO_4. Aqueous 0.1 M sodium pyrophosphate solution was prepared by dissolving $Na_4P_2O_7.10H_2O$, while sodium selenite 0.1 M , solution was prepared from Na_2SeO_3 in water.

3.2. Synthesis

3.2.1. Cerium pyrophosphate

The exchanger with cerium(IV) pyrophosphate mixing ratio of 1:2 was prepared by adding 0.1 M sodium pyrophosphate (100 ml) dropwise from a burette into a flask containing 50 ml solution of 0.1 M cerium(IV) sulfate with constant stirring at room temprature (20°C). The precipitate so obtained was kept for twelve hours, filtered and washed with distilled water until it was free from sulfate ion and to pH 4, dried at 50°C for 3 days. The material was ground and sieved to 72 - 150 mesh, soaked in

1 M HNO_3 overnight , washed with distilled water and dried again at 50°C and kept over Phosphorous pentoxide. Three different samples (1:2, 2:1, 1:1) were prepared similarly by changing the mixing mole ratio of cerium(IV) : pyrophosphate. The molar mixing ratio are given in Table 1.

3.2.2. Cerium(IV) selenopyrophosphate

The exchanger with cerium(IV) : selenite : pyrophosphate mixing ratio of 1:1:2 was obtained first by mixing thoroughly tetrasodium pyrophosphate solution with sodium selenite (0.1 M) with constant stirring. The mixture obtained was added with constant flow from a burette into a flask containing 50 ml solution of cerium(IV) sulfate (0.1 M) with constant vigorous stirring at room temperature(20°C). The precipitate so obtained was kept for 12 hours, filtered and washed with distilled water until it was free from sulfate ion and to pH of 4, dried at 50°C for 3 days. The sample was ground and sieved to 72 - 150 mesh, soaked in 1 M HNO_3 overnight, washed with distilled water and dried again at 50°C. It was kept over phosphorus pentoxide. Three different samples (1:1:1, 1:2:2, 1:1:2) were prepared similarly by changing the mixing mole ratio of cerium: selenite: pyrophosphate. The molar mixing ratio are given in Table 1.

3.3. Ion-Exchange Capacity

The ion-exchange capacity of cerium pyrophosphate and cerium selenophyrophosphate was determined by batch operation as follows (65). A 50-ml volume of 1 M sodium chloride solution was shaken with 100 mg of exchanger for 12 hours continuously. After equilibration a 10 ml portions of aliquot were taken and titrated with standard alkali solution using phenolphtalein as indicator. The effect of the concentration of neutral salt solution on the exchange capacity in batch operation is shown in Figs 3. and 4. The results obtained with the use of 1 M sodium chloride solution are reported in Table 1.

3.4. Ion Uptake Curves

Ion uptake curves were obtained by equilibrating cerium(IV) selenopyrophoshpate or cerium(IV) pyrophosphate samples (50 mg) with 5 ml of 0.1 N (MCl + MOH) solutions (M = Na^+, K^+ , Li^+) After shaking for 5 days at 20°C with orbital shaker, the supernatant liquids were analyzed for the alkali metals with atomic absorption spectrophotometer.

3.5. pH - Titration Curves

A 5 - ml volume of solution containing different amounts of (MCl + MOH) ($M = Li^+$, Na^+ or K^+) keeping the metal ion concentration constant at 0.1 M, was added to 50 mg of the exchanger. After continuous shaking for five days at constant temperature (20±1°C) the pH was recorded.

3.6. Phosphate Release at Different pH Values

To measure the amount of phosphate released at different pH values, 50 mg of each of the exchangers were shaken for 5 days with sodium hydroxide and sodium chloride mixtures and the phosphate released was measured spectrophotometrically with vanadomolybdophosphoric acid using colorimetric method as follows (66).

Appropriate amount of the phosphate containing sample was placed in a 50 ml volumetric flask. 10 ml of vanadate-molybdate mixture reagent was added and diluted to the mark with distilled water. A blank was prepared in which a 35 ml distilled water substituted for the sample. Ten minutes after adding the vanadate-molybdate reagent, the transmittance of the sample versus the blank at a wavelength of 465 nm was measured. The concentration was obtained from the calibration curve.

3.7. Chemical Stability

To see the stability of the exchangers in several solvents, 50 mg of the exchanger was equilibrated with 10 ml volume of solvents for 18 - 20 hours with constant shaking. The phosphate released was measured spectrophotometrically as in section 3.6. While cerium was measured as follows (67) appropriate amount of the supernatant solution was taken into 50 ml volumetric flask and 2.5 ml of 10 % hydrogen peroxide was added. This was diluted to 50 ml with 1 N H_2SO_4. The blank was prepared by carrying out through the same procedure used for the sample. The Ce(III) concentration was read from a calibration curve prepared by taking known Ce(III) standards through the same procedural steps used for the samples.

3.8. Composition of Cerium(IV) pyrophosphate and Cerium(IV) selenopyrophosphate

In both of the exchangers, phosphate was determined spectrophotometrically after dissolving the exchangers in concentrated acids as in section 3.7. Selenium was determined (68) by dissolving 50 mg of the exchanger in 40 ml of cold HCl, (5 N) and diluted to 100 ml. 10 ml of a 25 % solution of hydroxylamine hydrochlochloric acid added and heated at 90°C for 4 hours. The precipitate was transferred to a tared Gooch

crucible, washed with water and then alcohol, dried at 100°C and weighed. Cerium was determined titrimetricaly (69). To the weighed amount of the exchangers sulfuric acid was added and boiled. To the cooled solution, excess ferrous ammonium sulfate standard salt solution was added, and the excess iron(II) salt was titrated with standard potassium permanganate to the first appearance of pink colour.

3.9. Distribution Coefficient Values Determination

50 mg of the exchanger equilibrated with 10 ml of 10^{-3} M of the salt of interest for 18 - 20 hours. And the concentration difference between the original and that of the equilibrated compared using the following relation

$$Kd = \frac{\text{Amount element in exchanger}}{\text{Amount of element in solution}} \times \frac{\text{ml of solution}}{\text{g. of exchanger}}$$

3.10. Thermal Treatment of the Exchanger

To see the effect of temperature on the weight loss, 1 g of each of the cerium(IV) pyrophosphate and cerium(IV) selenopyrophosphate was heated in a furnance at different temperatures starting at 110°C (for the same duration) and the mass loss was calculated based upon the original mass. The furnance accuracy

was ±5°C, and the exchangers were heated to a maximum of 600°C with an interval of 100°C.

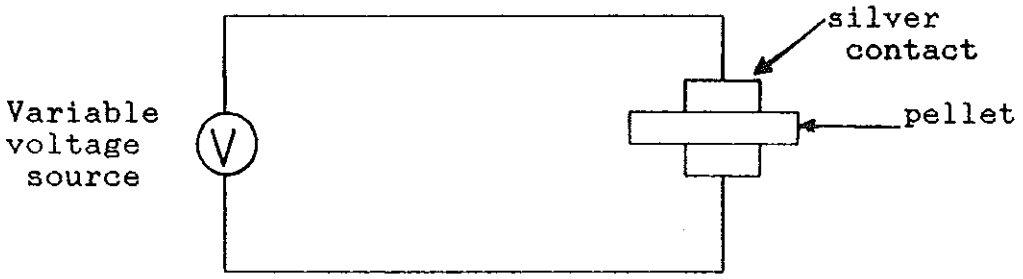
3.11. Column Operation

The ion exchange column was prepared as follows. A 250 mg of the exchanger in hydrogen form was taken into a glass column of internal diameter of 0.66 cm and height of 1.7 cm. Sufficient distilled water was added to allow thorough mixing to expel bubble. Glass-wool was used as a column support. Mixture of the metal ions was then applied and allowed to pass through the column with a slow rate. The metal ions absorbed on the exchanger were then eluted with suitable eluting reagent. The average flow rate of the effluent was 0.3 ml/min. The metal ions in fraction of the effluent were collected and determined by atomic absorption spectrophotometer. The results are summarized in Tables 6 and 7.

3.12. Electrical Beheviour

The conductivity of cerium(IV) pyrophosphate and cerium(IV) selenophyrophospahate and current voltage relation of the latter were measured by application of variable voltage as shown below. The exchangers pellet were prepared at a pressure of 7 Mpa

without any binder. Silver paste was used to make contact with the pellet.



4. RESULT AND DISCUSSION

4.1. IR Results and Composition

4.1.1. Cerium(IV) pyrophosphate

Studies (46, 47,) indicated that the properties of amorphous inorganic ion exchangers are dependent on the conditions of preparation. The method of preparation has a considerable effect on the degree of hydration and the composition of the sample. These factors are responsible for the shape and size of cavities inside the exchanger and chemical stability. Cerium(IV) pyrophosphate was prepared by mixing cerium(IV): pyrophosphate at 1:1, 1:2, 2:1, mole proportions (see Table 1A). The external texture of the three exchangers were the same, but the colour varied with the difference in the mixing ratio. Exchanger with high cerium ion proportion has a yellowish colour while with less cerium mixing ratio has light yellow colour. The preparation was arranged so as immediate precipitation of the compound to occur before hydrolysis in the media. It was observed that as the exchanger was washed repeatedly the amount of phosphate decreased. When the exchangers were tested for sulfate after drying, they have showed negative result. Elemental analysis showed that Ce : PO_4^{3-} ratio is 1 : 2 for cerium(IV) pyrophosphate (CP_3).

The infrared spectrum of cerium(IV) pyrophosphate showed four peaks at Ca. 3400, 1600, 1200 and 200-300 cm^{-1}. The strong broad peak at 3400 cm^{-1} is characteristics of interstitial water (or free) water and hydroxyl groups. The strong peak at 1600 cm^{-1} is due to the bending mode of interstitial water molecules. The peak at around 1200 cm^{-1} is due to the phosphate and the band between 200 - 300 cm^{-1} is assigned to Ce - O stretching vibrations (61). A band at 980 cm^{-1} is due to P-O-P structure (70), which is observed as one sharp peak in normal sodium pyrophosphate (cf Figs. 15, 16, 18). Besides, the peak around 1200 cm^{-1} (broad) is due to the ionic phosphate, and the multiple peaks at 1200 cm^{-1} indicate the formation of polymer (65).

4.1.2. Cerium(IV) selenopyrophosphate

Three proportions (1:1:1, 1:1:2, 1:2:2; Ce(IV) : SeO_3^{2-} : $P_2O_7^{4-}$) of the exchanger mixture were prepared as explained in the experimental (see Table 1B). Elemental analysis showed that Ce : PO_4^{3-} : SeO_3^{2-} ratio is 0.47 : 1 : 0.03 for CSP_2. The colour of ceriumn(IV) selenopyrophosphate was more yellowish than cerium(IV) pyrophosphate in all proportions. In the preparation of all of the samples, a well stirred mixture of sodium selenite and sodium pyrophosphate were added dropwise to the cerium(IV) ion in 1 M H_2SO_4 with constant stirring. The compound precipitated as soon as the pyrophosphate and selenite mixture fell into the cerium ion. This might reduce the possibility of

hydrolysis before precipitation. It is presumed that the presence of two anionc groups; i.e., pyrophosphate and selenite affects the selectivity of the ion exchanger towards certain metal ions (71), and stability towards chemical action.

The IR spectrum of the cerium(IV) selenopyrophosphate was almost similar to that of cerium(IV) pyrophosphate. The frequencies due to selenite overlap with that of phosphate group (see Figs. 14, 17).

Table 1. Synthesis and ion exchange properties of the exchangers

A. Cerium(IV) pyrophosphate

Sample	0.1 M $Ce(SO_4)_2.4H_2O$ ml added	0.1 M $Na_4P_2O_7.10H_2O$ ml added	Hydrogen ion libration capacity (meq/g)
CP_1	100	100	0.74
CP_2	200	100	0.84
CP_3	100	200	1.40

B. Cerium(IV) selenopyrophosphate

Sample	0.1 M $Ce(SO_4)_2$ $4H_2O$ ml added	0.1 M $Na_4P_2O_7.10H_2O$ ml added	0.1 M Na_2SeO_3 ml added	Hydrogen libration capacity (meq/g)
CSP_1	100	100	100	0.98
CSP_2	100	200	100	1.13
CSP_3	100	200	200	0.73

4.2. Ion Uptake Curves and Exchange Capacity

The curves which were obtained as pH versus milliequivalent of alkali metals were shown in Figs. 1 and 2. The major interest in these graphs was to obtain information on the ion-exchange properties of the exchangers in the whole range of pH and to see the point where maximum exchange occurs.

It was seen that the shape of the uptake curves and the maximum ion exchange capacity depend on the nature of the exchanging ion. At low pH values the exchanger prefered the ion with the larger crystalline radius; i.e., K^+ in both exchangers. The selectivity sequence of cerium(IV) selenopyrophosphate was $K^+ > Na^+ > Li^+$ until pH of about 6.5 , $K^+ > Li^+ > Na^+$ between 6.5 and 8.0 and $Li^+ > K^+ > Na^+$ above pH 8. The selectivity series of alkali metal ions on cerium(IV) pyrophosphate was found to follow the order $K^+ > Na^+ > Li^+$ to pH 8, above pH 8 the order was $Li^+ > Na^+ > K^+$, i.e., a complete reversal of selectivity. At the same time the maximum exchange capacity decreases as the crystalline radius of the alkali metal ion increases at higher pH. For the H-Li exchange maximum exchange has been obtained above pH 10, but precipitation of trilithium phosphate is likely to occur at this pH (54). Inversion in the selectivity sequence have been also found in other exchangers (54, 72).

Using a model, Torracca et al. (72) explained that amorphous zirconium arsenate, due to its disordered structure, exchanges 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 at first and the exchanger will prefer the counter ion with the smallest hydrated volume, since smaller and smaller cavities have to be involved as conversion proceeds, the affinity order will gradually change and the exchanger will finally prefer the ion with the smallest crystaline radius. This explanation is also true for what is observed with cerium(IV) pyrophosphate and cerium(IV) selenopyrophosphate.

The capacities determined by base titration are quite large in terms of milliequivalent per gram of solid, higher capacities can be realized if the solids are treated with more basic solutions or with anions which are more strongly adsorbed (1). Similarly, higher exchange capacities are observed in base titration for cerium(IV) pyrophosphate and cerium(IV) selenopyrophosphate samples, as shown in Figs. 1 and 2. The exchange capacity of cerium(IV) pyrophosphate increased from about 1.40 meq/g with batch experiments to about 3.0 meq/g in the ion uptake curve, while cerium(IV) selenopyrophosphate's increased from 1.12 meq/g to 2.80 meq/g at pH 8 with Na^+ ion. The exchange capacities

of the samples are shown in Table 1. The results also suggests that, exchange capacity increases as the amount of anionic group increase; i.e., pyrophosphate. This result is in agreement with other works which have demonstrated that the exchange capacity increases as the ratio of metal to anion incecreases (73, 74). Ion exchange capacity of CP_3 and CSP_2 with molarity of NaCl are shown in Figs. 3 and 4. Apparently the exchange proceeds rapidly in the beginning.

4.3. pH Titration Curves

The pH titration of both exchangers were performed in the presence of alkali metal chlorides. As it is observed from Figs. 5 and 6, the shape of the titration curves (MOH + MCl , M = Li^+, K^+, Na^+), exhibits a slight bending at about pH 3. These curves resemble those synthesized for cerium phosphate (45). The nature of the alkali ions affects the shape of the titration curves of both CSP_2 and CP_3 . This indicates the different affinity of the exchangers for the metals at different pH. It is not possible to derive the precise value of the exchange capacity of the exchangers with pH titration, because the hydroxide is consumed to release phosphate. It is for this reason the uptake of alkali metals at differnt pH values were measured to obtain the exchange capacity in Section 4.2.

4.4. Phosphate Release With pH Values

When the exchangers were equilibrated with 0.1 N (NaCl+NaOH) for five days, it was seen that the amount of phosphate ion released into the solution increases as pH increases. The hydrolysis of phosphate groups increases substantially at pH values higher than 7.6, see Figs. 7,8 . The hydrolysis at more alkaline pH lowers the phosphate content of the exchangers and therefore the alkali metal uptake.

4.5. Chemical Stability

In order to evaluate the stability of the exchangers against different solvents, the amount of phosphate and ceric ion dissolved in these media were determined by means of the method described in the experimental part. Solubility of both exchanger increases as the concentration of the acid or base increased and dissolve completely in concentrated acids (see Tables 2 and 3). The observed solubility in the various acids can be related to the complexing power of these acids towards the central metal, i.e., cerium (37). In H_2SO_4 the colour of the exchanger was yellow as compared to hydrochloric acid and nitric acid. It was observed to produce cloudy solution in bases especially as the concentration of the base increases. This might be due to the formation of cerium oxide. The exchangers are fairly unstable in 0.1 M sodium hydroxide solution than in acids of similar

concentration. It is apparent that phosphate ion selectively dissolved in the media's studied. It was also observed (Table 2) that the solubility of cerium(IV) selenopyrophosphate was lower than that of cerium(IV) pyrophosphate, which may be ascribed to the presence of two anionic groups in the former exchanger. The materials can be used in 0.05 N HNO_3 without suffering great deterioration.

Table 2. Chemical stability of cerium(IV) selenopyrophospate and cerium(IV) pyrophospahte

(equilibration time 26 hrs at 20±1 °C;
quantity of exchanger 50 mg;
volume of solvent 10 ml)

Solvent	Phosphate released (mg/10 ml)	
	CSP_2	CP_3
4 M acetic acid	1.51	1.64
0.1 N NH_3	8.12	8.23
0.05 N NaOH	9.05	10.37
0.1 N NaOH	11.43	14.1
6% $HClO_4$	1.73	1.88
0.5 M H_2SO_4	6.11	7.05
1 M H_2SO_4	7.79	9.20
1 M HCl	**2.19**	**2.48**
0.5 M HCl	1.84	2.15
0.5 M HNO_3	2.08	2.46
1 M HNO_3	**2.73**	**2.93**
2 M $NaNO_3$	1.17	1.19

Table 3. Chemical stability of cerium(IV) pyrophosphate and cerium(IV) selenopyrophosphate
(equilibration time 20 hours at 20±1°C;
quantity of exchanger 50 mg;
volume of sovent 25 ml)

Solvent	Cerium released (mg/25ml)	
	CSP_2	CP_3
1 M H_2SO_4	4.92	4.18
0.5 M H_2SO_4	3.09	3.08
1 M HCl	2.38	2.87
0.5 M HCl	1.56	2.31
H_2O	1.25	1.24
6% $HClO_4$	1.82	2.66
0.01 N NaOH	2.16	1.82
0.1 N NaOH	2.52	2.94
0.1 N NH_3	2.69	2.42
4 M acetic acid	1.93	2.24

4.6. Thermal Treatment

To see the effect of heat, both exchangers were subjected to heat starting from 110°C through 600°C (see Fig. 9) . The weight loss started at low temperature (110°C) and reaches to about 200°C. Above this temperature small change in weight has been observed. The weight loss up to ~ 200°C may be due to the loss of external water molecules. It has been observed that after heating the sample in the range of 165-180°C for 8 hours, the IR spectrum showed no change. When the temperature was increased above 200 °C the colour of the exchanger changed to white gradually. The ion exchange capacity of the exchangers was completely lost at 600 °C and the external texture also changed. The infrared spectrum taken after heating at temprature 600 °C, showed that the peak due to P-O-P stretching at 980 cm^{-1} further enhanced (see Fig. 19). This may be referred to the condensation of hydroxyl groups present in the exchangers. The broad peak at 3400 and 1600 was almost disappeared. The weight loss curve obtained for cerium (IV) pyrophosphate showed almost the same pattern of weight loss with that of cerium(IV) phosphate after irradiation with γ - rays (70).

4.7. Distribution Coefficient

The distrbution coefficients (K_d) for some important metal ions have been determined at different pH values. In 0.01 N HNO_3

the adsorption of metal ions on cerium(IV) selenopyrophospahate showed the following selectivity series Pb^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Cd^{2+} > Ni^{2+}, in H_2O the order become Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}, while at pH 6 it become Pb^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}. The selectivity series of metal ions on cerium(IV) pyrophosphate in 0.01 N HNO_3 was found to follow the order Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} ≈ Ni^{2+}, in H_2O the order was pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}, at pH 6 the order is Pb^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}. At low pH (0.1 N HNO_3) Bi^{3+} was adsorbed well as shown in Table 5. It has been observed that the concentration of nitric acid has effect on the adsorption ability of both exchangers. It was observed that the adsorption ability of almost all metal ions was very low in concentrated HNO_3 (0.1 N). The Kd values increases as the nitric acid concentration decreases in the medium. Distribution coefficients become almost negligible with an increased concentration of nitric acid for the metals determined. Table 5 shows that cerium(IV) pyrophosphate and cerium (IV) selenopyrophosphate have higher affinity for Pb^{2+} and both exchangers have almost the same selectivity except in 0.01 N HNO_3. This can be ascribed to their major common component; i.e., pyrophosphate. It was also seen that Co^{2+} selectivity increased in 0.01 N HNO_3 with cerium(IV) selenopyrophosphate, which may be due to the presence of selenite. Similar selectivity for cobalt was observed on Zirconium selenite (76). At all pH values, distribution coefficients are higher for lead than for other metals, and it is therefore

possible to separate this metal from the metals that have much lower distribution coefficients.

For a given series of comparable ions such as the alkali earth metal ions, the affinity of the exchange sites sometimes increases with decreasing radii of the hydrated ion (which is the reverse of the order of crystal radii) giving the following series of affinities $Ba^{2+} > Ca^{2+} > Mg^{2+}$ (65) . The data which shows the relationship adsorption and hydrated ionic radius is given below.

Table 4. Distribution coefficient values of alkaline earth metal ions

Metal Ion	Hydrated ionic radius (A^0)	Distribution coefficient (ml/g) CSP2	CP3
Mg^{2+}	7.00	20	5
Ca^{2+}	6.30	46.6	27.8
Ba^{2+}	5.90	275	200

CSP2 : cerium(IV) selepyrophosphate.

CP3 : Cerium(IV) pyrophosphate.

Exceptions to these tendencies are not rare; thorium arsenate for example, possesses interesting ion-sieve properties;

the protons being exchanged only by anhydrous Li^+ (37) . This type of behaviour was not observed by cerium(IV) pyrophosphate and cerium(IV) selenopyrophosphate.

The marked difference in behaviour towards transition metal ions is very difficult to explain without the knowledge of the structure of the exchangers. Unfortunately it is not possible to work out the structure of these exchangers, since these materials are obtained as amorphous powder.

Table 5. Distribution coefficients of some metal ions in ml/g
(Time of equilbration: 12 hrs,
10 ml equilibrated with 50 mg of exchanger,
average deviation: 10.9,
analysis : twice.)

Metal	0.01 N HNO_3		H_2O		pH 6		0.1 N HNO_3	
Ion	CSP_2	CP_3	CSP_2	CP_3	CSP_2	CP_3	CSP_2	CP_3
Ni^{2+}	3.7	0	20.2	13.25	141.9	121.2	-	-
Cd^{2+}	5.7	13.73	141.6	102.8	2766	2816.5	16.0	16.3
In^{2+}	12.9	6.25	96.5	91.1	2360	1933	0	0
Cu^{2+}	11.3	7.6	163	163.3	-	-	0	0
Pb^{2+}	1431.9	1622	2378	2641	5566	3685	86.9	99.3
Co^{2+}	8.8	0	32.5	33.75	370.7	243.2	0	0
Bi^{3+}	-	-	-	-	-	-	220.2	228.8

- => not determined

0 => distribution coefficient values are zero

4.8. Column Operaiton

The potentiality of exchange of cerium(IV) pyrophosphate and cerium(IV) selenopyrophosphate have been investigated for the separation of some metal ions based on the distribution coefficient values. Some quantitive separtions of lead from

other divalent transition metal has been achieved. From the elution curve, it seems possible to separate transition metals such as Cd^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, from lead. As shown in the Figs. 10a and 10b, the separation of each element was carried out by a stepwise elution techinique in which different concentrations of HNO_3 with $NaNO_3$ were used as eluent. Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} were eluted with 0.01 N HNO_3 , while lead was eluted with (1:1) mixture of 0.1 N HNO_3 and 2 M $NaNO_3$.

Although lead could be separated from other metal ions, a long tailing effect and low elution yields were observed, which was also a problem on SnO_2 column (74). Low yields (81 % recovery) see Tables 6 and 7 , were attributed to the strong retention of cations to the exchanger particle during the time between elution and feeding periods. This problem seen in separation of calcium from lead; overlapping of each fraction occured and separation was not complete. The absence of any colour change of the exchangers through out the process indicates that Ce(III) has probably not been formed.

The exchanger showed affinity for Bi^{3+}, it was tried to separate it from Ni^{2+} as showen in the elution curve Fig. 10 C. With a recovery of Bi^{3+} 70 % and Ni^{2+} 96 %. The separation of Pb^{2+} from triplicate mixture was tried, but it was not possible to separate the other two from each other since they have close distribution coefficient while Pb^{2+} was separated out see Fig. 10d. It is seen from Tables 6 & 7 that the recovery of the

transition metals are satisfactory. Therefore both exchangers can be utilized for the separation of lead from salt solutions of transition metals.

Table 6. Separation of lead from other metals on cerium(IV) pyrophosphate column

(average flow rate 0.3 ml/min,
diameter = 0.66 cm,
packed height 1.7 cm)

Mixture separated	Eluent	Taken (mg)	Found (mg)	Recovery* (%)	
1. Pb(II) and Cd(II)	0.01 M HNO_3	0.562	0.56	99.9	(Cd)
	2 M $NaNO_3$ + 0.1 M HNO_3	1.04	0.87	84	(Pb)
2. Pb(II) and Zn(II)	0.01 M HNO_3	0.46	0.45	98.9	(Zn)
	2 M $NaNO_3$ + 0.1 M HNO_3	1.036	0.85	82	(Pb)
3. Pb(II) and Cu(II)	0.01 M HNO_3	0.3	0.275	89	(Cu)
	2 M $NaNO_3$ + 0.1 M HNO_3	1.04	0.864	83	(Pb)
4. Pb(II) and Co(II)	0.01 M HNO_3	0.28	0.27	96.4	(Co)
	2 M $NaNO_3$ + 0.1 M HNO_3	1.036	0.88	85	(Pb)
5. Pb(II) and Ni(II)	0.01 M HNO_3	0.28	0.28	100	(Ni)
	2 M $NaNO_3$ + 0.1 M HNO_3	1.04	0.87	83	(Pb)

* deviation = 0.01 - 0.12,
Number of analysis = 2.

Table 7. Separation of lead from other metals on cerium(IV) selenopyrophosphate
(Average flow rate = 0.3 ml/min,
diameter = 0.66 cm,
Packed height = 1.7 cm)

Mixture separated	Elluent	Taken (mg)	Found (mg)	Recovery* (%)	
1. Pb(II) and Cd(II)	0.01 M HNO_3	0.52	0.51	98	(Cd)
	2 M $NaNO_3$ + 0.1 M HNO_3	1.04	0.88	83	(Pb)
2. Pb(II) and Zn(II)	0.01 M HNO_3	0.326	0.324	97	(Zn)
	2 M $NaNO_3$ + 0.1 M HNO_3	1.036	0.85	81	(Pb)
3. Pb(II) and Cu(II)	0.01 M HNO_3	0.3	0.26	86	(Cu)
	2 M $NaNO_3$ + 0.1 M HNO_3	1.04	0.89	85	(Pb)
4. Pb(II) and Co(II)	0.01 M HNO_3	0.28	0.26	93	(Co)
	2 M $NaNO_3$ + 0.1 M HNO_3	1.036	0.92	89	(Pb)
5. Pb(II) and Ni(II)	0.01 M HNO_3	0.28	0.28	100	(Ni)
	2 M $NaNO_3$ + 0.1 M HNO_3	1.04	0.896	86	(Pb)

* devation 0.01 - 0.10,
Number of analysis 2.

4.9. X - Ray Analysis

X- ray photographs of cerium(IV) selenopyrophosphate and cerium(IV) pyrophosphate dried at 50°C, using Nickel - filtered CuK_{α} radiation, show that they are all non crystalline. (Figs. 21 and 22).

4.10. Electrical Behaviour

A part from investigaions on the synthesis and ion exchange properties of the exchangers, conductivity of these materials have been studied. The study of electrical properties of these exchangers is of considerable significance for two major points of view: firstly, for the major functions of energy storage and transmition and of communicaiton; secondly, for the information such study can provide on the dynamic processes proceeding with in the solid and its surfaces and to develop understanding of those processes and their control for specific purposes (75).

Therefore, the present data might give some information on the exchangers property. It has been found that cerium(IV) selenopyrophosphate show a semiconductor behaviour due to selenium, while cerium(IV) pyrophosphate follows Ohm's law (Figs. 11 - 13). The conductivity of CSP_2 doubled as the voltage applied tripled, while CP_3 remained almost the same in the same range as CSP_2 (see table 8).

Table 8. Specific conductance of cerium(IV) pyrophosphate and cerium(IV) selenopyrophosphate in H^+ form

Exchange	Voltage	(Ω^{-1} cm^{-1})
CSP_2	20	1.5×10^{-6}
	60	3×10^{-6}
CP_3	20	30×10^{-6}
	60	36×10^{-6}

5. CONCLUSION

Cerium(IV) pyrophosphate and cerium(IV) selenopyrophosphate are found to be promising cation exchangers from studies of fundamental properties. The exchangers are found to be higly selective for lead and therefore, can be utilized for the separation of lead.

The electrical behaviour obtained for CSP_2 may help the renewed interest which has been driven by the potential use of such compounds in sensors, and other electrochemical properties.

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APPENDIX

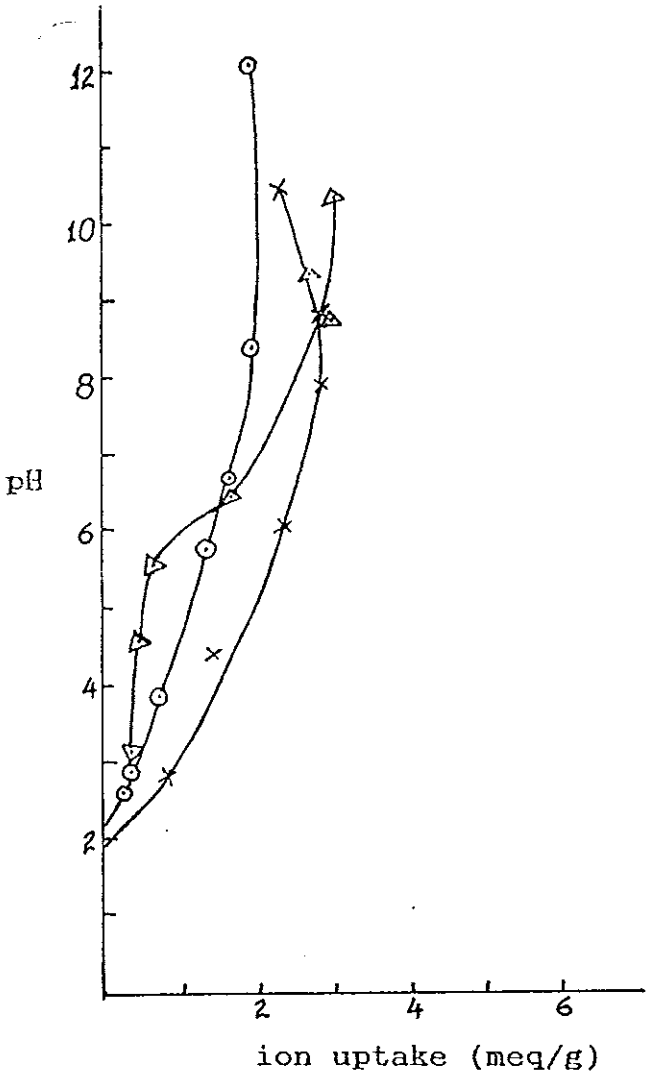


Fig. 1. Ion uptake of cerium(IV) selenopyrophosphate.

△ Li^+

× K^+

⊙ Na^+

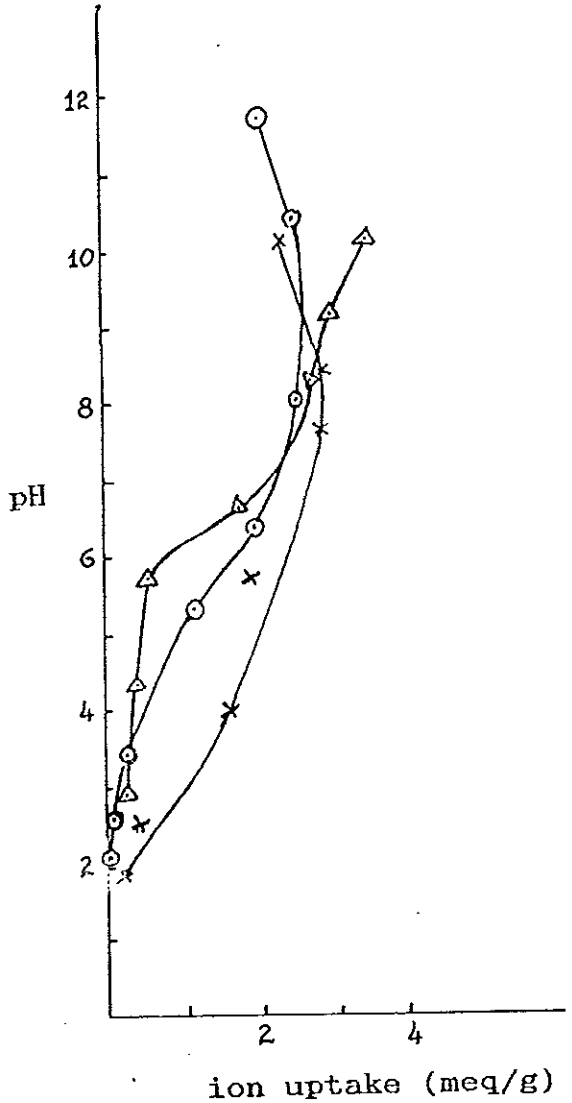


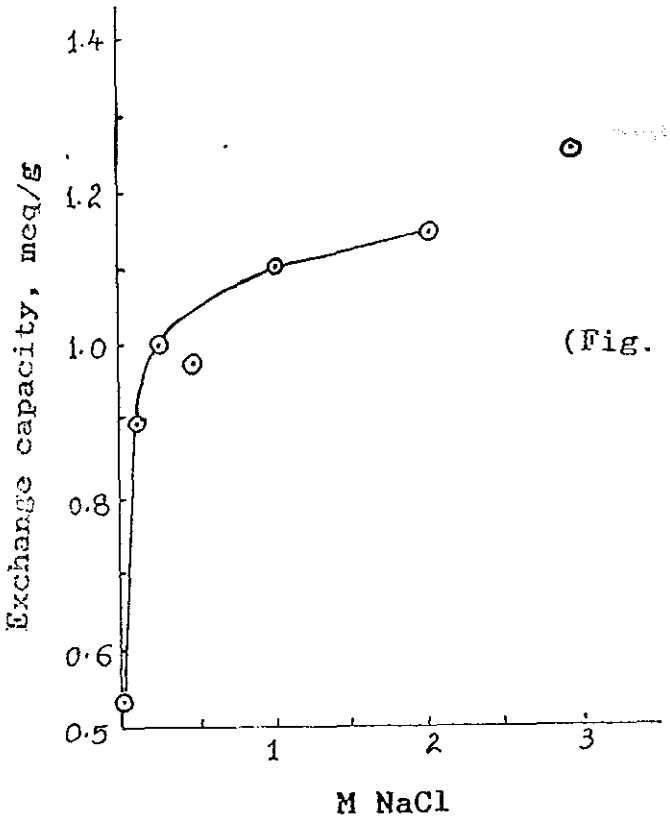
Fig. 2. Ion uptake of cerium(IV) pyrophosphate.

△ Li^+

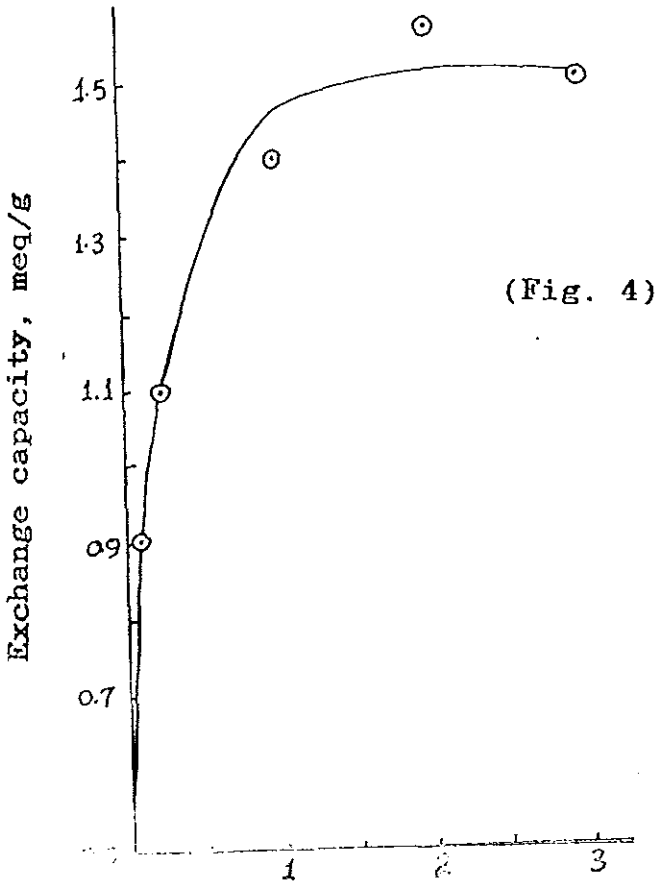
× K^+

⊙ Na^+

Fig. 3 & 4. Exchange capacity of cerinm(IV) selenopyrophosphate (Fig. 3) and cerium(IV) pyrophosphate (Fig. 4) as a function of concentration of Na^+ ions.



(Fig. 3)



(Fig. 4)

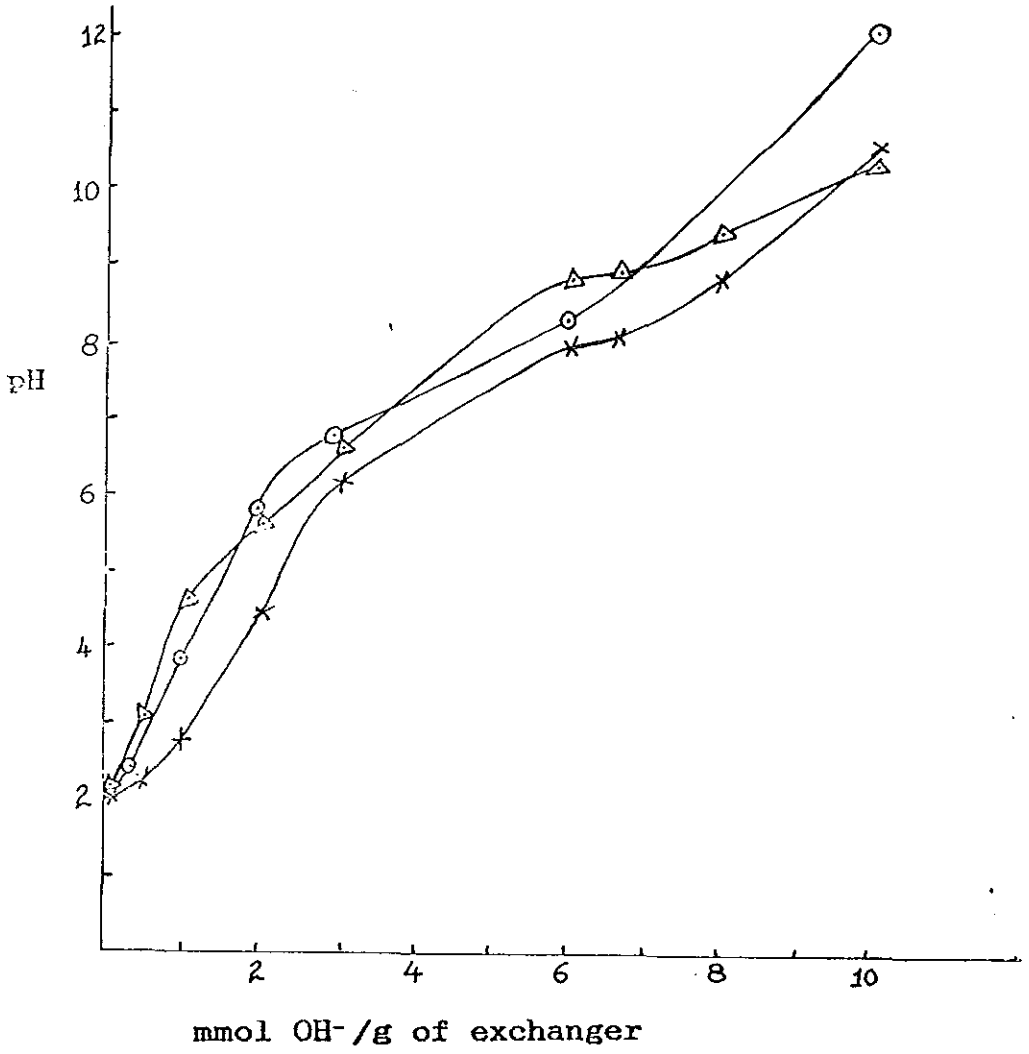


Fig. 5. Titration curves of cerium(IV) selenopyrophosphate.

△ Li^+

× K^+

⊙ Na^+

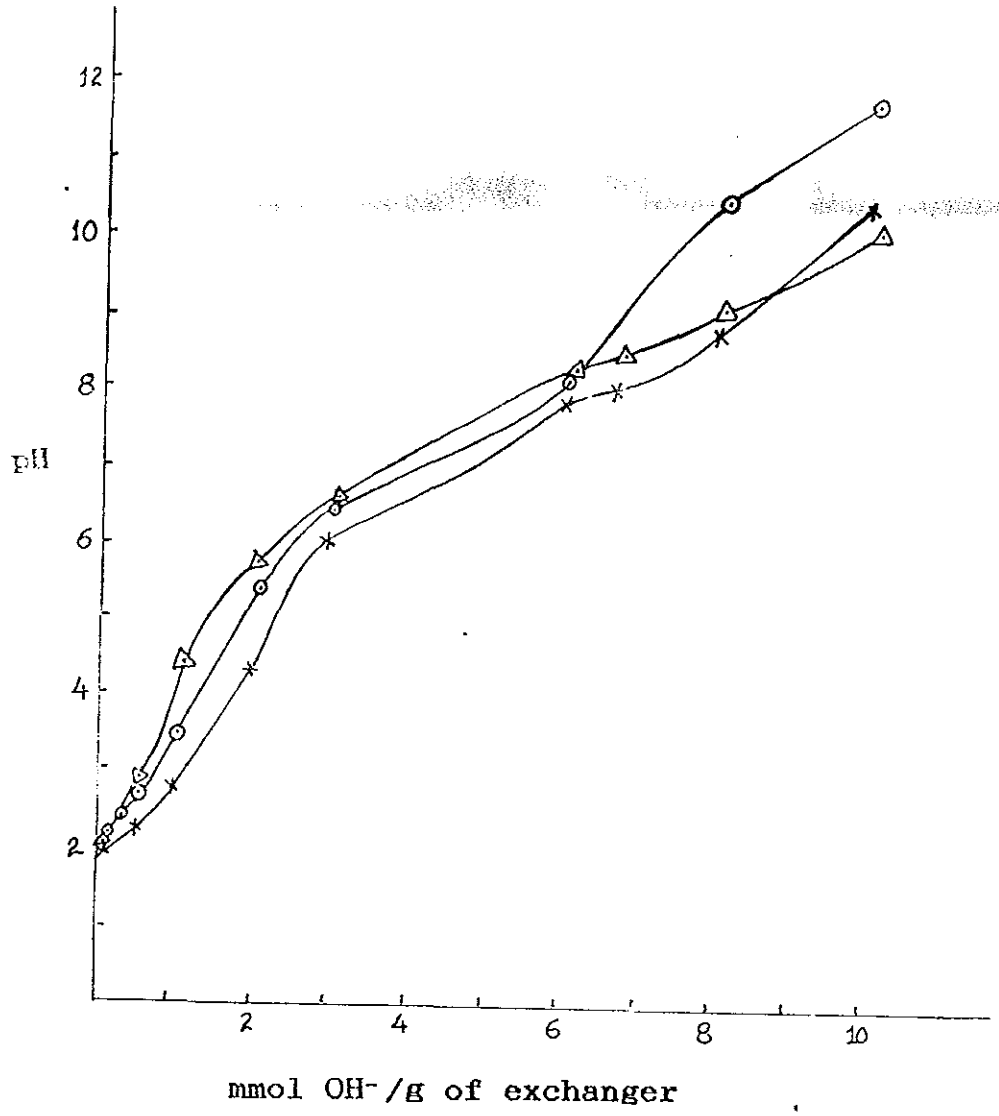


Fig. 6. Titration curves of cerium(IV) pyrophosphate.

△ Li+

× K+

⊙ Na+

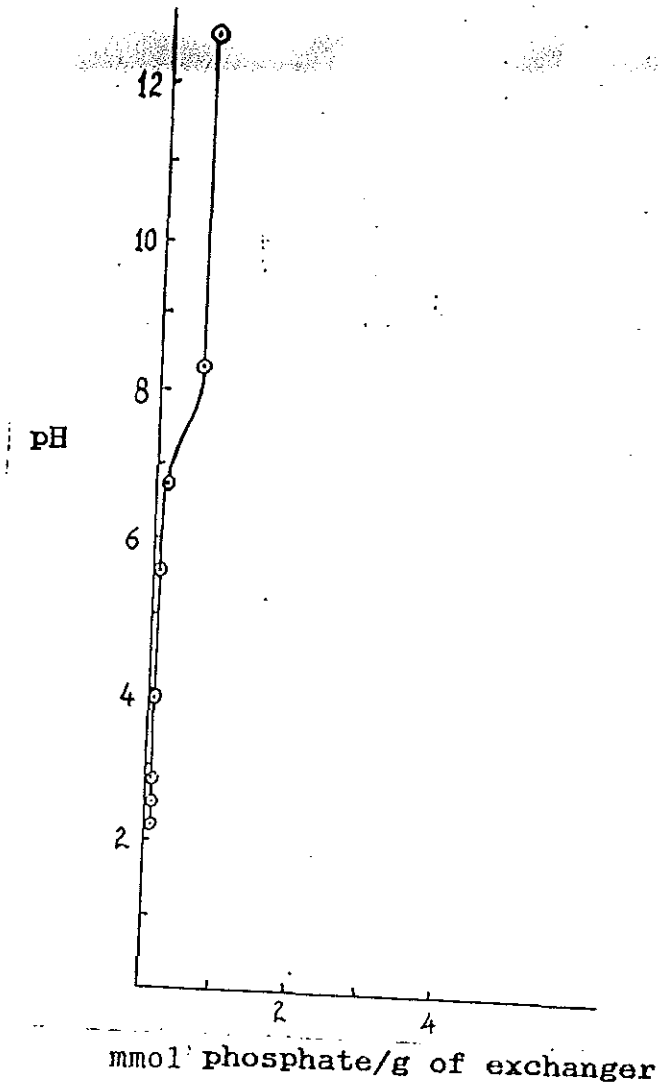


Fig. 7. Hydrolysis of cerium(IV) selenopyrophosphate.

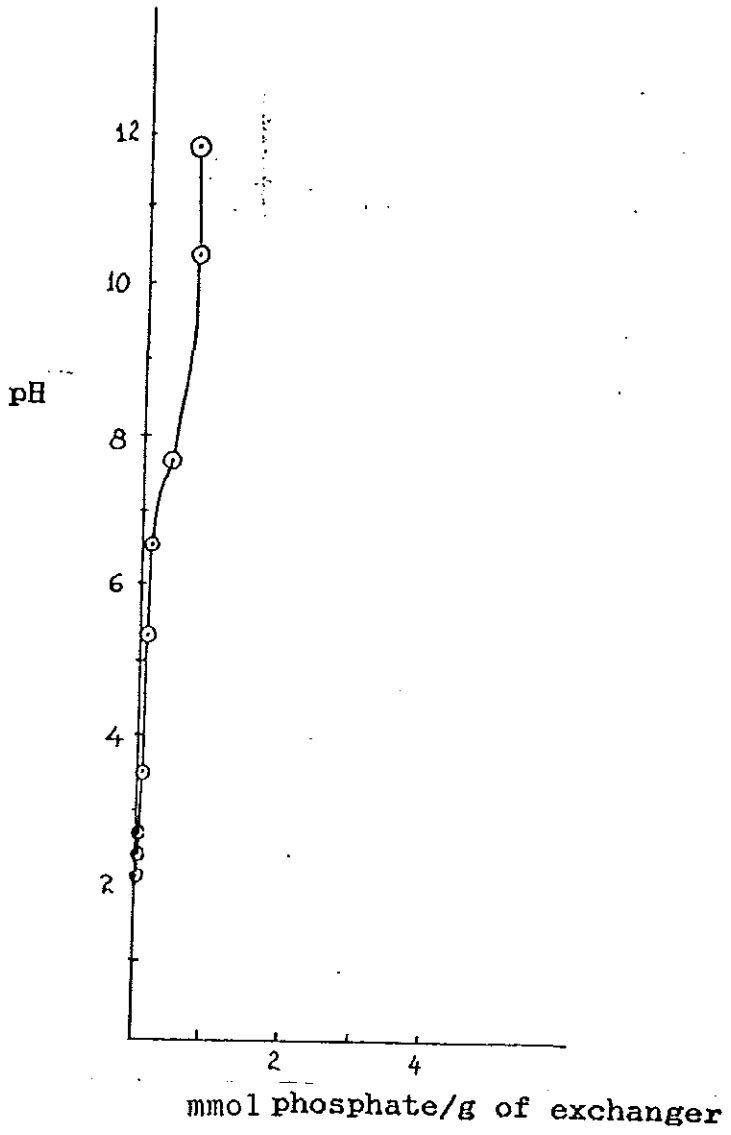


Fig. 8. Hydrolysis of cerium(IV) pyrophosphate.

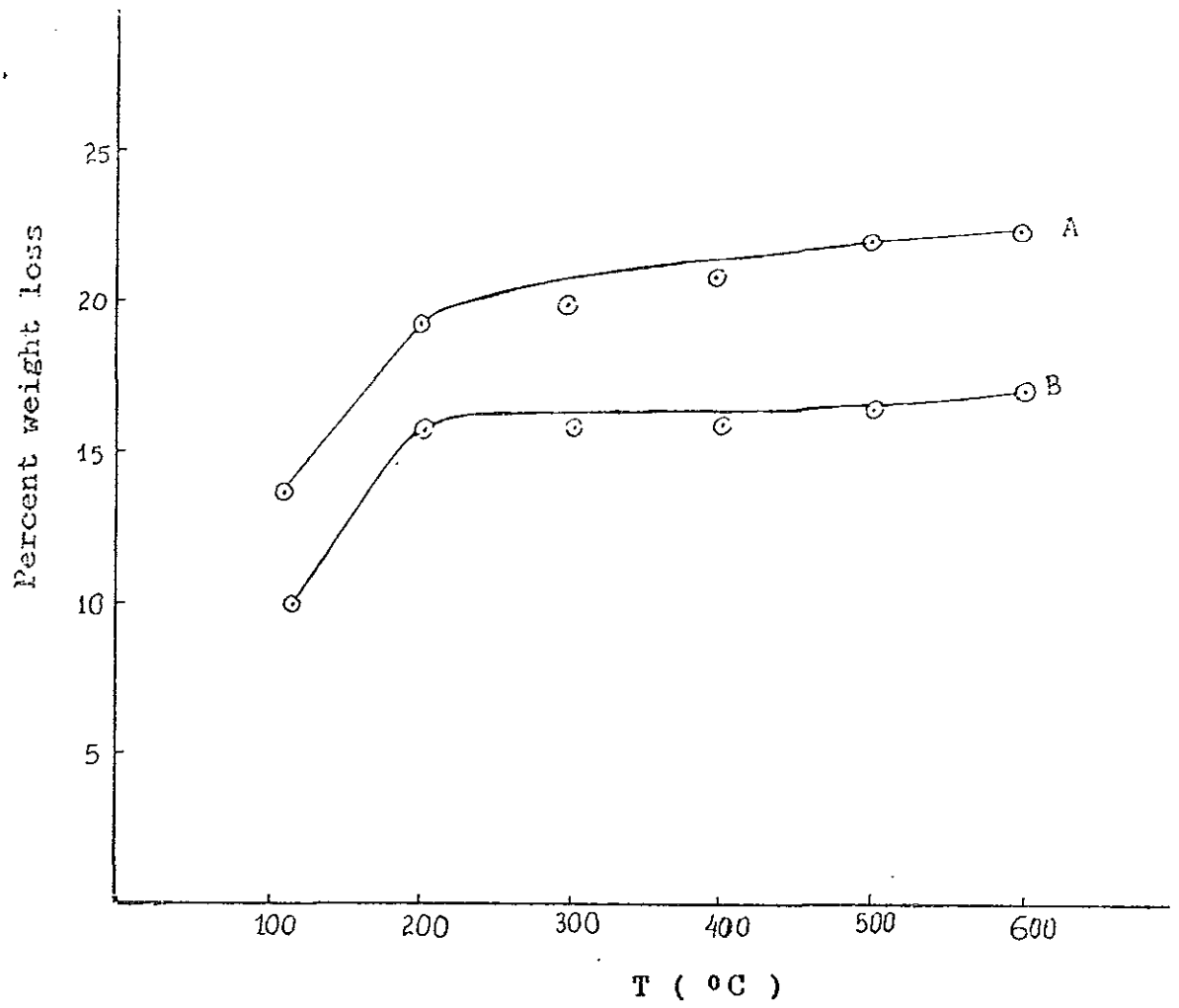
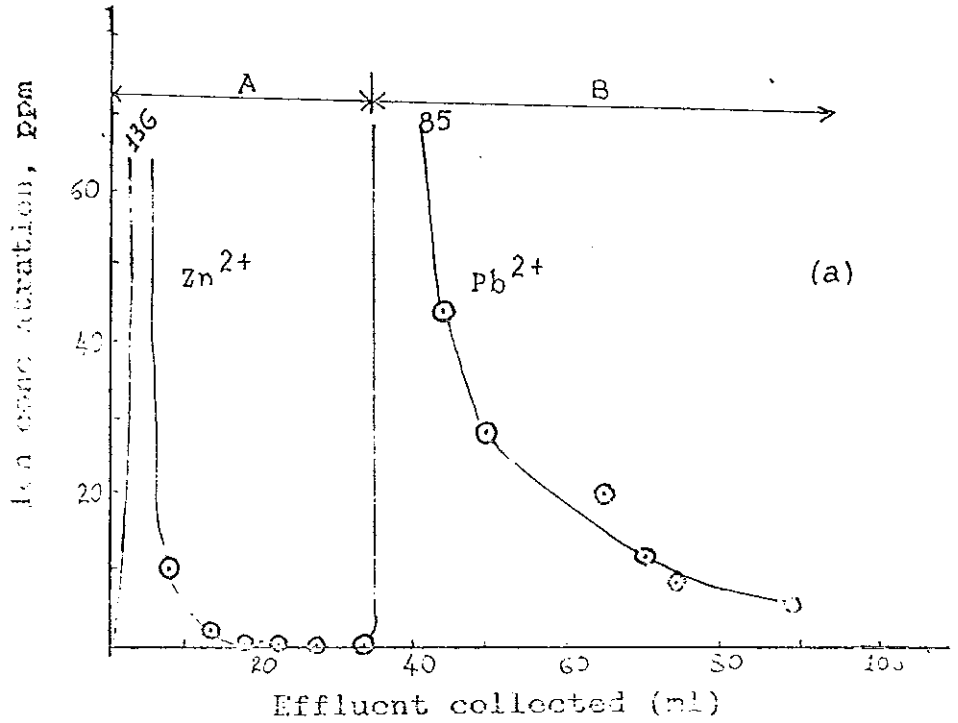
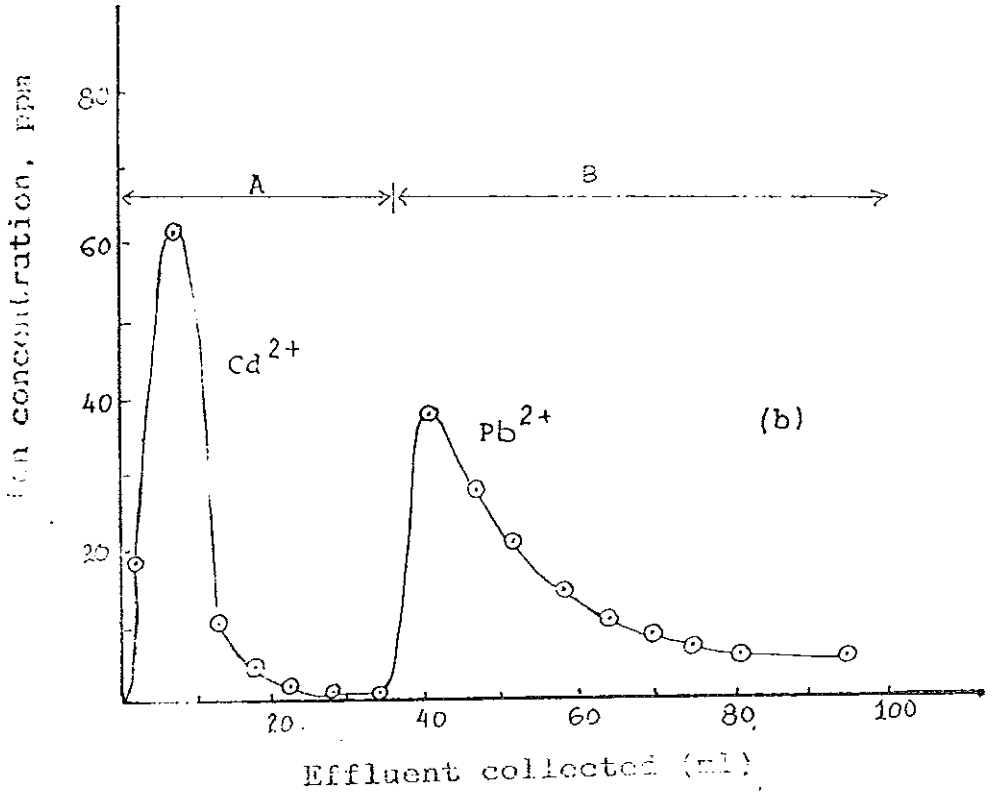


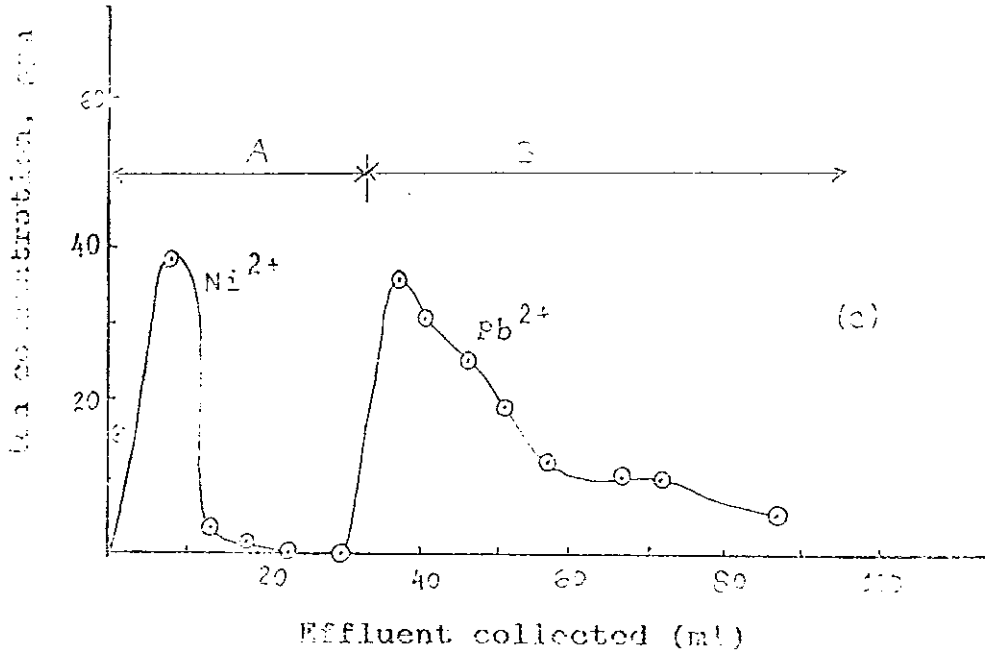
Fig. 9. Percent weight loss of CSP2 (A) and CP3 (B) as function of drying temperature.

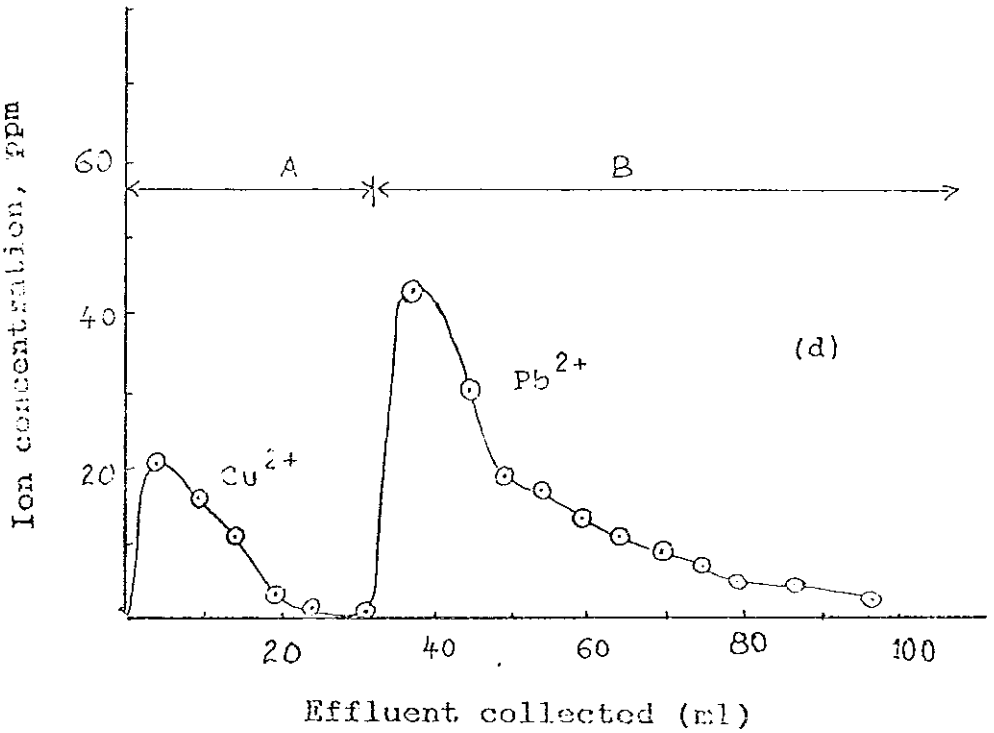
Fig. 10 a. Separation of (a) Zn^{2+}, (b) Cd^{2+}, (c) Ni^{2+}, (d) Co^{2+} and (e)Co^{2+} from Pb^{2+} on cerium(IV) selenopyrophosphate.

A = 0.01 M HNO_3 B = 2 M $NaNO_3$ + 0.1 M HNO_3 (1:1)






A
B
40
20
Ni^{2+}
Pb^{2+}
(c)
20
40
Effluent collected (ml)


Ion concentration, ppm
60
A
B
40
Pb^{2+}
(d)
20
Cu^{2+}
20
40
60
80
100
Effluent collected (ml)

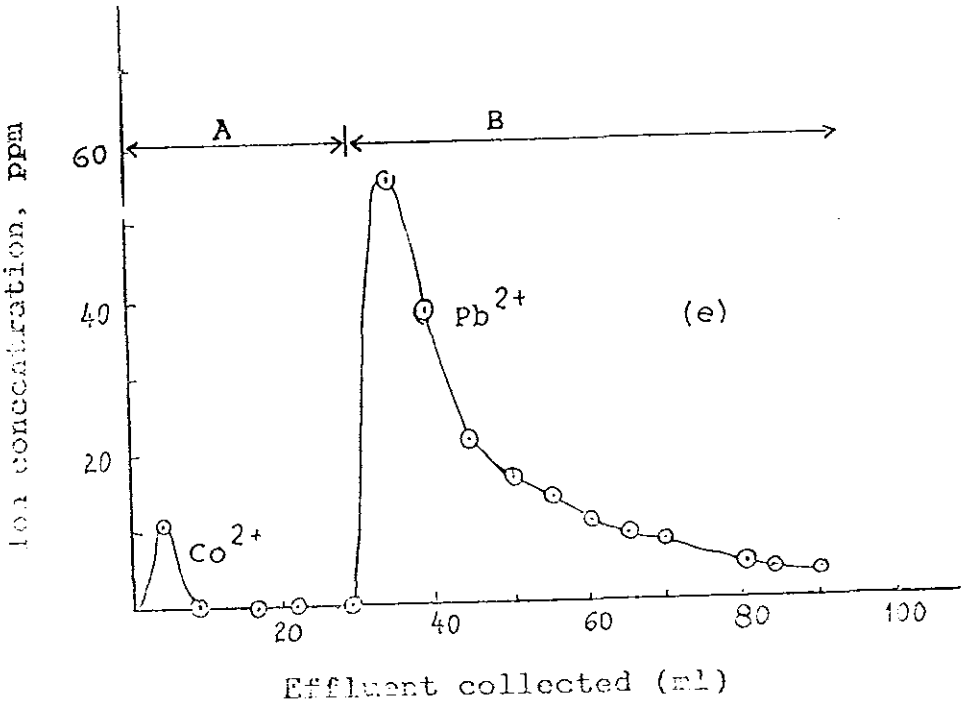
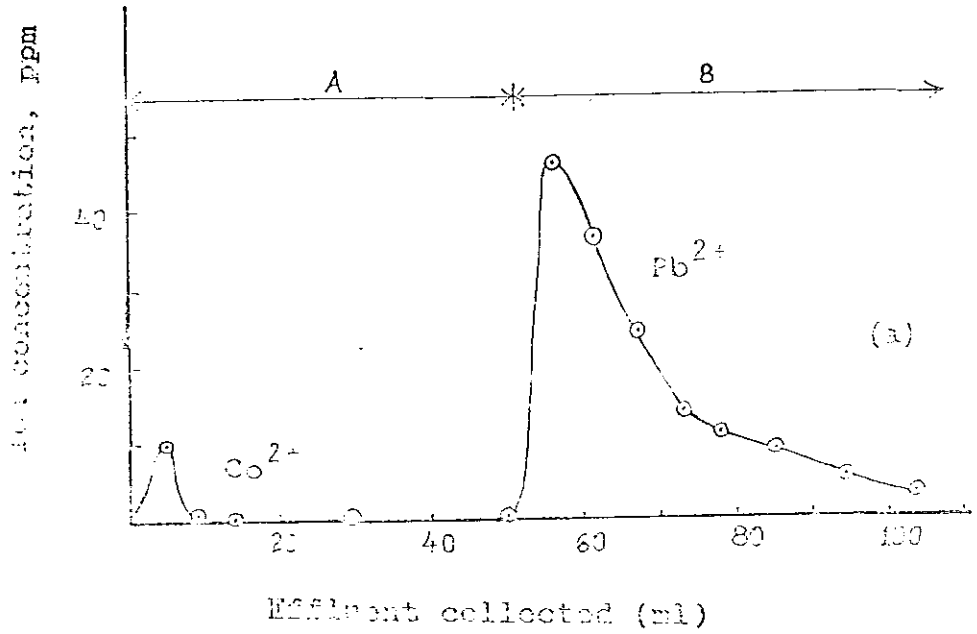
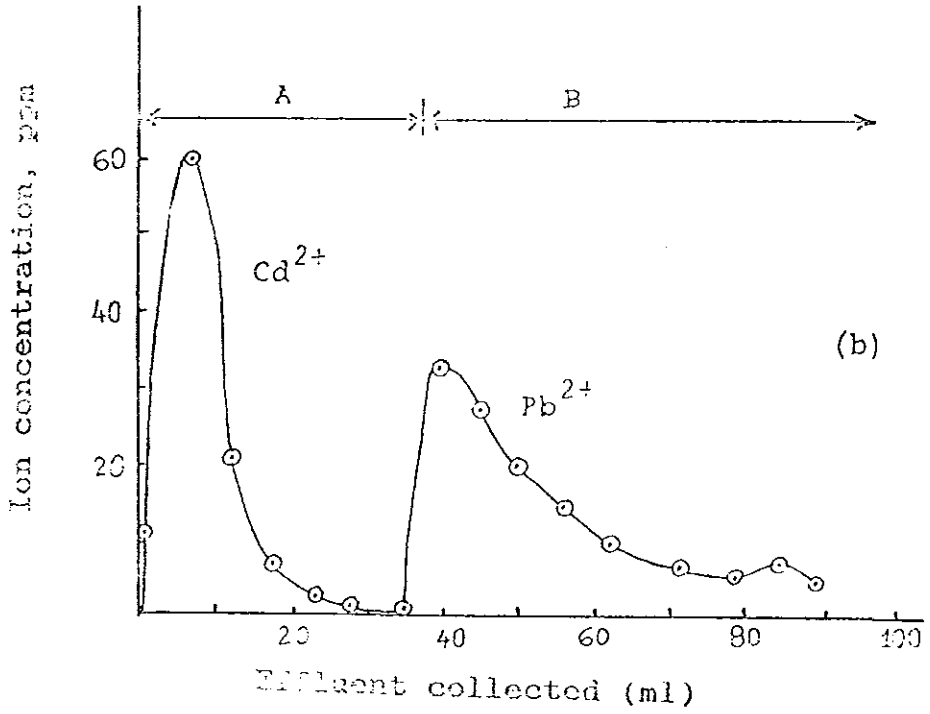
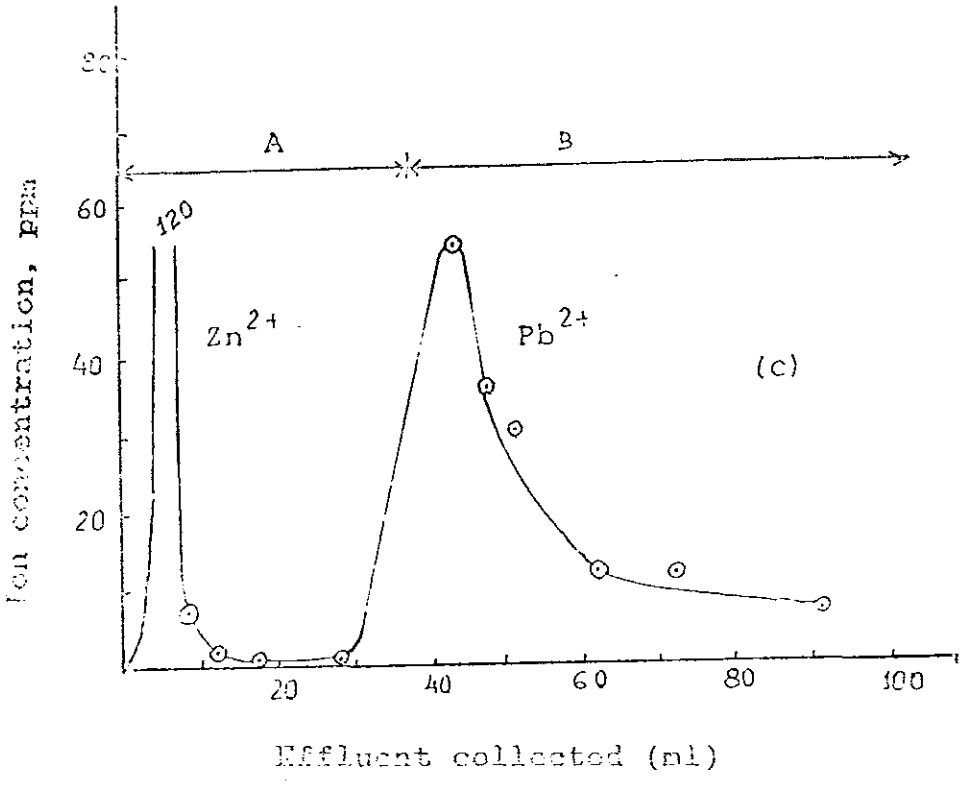

Ion concentration, ppm
60
40
20
A
B
Co^{2+}
Pb^{2+}
(e)
20
40
60
80
100
Effluent collected (ml)

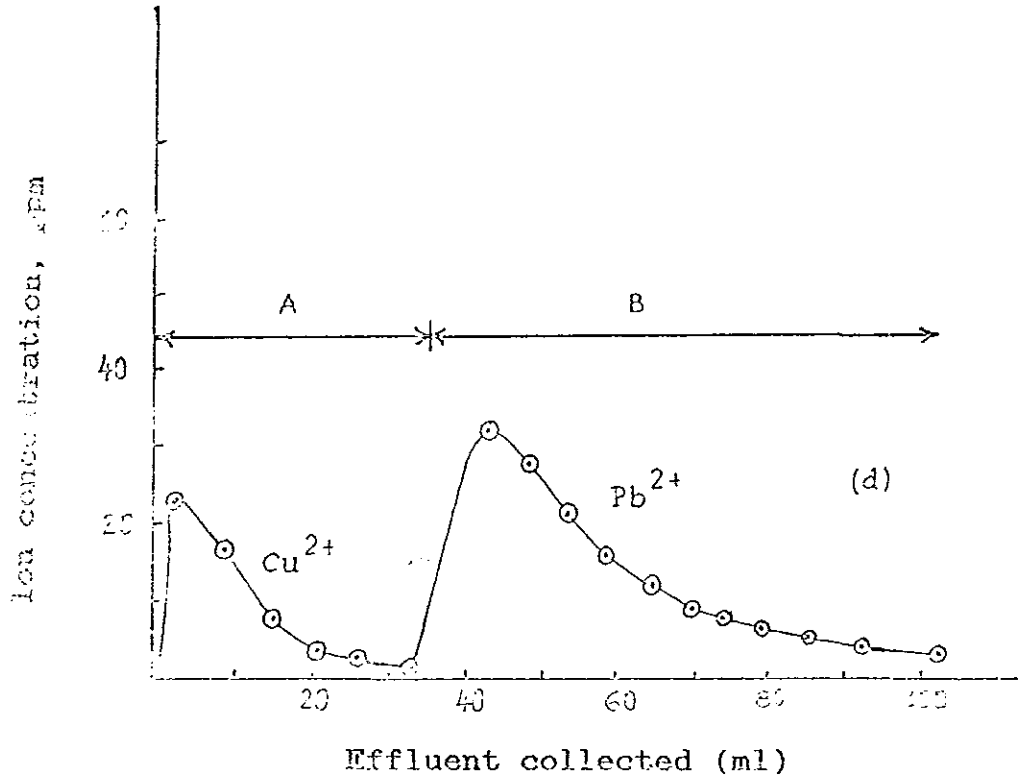
Fig. 10 b. Separation of (a) Co^{2+}, (b) Cd^{2+}, (c) Zn^{2+}, (d) [illegible] and (e) Ni^{2+} from Pb^{2+} on cerium(IV) [illegible]

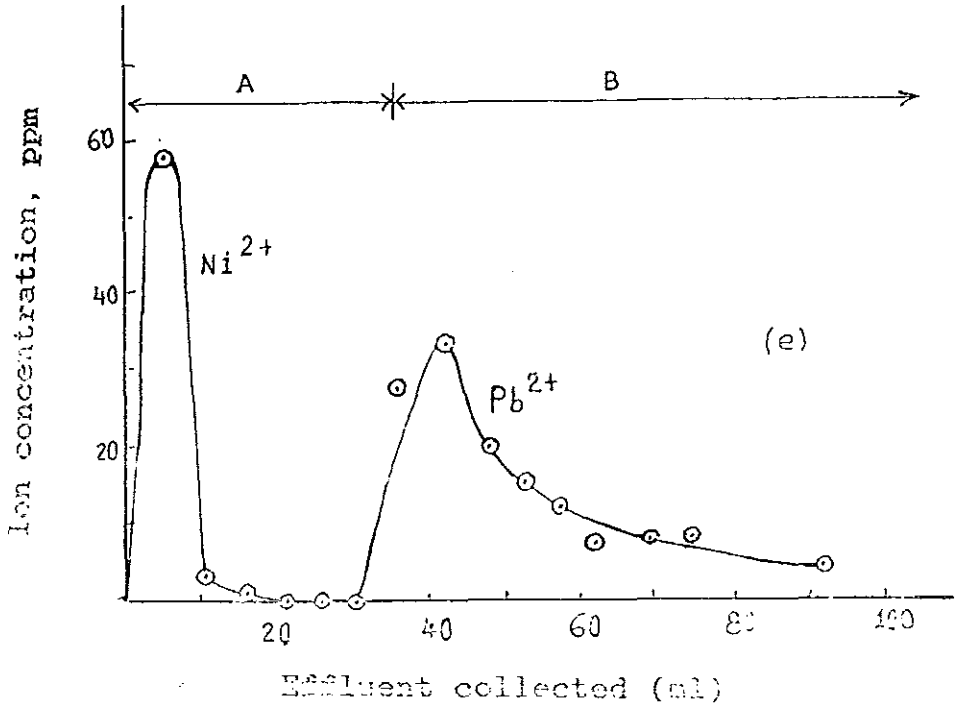
A = 0.01 M HNO_3 B = 2 M [illegible] + 0.1 M [illegible]






A
B
120
Zn^{2+}
Pb^{2+}
(c)
60
40
20
20
40
60
80
100
Effluent collected (ml)


A
B
40
Cu^{2+}
Pb^{2+}
(d)
20
40
60
Effluent collected (ml)


A
B
60
40
20
Ni 2+
Pb 2+
(e)
20
40
60
Effluent collected (ml)
Ion concentration, ppm

... pyrophosphate.

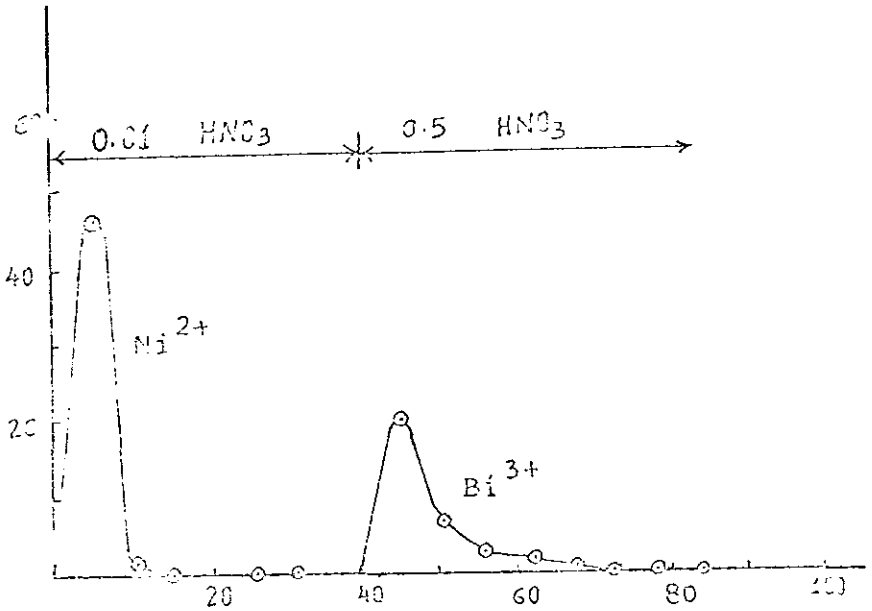
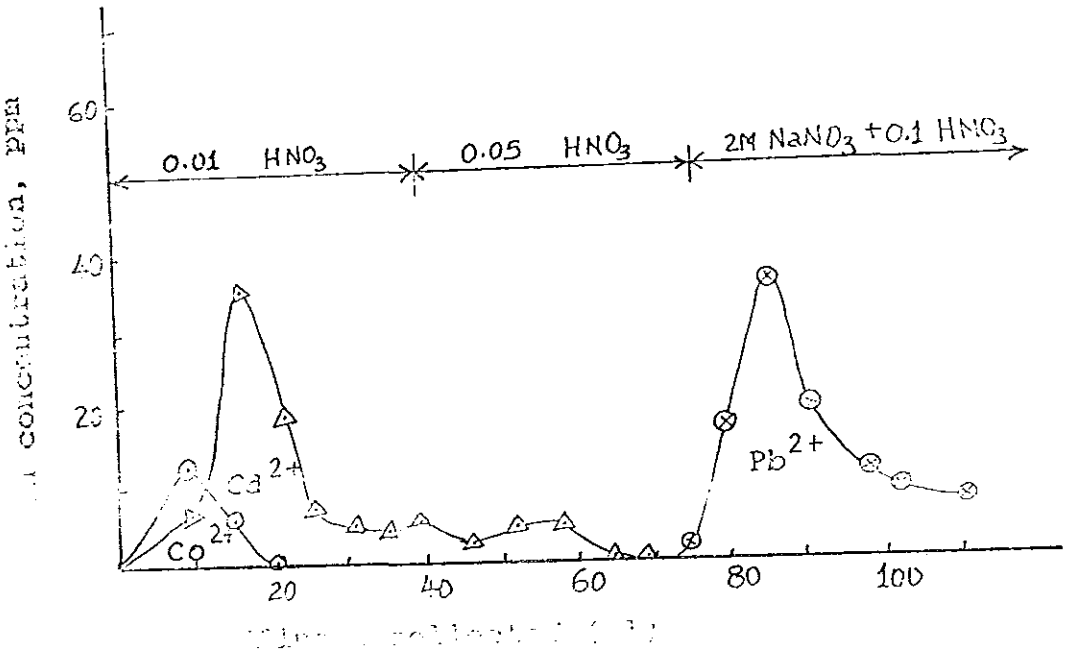


Fig. 10d. Separation of Pb^{2+} from Cd^{2+} and Co^{2+} on zirconium(IV) selenopyrophosphate.



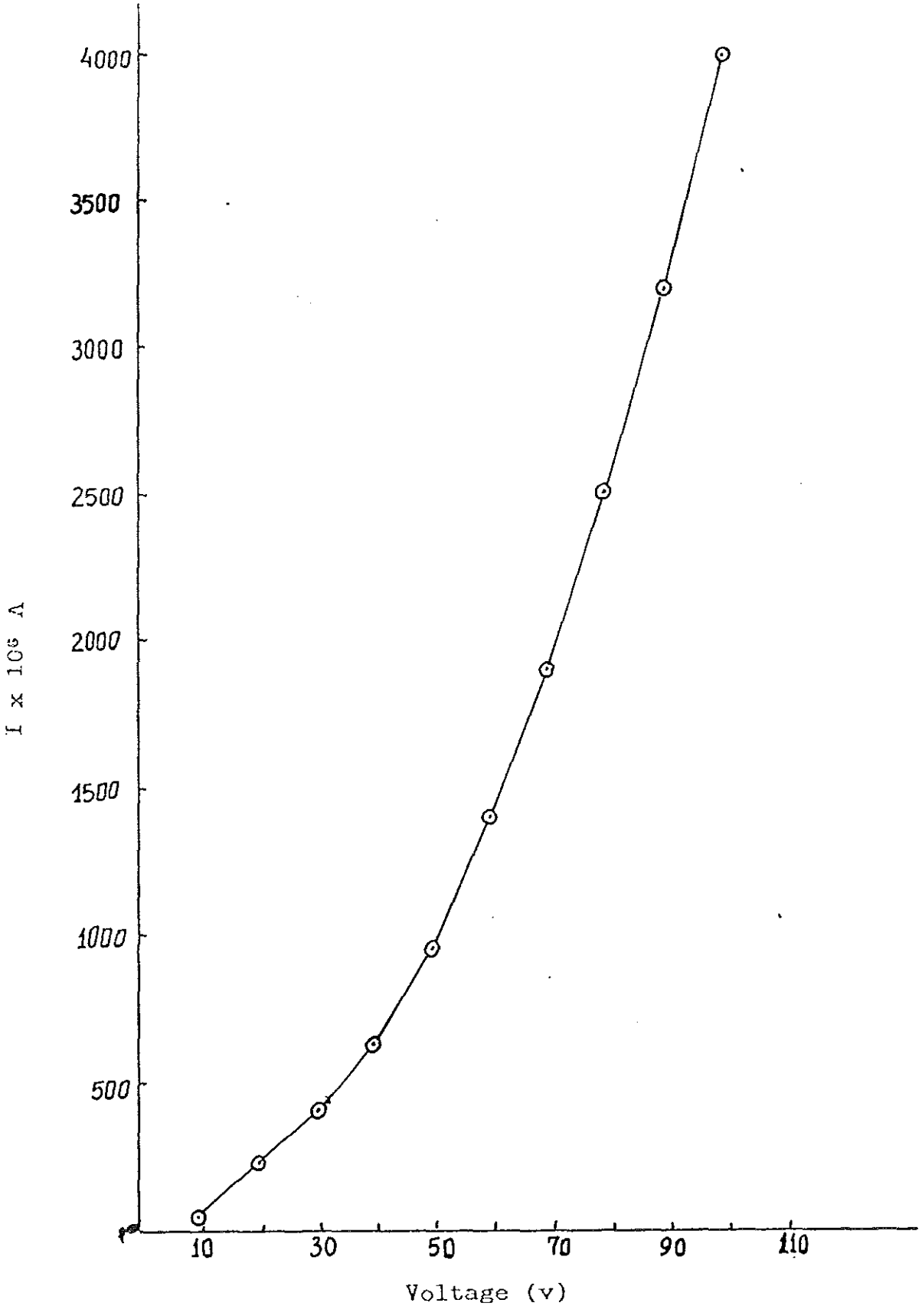


Fig. 11. Current voltage relation of cerium(IV) selenopyrophosphate.

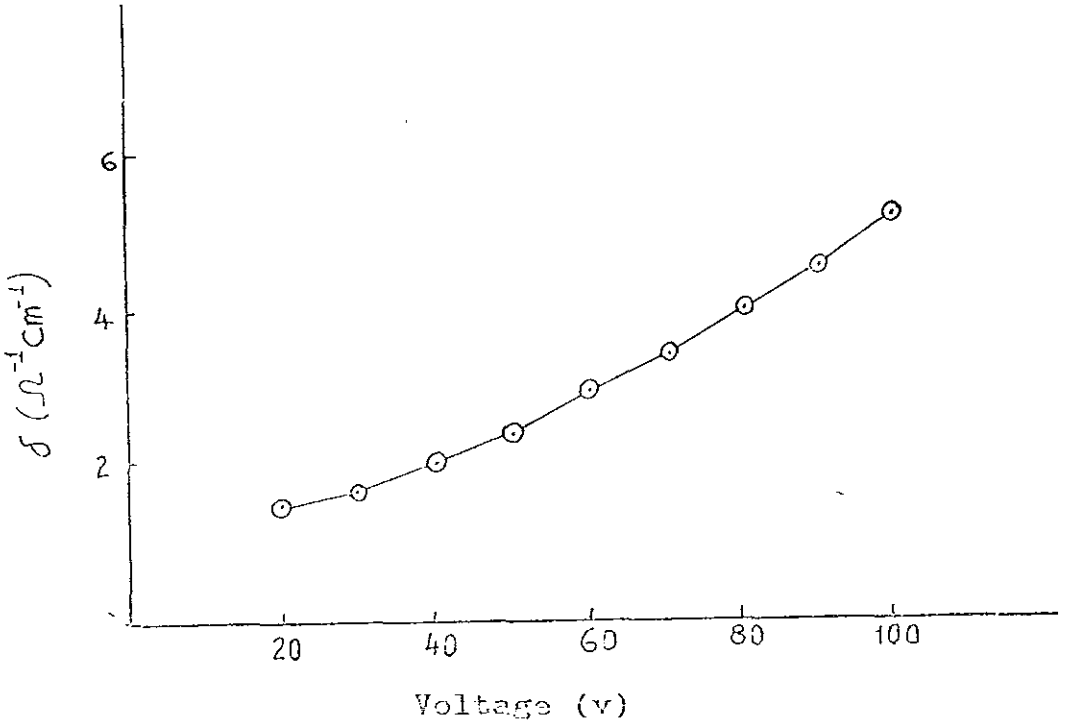
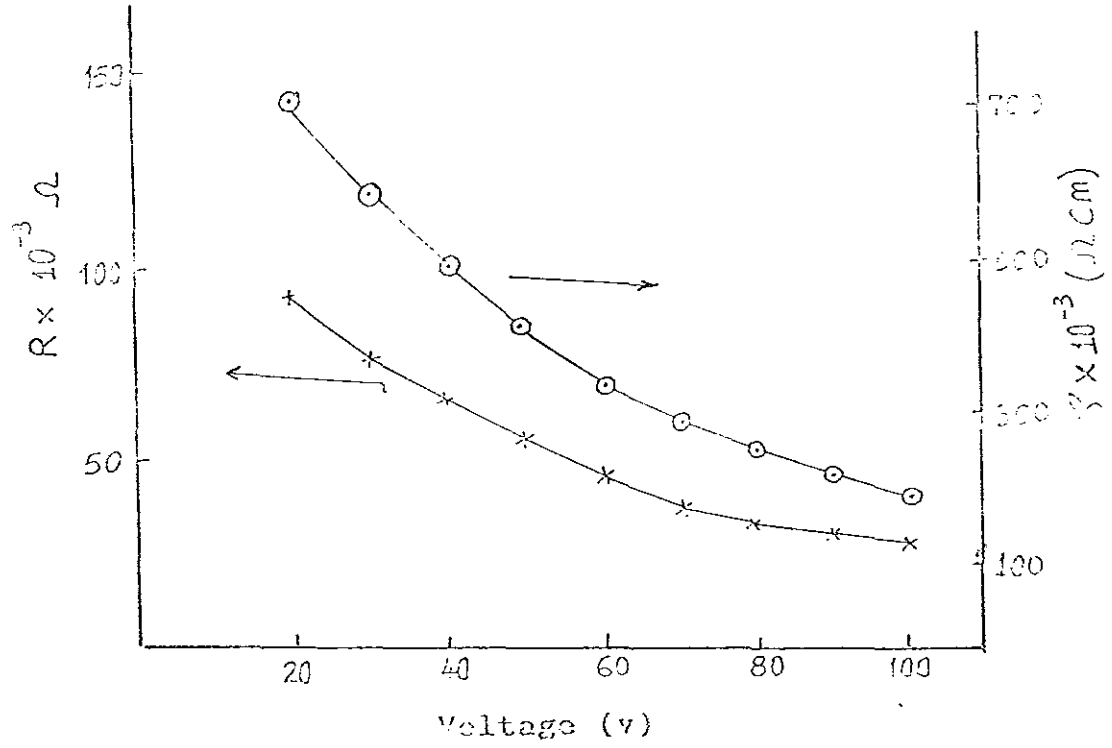


Fig. 12 a. Conductivity of cerium (IV) selenopyrophosphate in the given voltage range.



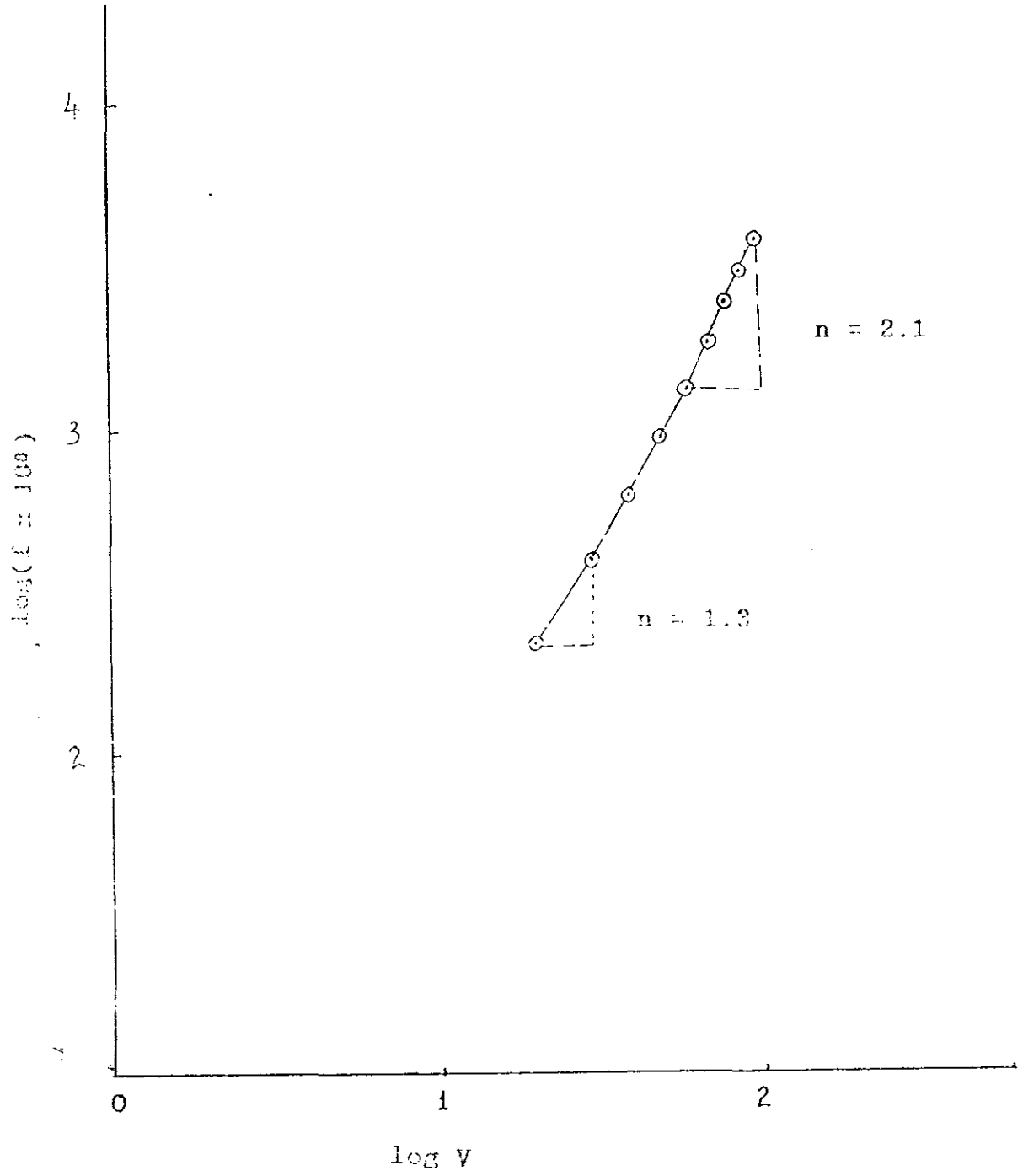


Fig. 13. Log of current and voltage of [illegible] phosphate; where n is the slope.

g. 14. IR Spectrum of Cerium(IV) selenopyrophosphate (CeP_2), (KBr).

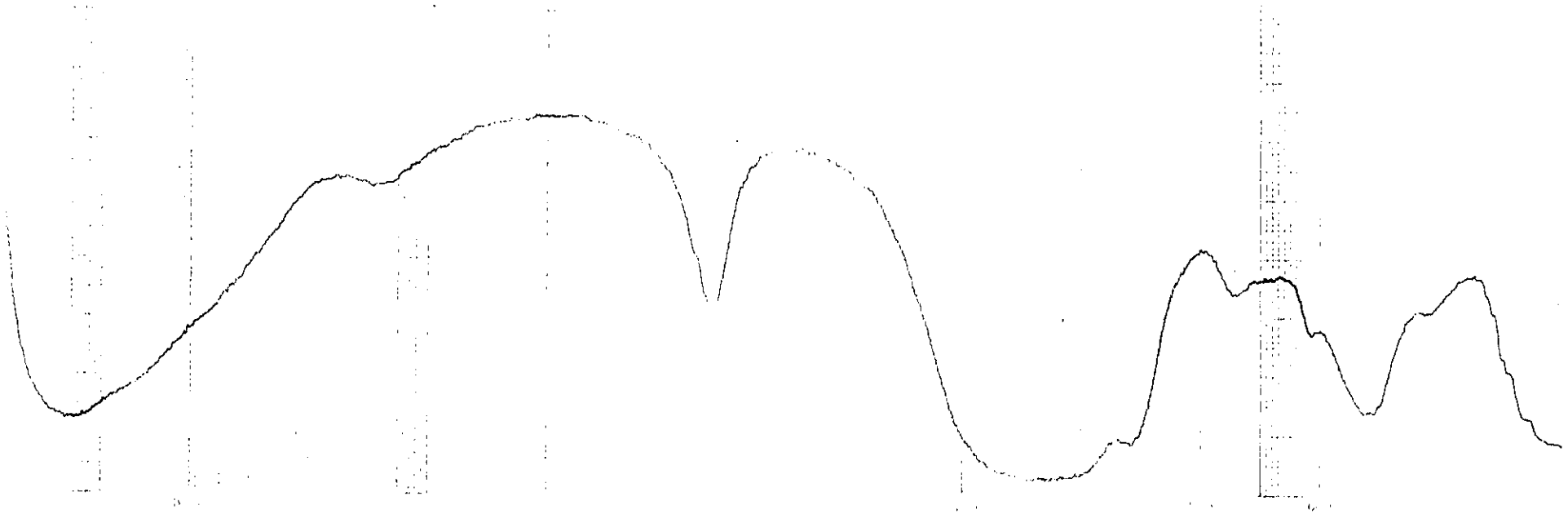
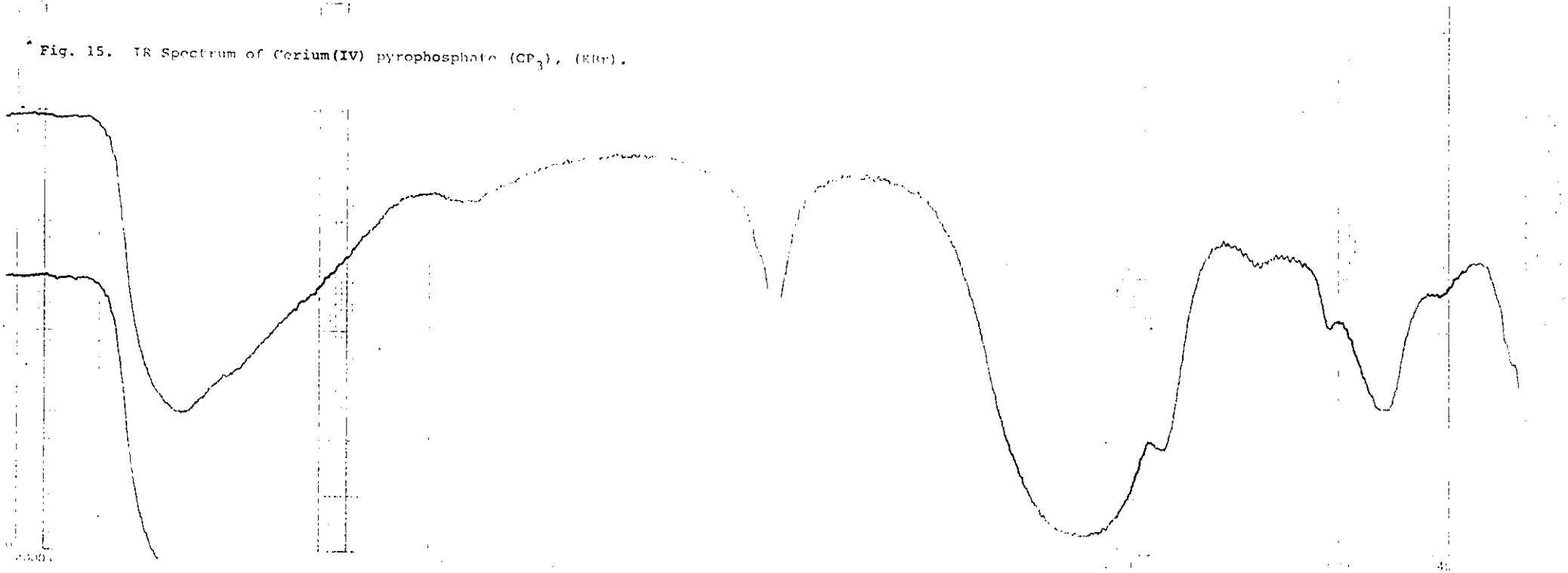


Fig. 15. IR Spectrum of Cerium(IV) pyrophosphate (CP_3), (KBr).



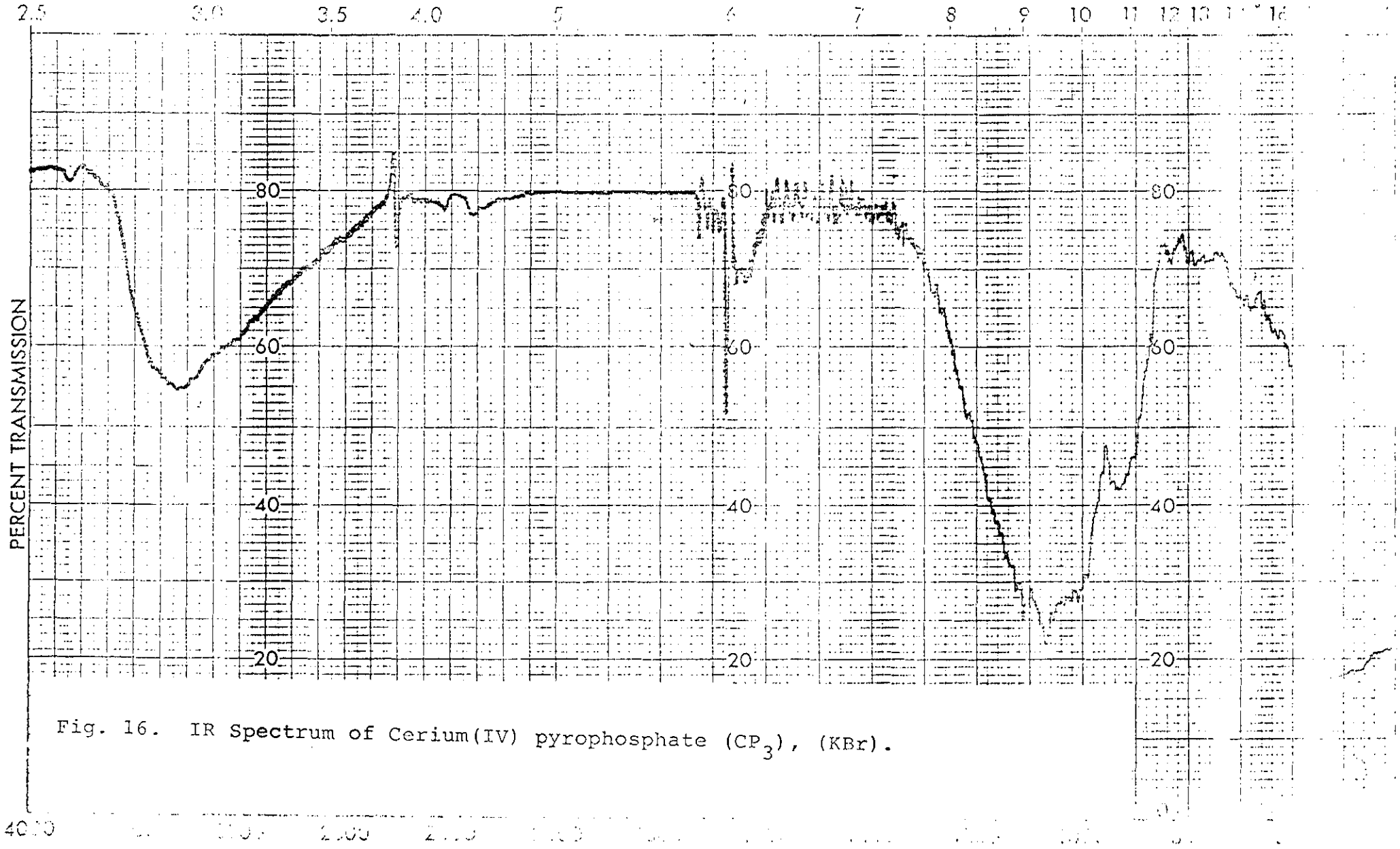


Fig. 16. IR Spectrum of Cerium(IV) pyrophosphate (CP_3), (KBr).

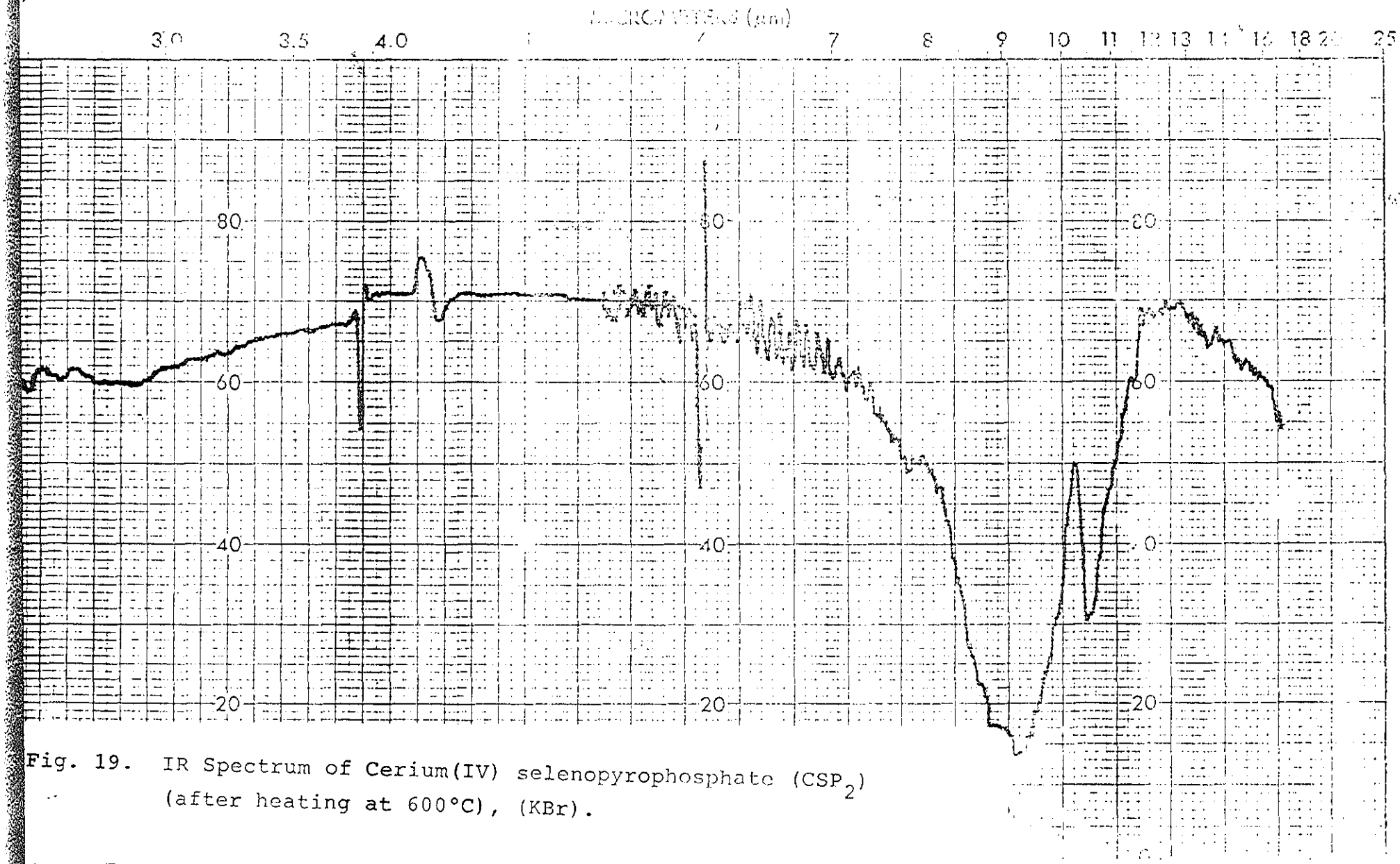


Fig. 19. IR Spectrum of Cerium(IV) selenopyrophosphate (CSP_2) (after heating at 600°C), (KBr).

Fig. 20. X-Ray Diffractogram of Cerium(IV) pyrophosphate (CP_3).

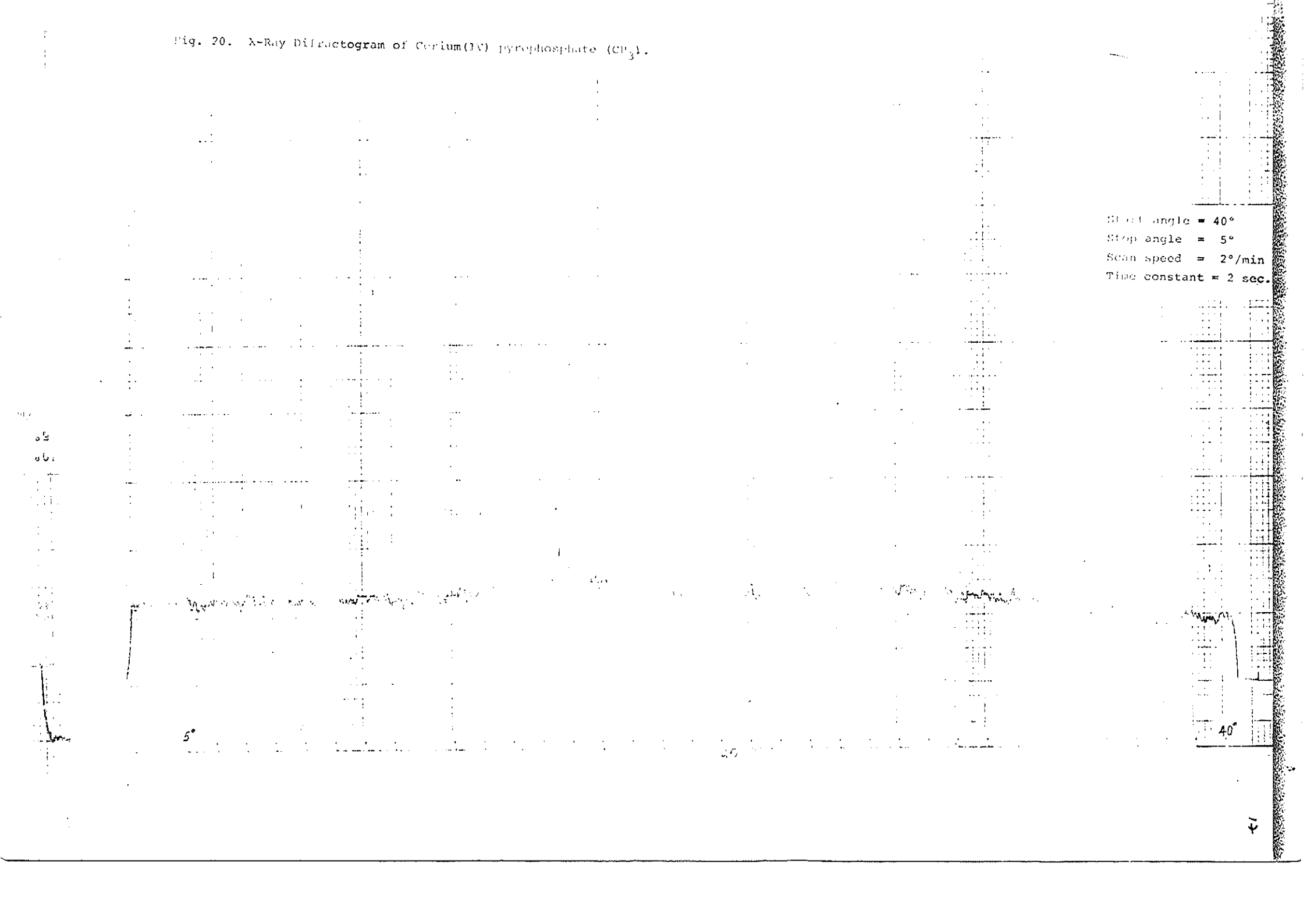


Fig. 21. X-Ray Difractogram of Cerium(IV) selenopyrophosphate (CSP_2).