CHEMICAL AND RADIOCHEMICAL SEPARATION OF SOME ACTINIDES AND LANTHANIDES

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By
DEEP CHAND M.Sc.

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SUPERVISOR'S CERTIFICATE

This is to certify that the work contained in this thesis entitled 'Chemical and Radiochemical Separation of Some Actinides and Lanthanides', submitted by Sri Deep Chand, M.Sc., Senior Lecturer in Chemistry, K.V. Degree College Machhra, Meerut (U.P.) was carried out at B.I.T.S., Pilani (Rajasthan)

This thesis embodies the work of the candidate himself and the candidate worked under both of us for the period required under Ordinance 14 and that he is a teacher in an affiliated College of Meerut University.

(S.P. Gupta)
Reader in Chemistry Deptt.,
D.N. Postgraduate College,
Meerut (U.P.)

R. S. Rai
(R.S. Rai)
Asst.Professor of Chemistry
B.I.T.S.,PILANI(Rajasthan).

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Deepchand
(DEEP CHAND)

CHAPTER 1

GENERAL INTRODUCTION

GENERAL INTRODUCTION

The chemistry of actinide elements attracted the attention of chemists and physicists after the discovery of nuclear fission by Hahn and Strassman in 1939. The metals thorium, uranium and plutonium are specially important in the field of nuclear technology and modern inorganic chemistry because these elements promise a vast source of energy which could successfully be utilised for the benefit of mankind. Although uranium fed reactors are useful, it leads to explore the possibility of other fissile material. Subsequently the chemistry of thorium along with uranium gained momentum for its usefulness in breeder reactors. Thorium is three times more abundant than uranium. In India the supply of uranium is very limited but thorium is found as very rich deposits in the form of rare-earths thorium orthophosphate. The radioactive mineral containing uranium, thorium and rare-earths are processed and utilised for extraction. Therefore, it has been thought worthwhile to develop some new analytical procedures for the separation of uranium, thorium and rare-earths in order to improve upon the previous data as well as to find out some suitable methods for their separation so that such study might be successfully utilised in the nuclear technology. The element protactinium could not be incorporated in this study because of the non-availability of the element or its compounds.

A very large amount of data is available in the form of research papers, reviews and books which describe a number of analytical techniques for the separation of actinides and lanthanides. Out of these analytical procedures, ion-exchange chromatography, thin layer chromatography, solvent extraction and heterogeneous exchange reactions on solid surfaces have been selected for the present study.

It has been found out from the survey of literature that Zeokarb 225 and 216 have been investigated along with De Acedite FF ion-exchange resins. It has also been found out that cation exchange resins in hydrochloric acid and organic solvent media have been used for specific separation problems. The data obtained by various workers cannot be correlated properly. Therefore, the adsorption behaviour of a number of ions has been studied. These ions include some actinides and lanthanides besides some other metal ions which are used in the construction of the reactors as well as they are present in fission products. Amberlite IRA-400 anion exchange resin has been selected for the present study and a complete picture of adsorption characteristics and separation possibilities of ions of some twenty elements in mixed solvents media have been studied. For this purpose a number of organic solvents have been mixed in hydrochloric acid in varying proportions. Similarly anion exchange behaviour of several elements in nitric acid organic solvents media has been studied to obtain a much more complete picture of the adsorption characteristics and separation possibilities of elements in mixed solvent system.

Two other procedures have been developed for the separation of uranium, thorium and platinum over Amberlite IRA-400. In one of these procedures primene JM-T was used as a solvent extractant for the separation of thorium. Uranium and platinum were separated over the resin column. These three metal ions were separated over the resin bed using different complexing and eluting agents.

The paper chromatography has been used seriously to the problems of inorganic separations only comparatively recently. It appears to have wide spread utility in inorganic field. The methods developed in paper chromatography are time consuming. Since 1958 thin layer chromatography has developed rapidly and it has its advantage in the fact that these separations can be easily performed in 1 to 2 hours. Further a clean separation of ions is possible over the plates. In this method the adsorption layer and the solvent can be changed, therefore this technique is better than the paper chromatography. Paper chromatography has been used for the separation of number of ions using both normal and reversed phase techniques. Various solvents and mixture of solvents have been used for the paper chromatographic separation of thorium and uranium ions from other metal ions. The paper chromatographic separation are of considerable importance in the radio-chemistry, because a number of ions using both normal and reversed phase techniques were separated. The identical information in the area of thin layer chromatography is insufficient although this method is rapid and its separation capacity is higher than the paper chromatography. Therefore, the present work was undertaken to improve upon some of the separations achieved on paper chromatography. Further an attempt has been made to find out an alternative system of solvents for better separations of some actinides and lanthanides including some other metal ions. However protactinium could not be used due to the reason stated in the preceding paragraph.

A number of amines and phosphines have been used for extraction separately. Tri-n-butyl phosphate has been studied very extensively than any other organophoephorous extractant. A number of physicochemical properties, i.e., dipole moment, nonvolatility, high boiling point and density make it a useful extractant. A number of elements have been extracted under different conditions. TBP forms a number of complexes with water in different stoichiometric ratio. It also forms a number of molecular complexes with metal nitrates. The trivalent metals form trisolvates with TBP and the lanthanides form anhydrous trisolvates. Tetravalent metals are extracted as disolvates of TBP. In addition to this other solvates have also been detected. The hexavalent actinides are extracted as disolvates. It is generally agreed that nitric acid and TBP form a number of complexes.

Therefore tri-butyl phosphate along with hydrochloric acid has been used for the separation of uranium and thorium. The system studied is uranyl perchlorate in presence of perchloric acid, sodium perchlorate and hydrochloric acid. The sulphoxides as extractants are quite recent and aliphatic sulphoxides have been used for the estimation of mineral acids and uranium salts. Dimethyl sulphoxides - aqueous hydrochloric acid have been used in ion-exchange chromatography and di-n-pentyl sulphoxides was used as a solvent extractant. Therefore diphenyl sulphoxide has been selected for the extraction of thorium under varying conditions. The species formed could not be investigated due to breakdown in the IR recording spectrophotometer.

The adsorption phenomenon has played an enormous role in the radiochemical analysis. This process is always associated with the precipitation techniques. Isotopes can be separated by exchanging them at a solid surface. The rate of the exchange between the solid phase and aqueous phase depends not only on the rate of the adsorbing atoms at the interface but also on recrystallisation and self diffusion process. This leads to a heterogeneous isotopic distribution in the solid phase.

When a nascent or a previously prepared precipitate is mixed with a radioactive element present in the form of cation or anion containing identical ions or ions isomorphous to them, exchange takes place. The distribution of these radioactive ions in the precipitate is heterogenous.

In radiochemistry the tracer is rapidly adsorbed either by exchanging with the counter ions or lattice ions on the surface of crystal. Therefore, heterogeneous exchange reaction and co-precipitation techniques have been used for a fast radiochemical separation. Here the exchange is very rapid, but the completion of the process takes some time. Numerous heterogeneous exchange reactions involving the separation of own or related ions by rapid exchange reactions on the surface layer of the precipitate are described. A number of isotopes have been separated rapidly. Since the separation of thorium and uranium on lead sulphide and bismuth sulphide was recently reported in the literature, therefore antimony tri-sulphide and tin (IV) sulphide were selected for the separation of uranium and thorium over them using Th^{234} as well as Sb^{120m} as a tracer. It gives a good separation of uranium and thorium over the precipitate.

The relevant scientific literature relating to these four analytical techniques is given separately at the end of different chapters to avoid duplication and repetition.

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CHAPTER 2

ION-EXCHANGE CHROMATOGRAPHY

INTRODUCTION:

In 1850 Thompson[1] and Way[2] reported that cultivated soil can exchange ammonium ions for calcium and magnesium ions. This phenomenon was first called base exchange and it was explained by Henneberg and Stohmann[3] in 1858. They succeeded in confirming the reversibility and equivalence of such ion-exchange processes. In 1870 Lemberg showed that several naturally occurring mineral specially the zeolites have the property to exchange ions. These and similar other observations remained the subject of basic research for about fifty years until Gans[4] in 1905 synthesized inorganic ion exchangers, among which sodium perutite found practical application in water treatment.

Adams and Holmes[5] discovered in 1935 that ion exchanging properties were noticed with synthetic resins. This was really a turning event in the history of ion exchangers because considerable developmental work was started since 1936 and a number of synthetic ion-exchange resins with the desired properties were prepared in the laboratory. In 1945 d'Alelio[6] incorporated sulphonic acid group into a crossed linked polystyrene resin and this replaced the polycondensation products by polymerisation products. These resins were further improved and ion exchangers with specific ion exchanging properties were synthesized. The research in this field gained momentum after 1945 when a number of publications on ion-exchange reached to about eight hundred per year. Thereafter the main attention was concentrated over synthetic resins exchangers.

Ion-exchange chromatography was very extensively applied to separation problems in nuclear technology. Such properties as ionic size, difference in the acidity or basicity and conversion of the ions into complex species were successfully applied to analytical problems like separation of interfering ions of opposite charge, determination of total salt concentration, isolation of tracer constituent and separation of ions from non-electrolytes. Ion-exchange chromatography has been very widely used in the nuclear technology for the separation of actinides and lanthanides. A number of reviews on the ion exchanging properties of actinides have appeared[7-11]. The separation of thorium from ions like uranium, actinium, plutonium, platinum and palladium was done using various ion-exchange resins. Thorium is strongly adsorbed on cation exchange resins and is not eluted to a significant extent with nitric acid or hydrochloric acid[12]. This property has been utilized for the separation of thorium from a number of metal ions. Several highly acidic hydrogen form resins were used for the separation of thorium. The most useful ion-exchange resins for this separation are: Dowex-50[13,14], Amberlite IR-100[15], Amberlite IR-120[16], KU-2[17,18], Ku-1[19] and Zeokarb-225[20-23], De-Acedite-FF[24].

Several eluting agents have been used for the separation of thorium ions, prominent among them being oxalic acid, buffered citric or lactic acids, fluoride ions, carbonate ions, oxalate ions, sulphate ions, sodium bisulphate and ammonium thiocynate. Korkisch and coworkers[25] have thoroughly studied the separation of a number of metal ions using nitric acid or hydrochloric acid in pure organic solvents and mixtures of solvents. A number of scattered data were available on the effect of organic solvent on strongly acidic cation exchangers as well as with mixed organic solvents. A comparative account of adsorption data of a number of ions on Dowex-50 in hydrochloric acid and nitric acid media are given. Thorium(IV), protactinium and uranium(VI) have been separated using Amberlite IRA-400 resin by eluting with hydrochloric acid. Thorium(IV) was separated with 9M hydrochloric acid, protactinium(V) with 1.0M hydrochloric acid/HF and uranium(VI) with 0.1M hydrochloric acid. From a survey of the literature it has been found out that cation exchange resins in hydrochloric acid and organic media has received attention only for specific separation problems. The data obtained by various workers cannot be correlated properly. Therefore the adsorption behaviour of a number of ions has been studied. These ions include a number of lanthanides and actinides.

From the literature surveyed, it is seen that cation exchange resin in HCl organic media has received attention only with respect to the solution of specific separation problems, and has been used to study the adsorption behaviour of several metal ion in only one solvent or of only one or small group of elements in several different organic solvents. The data obtained by various worker cannot be correlated properly, therefore Amberlite IRA-400 has been selected because Zeokarb-216 and Zeokarb-225 and De Acedite FF has meanwhile been investigated. A complete picture of adsorption characteristics and separation possibilities of some twenty elements in organic solvent media have been studied. Similarly anion exchange behaviour of several elements in nitric acid, organic solvent media has been studied in order to obtain a much more complete picture of the adsorption characteristics and separation possibilities of elements in organic solvent media.

Amberlite IRA-400:

Amberlite IRA-400 is gelular strongly basic ion-exchange resin. Its basicity is derived from quaternary ammonium functionality. The porous gelular resin bead structure of this resin is based on a styrene-divinylbenzene copolymer, unquestionably the strongest polymer matrix available to this type of product synthesis. It exhibits the highest basicity available in ion-exchange resin. It offers maximum temperature stability and good resistance to loss of strong base capacity due to oxidation. Its cross-linking is durable. It has no pH limitation. It is supplied in the chloride form and may be used directly for many application or it may be converted to the hydroxide form with solution of sodium hydroxide (4%). Because of the tendency for ion-exchange resin to adsorb bacteria from the solution care must be taken to store Amberlite IRA-400 in the absence of materials which might nourish bacterial growth and to clean the resin bed completely prior to each start up to assure that bacteria are not present. Likewise precautions must be taken during use to avoid contamination of the resin with poisonous salts.

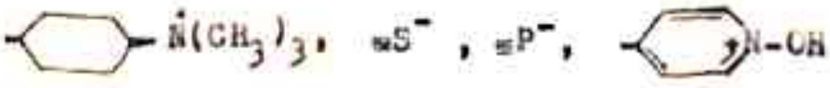
Principles and Experimental Procedure:

Ion exchangers are solid and suitably insolubilised high molecular weight polyelectrolytes which can exchange their mobile ions for ions of equal charge from the surrounding medium. The resulting ion exchange is reversible and stoichiometric with the displacement of one ionic species by another on the exchangers. Ion exchangers look like high molecular weight acids and bases with a high molecular cation. It can exchange its hydrogen or hydroxyl ions for equally charged ions and are thus converted into high molecular weight salts. If such a solid acid is neutralized with a base into the salt, however, the cations bound to the polyelectrolytes can again be displaced by other cations. This process is known as cation exchange and the polyelectrolyte is the cation exchanger. In the other case a solid base is obtained which is capable of OH^- ions-exchange and can be neutralized with an acid and the anion which was bound first can again be displaced by another anion. This process is known as anion exchange, and the polyelectrolyte is called anion exchanger.

An ion-exchanger is made of macro-molecules which form three dimensional network with a large number of attached ionisable groups. The high molecular weight skeleton made of different building blocks is known as the matrix to which the so-called functional groups are firmly and chemically bound. These are known as fixed ions. The exchangeable ions in a heteropolar bond are called the counter ions. In contrast, co-ions are all those ionic species which can be present in an exchanger, but have the same charge as the fixed ions, i.e., the functional group without its counter-ion. The monofunctional exchangers contain only one type of functional group, but the poly-functional ion exchangers contain different types of functional groups.

The synthetic resin ion exchangers are divided into three groups known as cation exchanger, anion exchanger and amphoteric ion exchanger. It is prepared by polymerisation and polycondensation process. The most important starting material is styrene which is crossed-linked with itself and with divinylbenzene into a polymeric network. Divinylbenzene, acrylic acid and methacrylic acid are used for the preparation of weakly acid cation exchanger. In polycondensation resins the matrix is usually constructed of phenol and formaldehyde. The entire matrix depends upon the cross-linking. The following functional groups have been incorporated in cation exchangers $-SO_3^-$, $-COO^-$, $-O^-$, PO_3^{2-}, $-PO_3H^-$, $-AsO_3^{2-}$, $-SeO_3^-$ and in anion exchangers

$$-\overset{+}{N}H_3, \; = \overset{+}{N}H_2, \; \equiv \overset{+}{N}, \; -\overset{+}{N}R_3$$



The functional groups confirm the property of ion -

exchange to the matrix. Depending on the acidity and basicity of the functional groups, a distinction is drawn between a strong and weak acid and between a strong and weak base ion-exchanger. Cation exchanger can also contain two different functional groups with the same charge such as sulphonic acid and carboxyl group and then they are known as poly-functional. In addition to cation and anion exchangers, amphoteric exchanger exists containing both acid and base groups. The condensation products of amines and phenols contain both very weakly acid phenolic OH-groups and basic amino groups. Bi-polar exchange resins have also been produced by introduction of acid and basic groups into the same skeleton of styrene-divinylbenzene copolymer.

Three techniques are used for the practical application of the ion-exchange: (1) batch operation, (2) column process and (3) continuous process.

Batch Operation:

It is the simplest ion-exchange process. The ion exchanger is brought into contact with the electrolytic solution in any desired vessel until an exchange equilibrium has been established between the counter ions of the exchanger and the ions of equal charge of the electrolyte. After the equilibrium has been attained, the ion exchanger is filtered. If additional ions are to be exchanged from the electrolyte solution by the exchanger, fresh ion exchanger must be added and the filtration must be performed again after the attainment of equilibrium. After the filtration, the filtrates are analysed chemically or radiochemically. This method is recommended in those cases where adsorption is favourable, time factor is prohibitive and where gas is evolved during the operation process.

Column process:

The column process is the most important and most frequently used laboratory technique. The ion exchanger is packed in a glass column and all necessary operations are carried out in this bed. Fundamentally two techniques can be distinguished in this case. The one is the descending flow process and the other is ascending flow process. In the first case, the liquid moves up through the exchanger bed. The solution is kept in an over head reservoir and the counter ions of the solution are exchanged over the resin. After a short time the exchanger in the upper part of the column is completely loaded with the counter ions from the solution. Additional ions flow unhindered through this part of the bed and reached the exchange zones farther down and exchange at the ion exchanger. If this process is continued, the exchange zone in the column continue to migrate until it reached the lower end and the overall process has come to the point where both ions are simultaneously eluted from the column. The breakthrough capacity of a column is the concentration of the exchangeable ions in the solution which flows without any exchange. It depends upon the particle size of the resin, the shape of the column, the flow rate, the temperature and the composition of the solution. During flow through the column the ions which are to be exchanged continuously contact fresh ion-exchanger, so that the equilibrium is increasingly shifted in the desired direction compared to the batch technique, ion-exchange in this process becomes a complete and simple process.

In the next step, the column is rinsed with de-ionised water in order to displace the solution, which is left over in the column. This also eliminates acids and non-electrolytes which tend to be reversibly adsorbed in the column. Finally the ions are eluted from the resin bed. This process consists of removal or separation of adsorbed ions from the ion-exchange resin. The elution depends upon the particle size of the resin, the eluent concentration, the flow rate and the temperature. Finally, K_d values are calculated from the formula given by Samuelson[26]:

$$K_d = \frac{\overset{+}{M}r}{\overset{+}{M}s} \times \frac{w}{g}$$

where, K_d = distribution coefficient

$\overset{+}{M}r$ = millimoles of M^+ in the resin phase

$\overset{+}{M}s$ = millimoles of M^+ in the external solution

w = volume of the external solution

g = amount of ion exchanger in grams.

<u>Continuous process</u>:

The continuous ion-exchange processes are normally reserved for industrial application. In this process the exchanger and liquid usually move in counter-current columns. In this process a large part of upper ion exchange bed remains in the column without utilising during the run while the lower part performs the ion-exchange. Therefore the exhausted part of an ion-exchange column should be continuously removed and regeneration performed immediately. This is the characteristic feature of continuous or fluid bed process. A number of technical difficulties are encountered.

Laboratory ion-exchange column:

In principle the ratio of diameter to height should be 1:10 -1:20. A simple ion-exchange column is home made. It consists of a simple glass tube provided with a bored stopper on both ends. The upper end of the column is provided with an ordinary dropping funnel as a reservoir. The lower stopper is equipped with a glass tube attached to a tip of a capillary as a dropping attachment with ground joint. The pinch cock permits the regulation of the dropping rate. Cotton balls, cellulose, synthetic fibre or glass fibre balls are inserted at the lower end of ion exchanger bed. To prevent plugging of the discharge tube by the ion-exchange particles, charging the ion exchanger into a column can be easily done with some practice. The exchanger presented in any form is treated with distilled water in a beaker. The resulting swelling must be carried out under all circumstances to prevent rupture of the column or too close a packing due to swelling in the column. Two hours are usually sufficient for swelling. The exchanger is subsequently poured into the column with care that rapid charging leads to a uniform packing of the different sized exchange particles and the exchanger is always covered with water to prevent the inclusion of air bubbles. Excess water is continuously suctioned from the column and the air has entered between the particles, it usually suffices to add water and swirl the ion exchanger bed by tipping the column. Finally a cotton ball is inserted on the top rim of the ion exchanger bed and the column is washed a few times with distilled water. During regeneration, the exchanger is transformed into its original form. If the ion which has been exchanged in the first run is to be recovered, it is eluted from the exchanger with a suitable liquid and collected in the eluate. Three parameters serve to describe the dynamic and chemical process taking place in exchange column, i.e., flow rate, pressure drop and breakthrough capacity. The pressure drop depends on the particle size of ion exchanger. The exchange of one species of counter ion for another in an ion-exchange column finally reaches a point where breakthrough occurs.

Solutions:

Solution containing five mg metal ions/ml were prepared using minimum amount of acid in conductivity water. The strength of the EDTA solutions were 0.05M and 0.01M. Various indicators were used for the estimation of metal ions. These are:

1. Pyrocatechol violet
2. Xylenol orange
3. Hamotoxylin
4. Eriochrome black T
5. Solochrome black T
6. PAR

One g dried resin was weighed in a conical flask and 20 ml solution mixture containing 1 ml metal ion solution, 1 ml hydrochloric acid, 18 ml alcohols (methanol, ethanol, iso-propanol or n-propanol), acetic acid or tetrahydrofuran with water were mixed with the resin. In the other set of experiments hydrochloric acid was replaced by nitric acid. The resin and the solution mixture were kept in the well stoppered flask and were shaken for two hours and were analysed for metal ions present. Some time the complexing agent did not give the colour in the presence of tetrahydrofuran and acetic acid. In this case the procedure was modified and the solution was transferred to an evaporating dish and evaporated slowly to dryness. It was redissolved and titrated with EDTA solution. All metal ions were analysed with standard solution of EDTA, using proper indicators[27,28], but UO_2^{+2} ions were estimated by PAR[29]. The result of these observations are given in the Tables 1-12 and are plotted in Figures 1-12. Similar plots for thorium have been given by Bunney, Ballou, Pascual and Foti[30].

In another set of experiments platinum, uranium and thorium were separated over Amberlite IRA-400 using primene JM-T. Primene JM-T is a liquid primary amine which has been shown to be effective for the removal of thorium from dilute sulphuric acid solutions. Amberlite IRA-400 is a strongly basic type anion exchange resin and is used in a number of uranium mills for the adsorption of uranium from sulphuric acid leach liquors. Therefore these facts tempted to use primene JM-T and Amberlite IRA-400 together for the separation of these three metals.

The adsorption of metal ions (from sulphate solution) on the resin was studied. pH was maintained near 1.8 using sodium hydroxide solution. A 10% solution of primene JM-T was dissolved either in kerosene or xylene and was mixed with sulphate solution containing metals in separatory funnel. After half an hour thorium was transferred as anionic sulphate complex to the organic phase. The uranium and platinum remained in the aqueous phase. The aqueous phase was then drained from the separatory funnel, then it is passed through a small column containing Amberlite IRA-400. This column adsorbs uranium as anionic sulphate complex, while the platinum passed through the column. Uranium was removed from the resin bed by tartaric acid or citric acid or it was washed with water.

In another set of experiments 4N hydrochloric acid was taken for the preparation of solution. The adsorption of metal ions on Amberlite IRA-400 was studied. The solution was passed through a column of resin. The chloride complexes of platinum and uranium were adsorbed over the resin bed and thorium ions passed out of it. Uranium was eluted from the column of Amberlite IRA-400 by washing with water. Subsequently platinum was removed with a 3N nitric acid.

Platinum was estimated by stannous chloride method[31]. A 5 ml 0.01% platinum solution was taken and 5 ml concentrated HCl and 10 ml of 1M stannous chloride in 3.5 M HCl was mixed. The volume was made up to 50 ml. The transmittance was measured at 403 mu. The amount taken in the mixture and the volume separated through the resin column agreed within 99.5%.

UO_2^{+2} ions and Th^{+4} ions were estimated using a G.M. counter. The samples were counted using the fixed geometry. The background counts were repeatedly taken and the average was calculated. Similarly samples containing standard UO_2^{+2} and Th^{+4} ions and eluted or extracted samples were counted for the same period and the average counts were determined. The difference of average counts and the background counts gave the gross counts. The data are given in Table 13 and 14.

TABLE 1: Distribution coefficients of metal ions on Amberlite IRA-400 in hydrochloric acid medium and aqueous methanol.

Sl. No.	Metal ion	% Methanol					
		90	80	60	40	20	0
1	UO_2^{+2}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
2	Th^{+4}	1.1	1.0	0.8	0.6	0.4	0.4
3	Fe^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
4	Al^{+3}	28.1	39.1	94.0	186.0	220.0	240.2
5	Zn^{+2}	735.0	780.0	826.0	872.0	910.0	940.0
6	Cd^{+2}	18.6	24.2	32.8	38.5	42.3	48.0
7	Ba^{+2}	3.2	4.6	4.9	3.9	5.2	3.8
8	Pb^{+2}	8.2	8.6	9.2	6.4	7.2	6.6
9	Bi^{+3}	0.8	0.7	0.8	0.6	1.2	2.1
10	Mo^{+6}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
11	Sr^{+2}	22.4	25.5	18.9	16.2	12.8	14.2
12.	La^{+3}	92.0	96.0	98.0	100.0	105.1	110.0
13	Nd^{+3}	85.2	88.0	90.0	92.7	96.0	102.0
14	Ce^{+3}	87.0	91.0	94.0	99.5	104.0	109.4
15	Zr^{+4}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
16	Pd^{+2}	80.0	42.0	38.2	38.2	38.2	38.2
17	Dy^{+3}	89.0	93.3	95.0	93.0	98.0	98.0
18	Yb^{+3}	91.6	92.0	96.0	93.2	92.0	89.0

TABLE 2: Distribution coefficients of metal ions on Amberlite IRA-400 in hydrochloric acid medium and aqueous ethanol.

Sl. No.	Metal ion	% Ethanol 90	80	60	40	20	0
1	UO_2^{+2}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
2	Th^{+4}	3.1	3.8	4.2	3.4	2.6	0.4
3	Fe^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
4	Al^{+3}	16.0	32.6	81.0	162.0	181.0	240.0
5	Zn^{+2}	642.2	671.6	710.0	760.0	815.3	940.0
6	Cd^{+2}	16.2	19.5	26.5	30.2	38.4	48.2
7	Ba^{+2}	1.8	2.6	3.4	4.0	4.3	3.8
8	Pb^{+2}	9.8	10.2	9.2	5.6	6.3	6.6
9	Bi^{+3}	1.0	1.2	0.7	0.6	1.1	2.0
10	Mo^{+6}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
11	Sr^{+2}	18.6	16.8	18.5	15.3	14.4	14.2
12	La^{+3}	110.0	122.0	129.0	120.0	125.0	110.0
13	Nd^{+3}	88.0	93.0	96.3	105.0	110.0	102.0
14	Ce^{+3}	89.0	93.0	96.0	103.1	105.0	109.4
15	Zr^{+4}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
16	Pd^{+2}	80.0	40.1	40.1	40.1	38.0	38.2
17	Dy^{+3}	86.0	86.0	90.0	91.0	94.2	98.0
18	Yb^{+3}	87.2	89.0	86.0	88.0	92.0	89.0

TABLE-3: Distribution coefficients of metal ions on Amberlite IRA-400 in hydrochloric acid medium and aqueous iso-propanol

Sl.No.	Metal ion	% Iso -propanol					
		90	80	60	40	20	0
1	UO_2^{+2}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
2	Th^{+4}	5.0	5.2	5.0	4.0	3.8	0.6
3	Fe^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
4	Al^{+3}	11.0	28.0	89.0	128.2	148.0	240.0
5	Zn^{+2}	715.0	775.0	790.0	810.0	850.0	940.0
6	Cd^{+2}	11.5	14.6	19.8	28.4	40.0	48.0
7	Ba^{+2}	0.8	1.1	1.8	2.8	3.4	3.8
8	Pb^{+2}	6.5	7.6	7.9	8.1	6.2	6.6
9	Bi^{+3}	1	1	1	1	1.2	2.1
10	Mo^{+6}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
11	Sr^{+2}	18.4	16.9	18.4	15.9	15.2	14.2
12	La^{+3}	104.0	110.0	118.0	124.0	108.0	110.0
13	Nd^{+3}	91.2	95.0	97.0	102.4	108.0	102.1
14	Ce^{+3}	91.0	94.0	97.4	101.0	103.0	109.4
15	Zr^{+4}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
16	Pd^{+2}	102.0	62.0	41.0	41.0	41.0	38.2
17	Dy^{+3}	86.0	89.0	90.0	90.0	98.2	97.9
18	Yb^{+3}	88.3	88.0	87.1	87.0	92.0	89.0

TABLE 4: Distribution coefficients of metal ions on Amberlite IRA-400 in hydrochloric acid medium and aqueous n-propanol.

Sl. No.	Metal ion	n-propanol					
		90	80	60	40	20	0
1	UO_2^{+2}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
2	Th^{+4}	2.5	2.8	3.2	3.6	2.0	0.4
3	Fe^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
4	Al^{+3}	20.0	45.0	98.2	180.0	212.0	240.2
5	Zn^{+2}	685.0	710.7	730.0	745.0	785.0	940.0
6	Cd^{+2}	13.5	16.2	19.8	28.0	43.0	48.0
7	Ba^{+2}	1.4	2.2	2.8	3.2	3.4	3.8
8	Pb^{+2}	6.8	8.8	8.5	5.8	6.6	6.6
9	Bi^{+3}	1.0	1.5	0.9	0.8	1.4	2.3
10	Mo^{+6}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
11	Sr^{+2}	16.5	17.2	17.8	16.0	14.8	14.2
12	La^{+3}	105.0	114.0	120.0	112.0	103.0	110.0
13	Nd^{+3}	93.0	96.0	99.0	103.1	106.0	102.0
14	Ce^{+3}	93.2	96.0	99.0	104.0	106.0	109.4
15	Zr^{+4}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
16	Pd^{+2}	64.0	42.0	42.0	42.0	41.0	38.2
17	Dy^{+3}	88.0	92.0	94.5	98.0	100.0	98.0
18	Yb^{+3}	84.0	88.0	88.0	88.0	91.0	89.0

TABLE 5: Distribution coefficients of metal ions on Amberlite IRA-400 in hydrochloric acid medium and aqueous tetrahydrofuran.

Sl. No.	Metal ion	% Tetrahydrofuran					
		90	80	60	40	20	0
1	UO_2^{+2}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
2	Th^{+4}	6.4	5.4	5.0	3.2	1.8	0.4
3	Fe^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
4	Al^{+3}	26.0	38.1	75.0	156.2	210.0	240.2
5	Zn^{+2}	610.0	666.0	716.6	768.0	900.2	940.0
6	Cd^{+2}	12.4	16.8	26.0	32.6	40.0	48.0
7	Ba^{+2}	0.9	1.1	1.6	1.6	2.1	3.8
8	Pb^{+2}	8.8	8.6	8.4	6.0	6.0	6.6
9	Bi^{+3}	1.4	1.4	1.4	1.4	1.4	2.1
10	Mo^{+6}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
11	Sr^{+2}	12.4	13.0	13.5	13.5	14.2	14.2
12	La^{+3}	100.2	100.2	104.0	106.0	108.0	110.1
13	Nd^{+3}	81.0	85.0	89.0	92.0	96.0	102.0
14	Ce^{+3}	83.2	87.0	89.0	94.0	99.1	109.4
15	Zr^{+4}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
16	Pd^{+2}	80.0	72.2	69.0	38.2	38.2	38.2
17	Dy^{+3}	81.0	84.0	88.0	91.0	93.1	98.0
18	Yb^{+3}	83.3	96.0	88.3	86.0	88.0	89.0

TABLE 6: Distribution coefficientsof metal ions on Amberlite IRA-400 in hydrochloric acid medium and aqueous acetic acid.

Sl. No.	Metal ion	% Acetic acid 90	80	60	40	20	0
1	UO_2^{+2}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
2	Th^{+4}	2.8	2.0	1.0	0.8	0.8	0.5
3	Fe^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
4	Al^{+3}	22.0	32.0	70.0	148.0	196.0	240.2
5	Zn^{+2}	620.0	660.2	692.0	705.0	880.0	940.0
6	Cd^{+2}	14.2	16.8	18.2	22.1	32.6	48.0
7	Ba^{+2}	1.0	1.6	2.2	2.7	3.0	3.8
8	Pb^{+2}	9.0	9.6	10.0	9.6	7.8	6.6
9	Bi^{+3}	1.0	1.0	1.4	1.8	2.0	2.1
10	Mo^{+6}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
11	Sr^{+2}	14.8	16.8	15.5	17.8	15.2	14.2
12	La^{+3}	98.0	98.5	100.5	104.0	108.0	110.0
13	Nd^{+3}	92.0	96.0	98.0	100.0	102.0	102.0
14	Ce^{+3}	87.0	91.2	94.0	97.0	100.0	109.0
15	Zr^{+4}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
16	Pd^{+2}	38.1	38.1	38.1	38.1	38.1	38.0
17	Dy^{+3}	87.0	89.0	90.0	90.0	98.0	98.0
18	Yb^{+3}	89.0	96.0	99.0	100.0	94.0	89.0

TABLE 7: Distribution coefficients of metal ions on Amberlite IRA-400 in nitric acid medium and aqueous methanol.

Sl. No.	Metal ion	% Methanol 90	80	60	40	20	0
1	UO_2^{+2}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
2	Th^{+4}	4.2	5.5	5.9	6.4	7.2	7.0
3	Fe^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
4	Al^{+3}	38.0	29.2	82.0	165.0	198.0	244.0
5	Zn^{+2}	724.0	520.0	520.0	280.0	280.0	300.0
6	Cd^{+2}	110.0	124.2	118.7	100.0	74.0	85.0
7	Ba^{+2}	6.5	7.2	8.5	9.0	10.2	12.5
8	Pb^{+2}	35.5	45.0	60.0	72.5	90.0	106.5
9	Bi^{+3}	1.5	2.8	2.0	1.6	1.4	1.9
10	Mo^{+6}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
11	Sr^{+2}	30.0	36.5	40.2	45.5	49.0	55.0
12	La^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
13	Nd^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
14	Ce^{+3}	920.0	920.0	920.0	940.2	940.2	810.0
15	Zr^{+4}	910.0	915.5	920.0	920.0	935.0	815.0
16	Pd^{+2}	125.0	125.0	110.0	90.0	70.0	75.0
17	Dy^{+3}	840.0	860.0	875.0	880.4	880.4	810.0
18	Yb^{+3}	842.0	865.5	875.0	885.0	892.0	812.0

TABLE 8: Distribution coefficients of metal ions on Amberlite IRA-400 in nitric acid medium and aqueous ethanol.

Sl. No.	Metal ion	% Ethanol					
		90	80	60	40	20	0
1	UO_2^{+2}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
2	Th^{+4}	3.5	4.6	5.8	6.9	6.9	7.0
3	Fe^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
4	Al^{+3}	42.0	48.0	71.0	148.0	210.0	244.0
5	Zn^{+2}	745.0	600.0	540.0	400.0	300.0	300.0
6	Cd^{+2}	105.0	105.0	110.0	116.1	100.0	85.0
7	Ba^{+2}	5.5	6.5	7.8	8.8	9.5	12.5
8	Pb^{+2}	45.0	41.0	36.0	48.2	92.0	106.5
9	Bi^{+3}	2.5	2.2	2.8	2.0	2.0	1.9
10	Mo^{+6}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
11	Sr^{+2}	50.0	50.0	54.0	60.0	55.2	55.2
12	La^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
13	Nd^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
14	Ce^{+3}	910.0	925.4	930.0	935.0	940.3	810.0
15	Zr^{+4}	900.0	915.0	922.0	930.0	935.5	815.0
16	Pd^{+2}	140.2	116.0	116.0	85.0	70.0	75.0
17	Dy^{+3}	860.0	860.0	850.0	890.0	900.0	810.0
18	Yb^{+3}	835.0	845.0	870.0	900.0	909.1	812.0

TABLE 9: Distribution coefficients of metal ions on Amberlite IRA-400 in nitric acid medium and aqueous iso-propanol.

Sl. No.	Metal ion	% Iso-propanol 90	80	60	40	20	0
1	UO_2^{+2}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
2	Th^{+4}	2.0	2.4	2.9	3.7	5.0	6.8
3	Fe^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
4	Al^{+3}	65.0	50.0	70.2	114.0	174.0	244.0
5	Zn^{+2}	710.0	680.0	540.0	540.0	400.0	300.0
6	Cd^{+2}	80.0	80.0	80.0	80.0	80.0	85.0
7	Ba^{+2}	16.8	15.0	15.0	14.1	13.2	12.5
8	Pb^{+2}	41.0	61.0	73.0	90.0	100.2	106.5
9	Bi^{+3}	1.0	1.5	1.8	2.0	2.4	1.9
10	Mo^{+6}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
11	Sr^{+2}	35.0	38.0	41.0	45.0	50.2	55.0
12	La^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
13	Nd^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
14	Ce^{+3}	810.0	915.0	915.0	915.0	925.0	810.0
15	Zr^{+4}	890.0	900.0	915.0	940.0	960.0	815.0
16	Pd^{+2}	123.0	114.0	94.2	88.0	90.0	75.00
17	Dy^{+3}	860.0	875.5	880.0	880.0	890.0	810.0
18	Yb^{+3}	855.0	860.0	870.0	870.0	880.0	812.0

TABLE 10: Distribution coefficients of metal ions on Amberlite IRA-400 in nitric acid and aqueous n-propanol.

Sl. No.	Metal ion	% n-propanol 90	80	60	40	20	0
1	UO_2^{+2}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
2	Th^{+4}	7.4	7.5	7.5	7.4	7.4	7.0
3	Fe^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
4	Al^{+3}	70.0	80.0	80.0	160.0	200.0	244.0
5	Zn^{+2}	700.00	680.0	641.0	600.0	390.0	300.0
6	Cd^{+2}	95.0	105.1	112.0	105.0	95.0	85.0
7	Ba^{+2}	8.2	7.8	8.3	10.7	13.0	12.5
8	Pb^{+2}	60.0	53.0	60.0	89.0	100.0	106.5
9	Bi^{+3}	1.0	1.8	3.0	2.5	2.0	1.9
10	Mo^{+6}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
11	Sr^{+2}	32.0	30.0	28.0	40.0	55.0	55.0
12	La^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
13	Nd^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
14	Ce^{+3}	930.0	935.0	935.0	490.0	940.0	810.0
15	Zr^{+4}	890.	900.0	905.0	915.0	947.0	815.0
16	Pd^{+2}	162.0	153.0	111.0	94.0	86.0	75.0
17	Dy^{+3}	745.0	800.0	840.0	840.0	880.0	810.0
18	Yb^{+3}	810.0	825.0	845.0	850.0	900.0	812.0

TABLE 11: Distribution coefficients of metal ions on Amberlite IRA-400 in nitric acid medium and aqueous tetrahydrofuran.

Sl. No.	Metal ion	% Tetrahydrofuran 90	80	60	40	20	0
1	UO_2^{+2}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
2	Th^{+4}	8.0	8.0	8.1	9.0	9.0	7.0
3	Fe^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
4	Al^{+3}	80.0	90.0	105.0	150.0	200.0	244.0
5	Zn^{+2}	720.0	680.0	490.0	440.0	400.0	300.0
6	Cd^{+2}	120.1	125.0	128.0	100.0	90.0	85.0
7	Ba^{+2}	6.0	8.5	10.9	12.0	12.0	12.5
8	Pb^{+2}	60.0	76.0	91.2	80.0	110.0	106.5
9	Bi^{+3}	2.0	2.0	2.0	1.5	1.5	1.9
10	Mo^{+6}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
11	Sr^{+2}	35.0	35.0	30.2	36.0	55.0	55.0
12	La^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
13	Nd^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
14	Ce^{+3}	900.0	900.0	920.0	920.5	940.0	810.0
15	Zr^{+4}	900.0	910.0	925.0	925.0	945.0	815.0
16	Pd^{+2}	148.0	125.0	117.0	97.0	86.0	75.0
17	Dy^{+3}	870.0	900.0	920.0	940.0	920.0	810.
18	Yb^{+3}	835.2	840.0	845.0	850.0	880.0	812.0

TABLE 12: Distribution coefficients of metal ions on Amberlite IRA-400 in nitric acid medium and aqueous acetic acid.

Sl. No.	Metal ion	% Acetic acid 90	80	60	40	20	0
1	UO_2^{+2}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
2	Th^{+4}	5.2	5.7	6.0	6.8	6.8	7.0
3	Fe^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
4	Al^{+3}	70.0	80.0	145.0	165.5	195.0	244.0
5	Zn^{+2}	740.0	540.0	300.0	400.0	350.0	300.0
6	Cd^{+2}	80.0	80.0	80.4	81.0	84.0	85.0
7	Ba^{+2}	10.5	11.0	11.5	13.0	12.5	12.7
8	Pb^{+2}	70.0	88.0	90.0	95.0	95.0	106.5
9	Bi^{+3}	1.0	1.7	1.9	2.3	2.4	2.0
10	Mo^{+6}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
11	Sr^{+2}	20.0	20.0	35.0	53.0	53.0	55.0
12	La^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
13	Nd^{+3}	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
14	Ce^{+3}	910.0	910.0	960.0	960.0	960.0	810.0
15	Zr^{+4}	880.0	900.0	920.6	920.6	935.0	815.0
16	Pd^{+2}	170.0	154.0	112.0	88.0	75.0	75.0
17	Dy^{+3}	876.0	878.0	900.0	900.0	875.0	810.0
18	Yb^{+3}	820.0	850.0	860.0	860.0	880.0	812.0

TABLE 13: Radiometric estimation of UO_2^{+2} and Th^{+4} using Primene JM-T and Amberlite IRA-400 resin.

Condition	Average background counts/minute	Average total counts/minute	Gross counts/minute	Percent activity
1 ml UO_2^{+2} solution	42	146	104	-
1 ml Th^{+4} solution	40	180	140	-
Th^{+4} activity in Primene JM-T	40	179	139	99.2
UO_2^{+2} activity eluted	41	143	102	98.0

TABLE 14: Radiometric estimation of UO_2^{+2} and Th^{+4} on Amberlite IRA-400.

Condition	Average background counts/minute	Average total counts/minute	Gross counts/minute	Percent activity
1 ml UO_2^{+2} solution	41	152	111	-
1 ml Th^{+4} solution	40	178	138	-
Th^{+4} activity passed out	42	178	136	98.5
UO_2^{+2} activity eluted	42	152	110	99.0

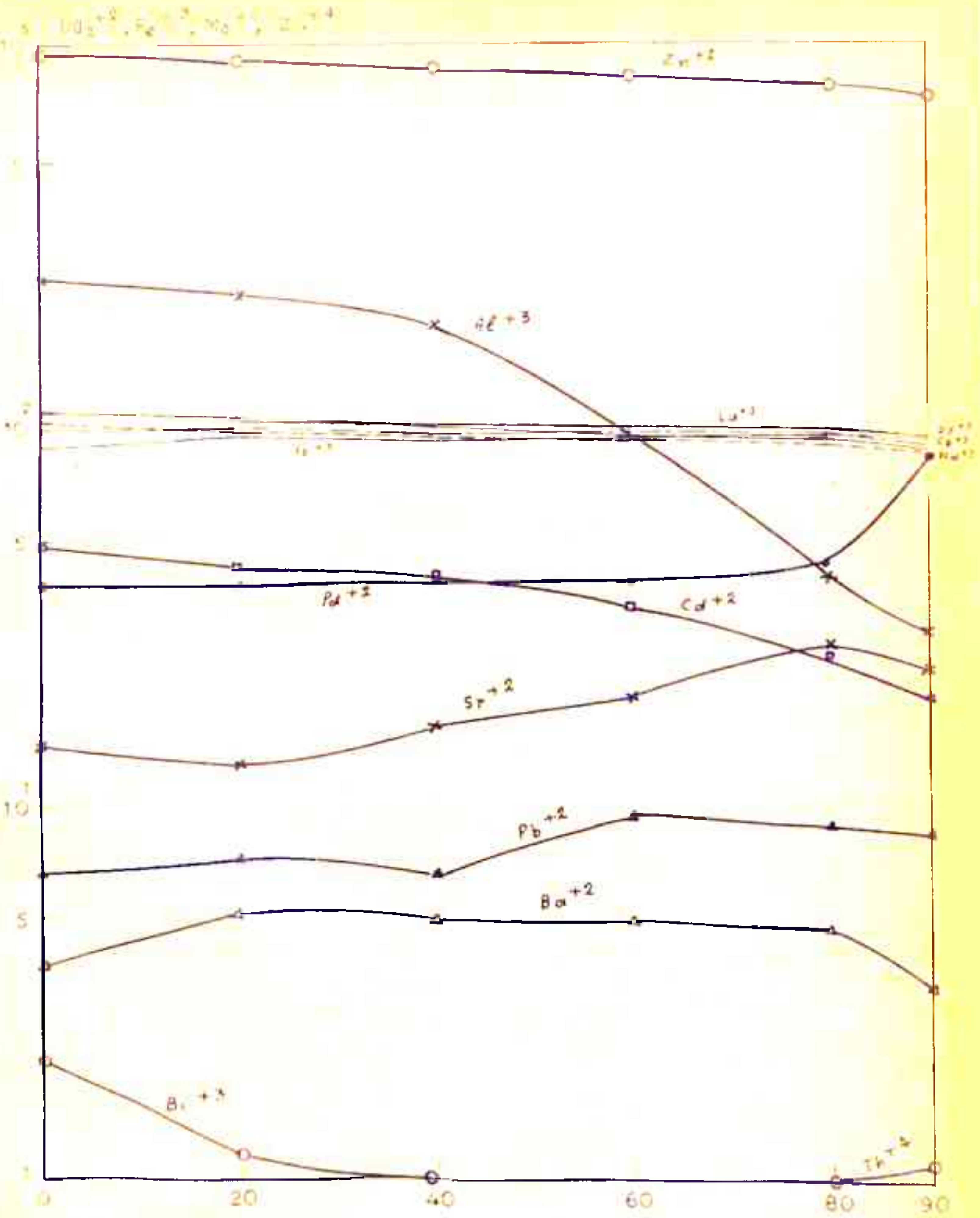
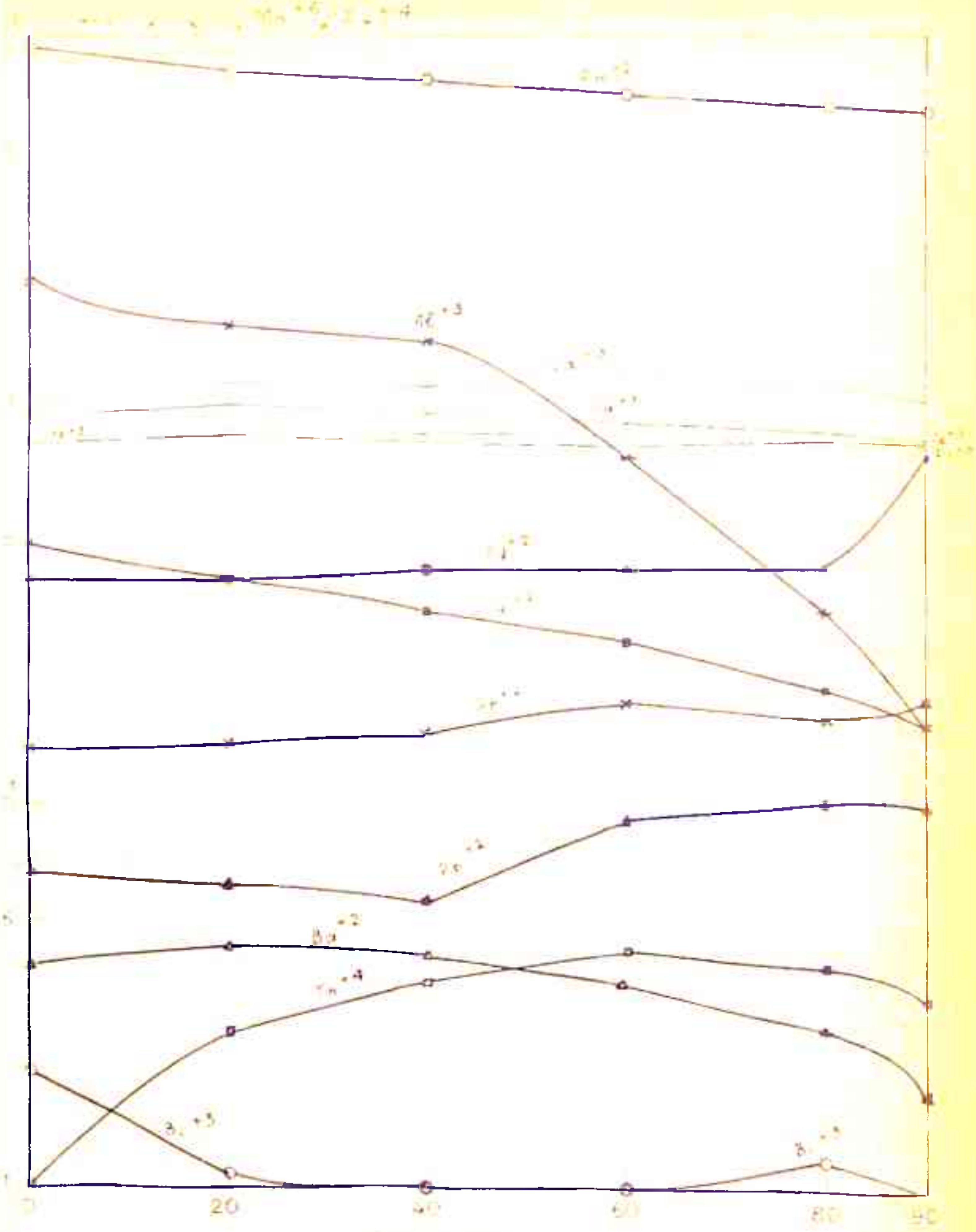


FIG. I DISTRIBUTION COEFFICIENTS OF METAL IONS IN AQUEOUS METHANOL (REF. TABLE I)



IG. 2 DISTRIBUTION COEFFICIENTS OF METAL IONS IN AQUEOUS ETHANOL (REF. TABLE 2)

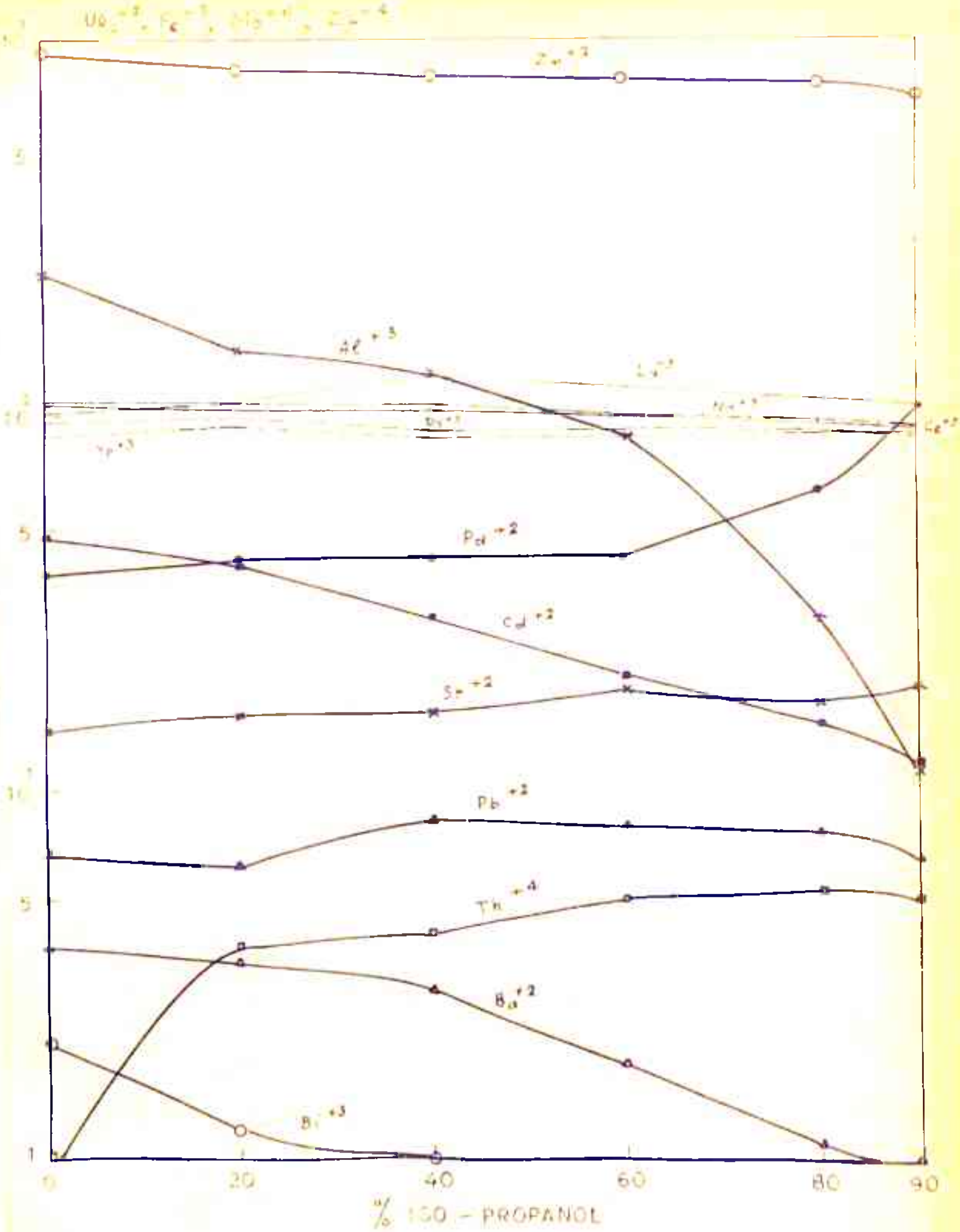
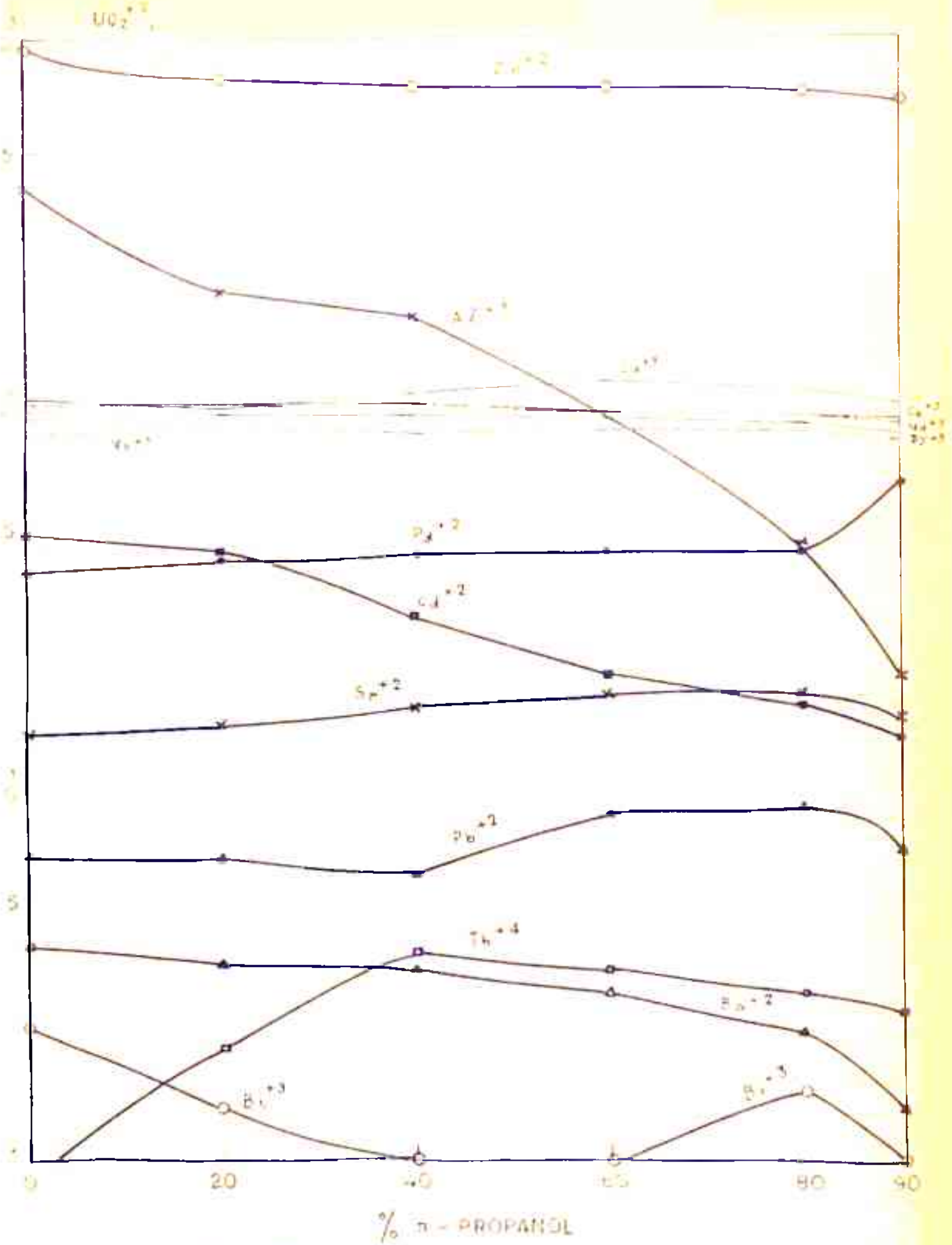


FIG. 3 DISTRIBUTION COEFFICIENTS OF METAL IONS IN AQUEOUS ISO - PROPANOL (REF. TABLE 3)



G. 4 DISTRIBUTION COEFFICIENTS OF METAL IONS IN AQUEOUS n - PROPANOL (REF. TABL. 4)

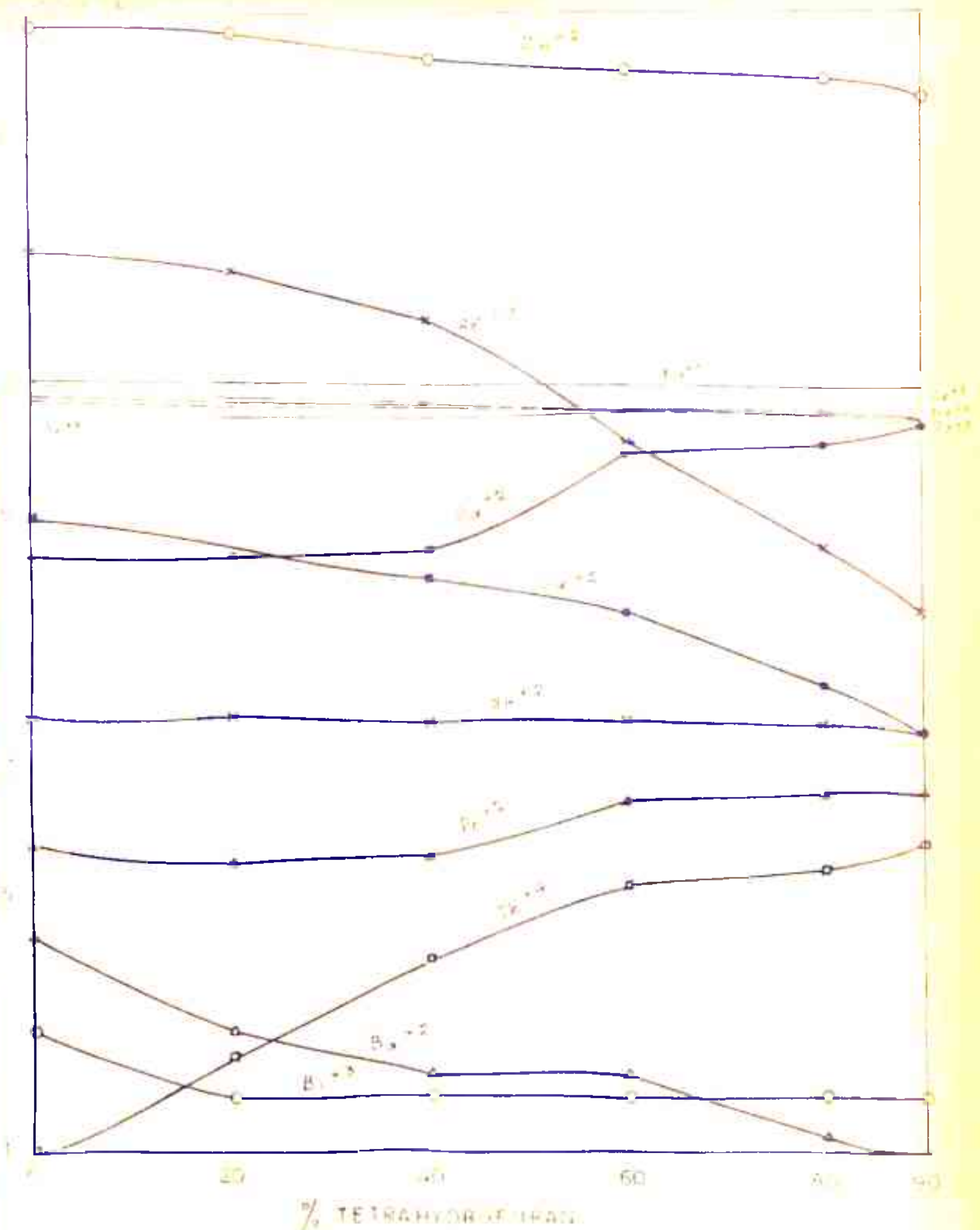
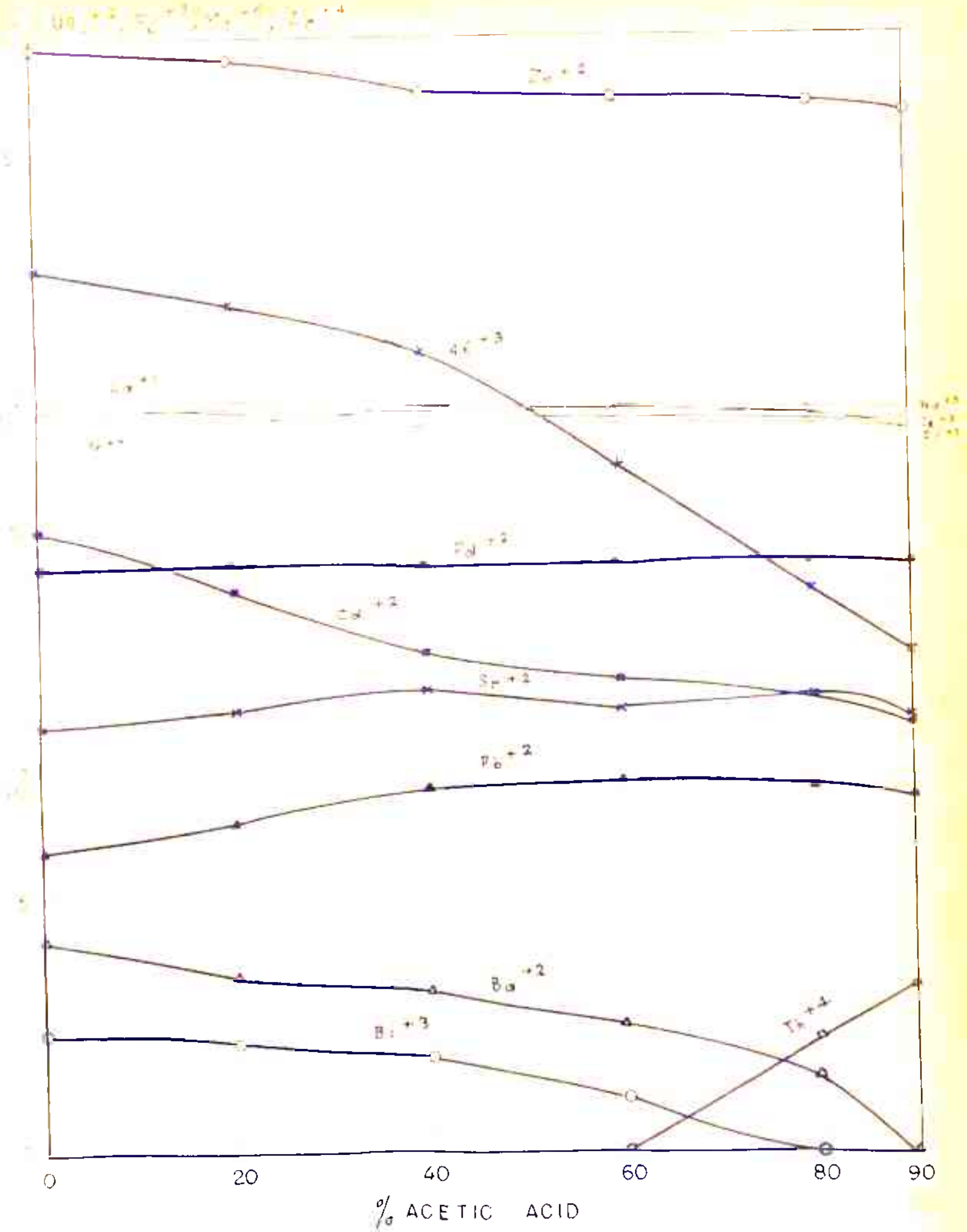
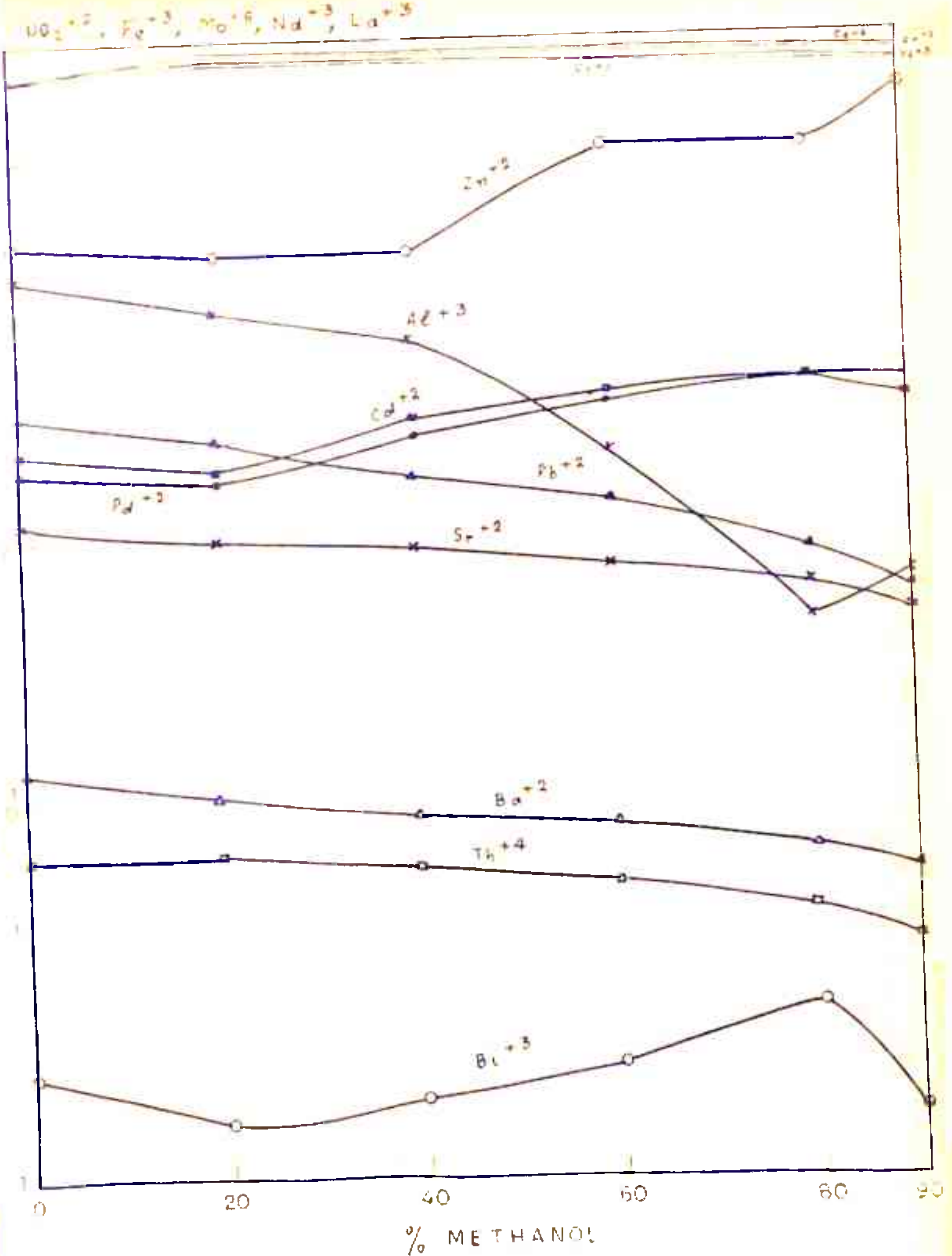


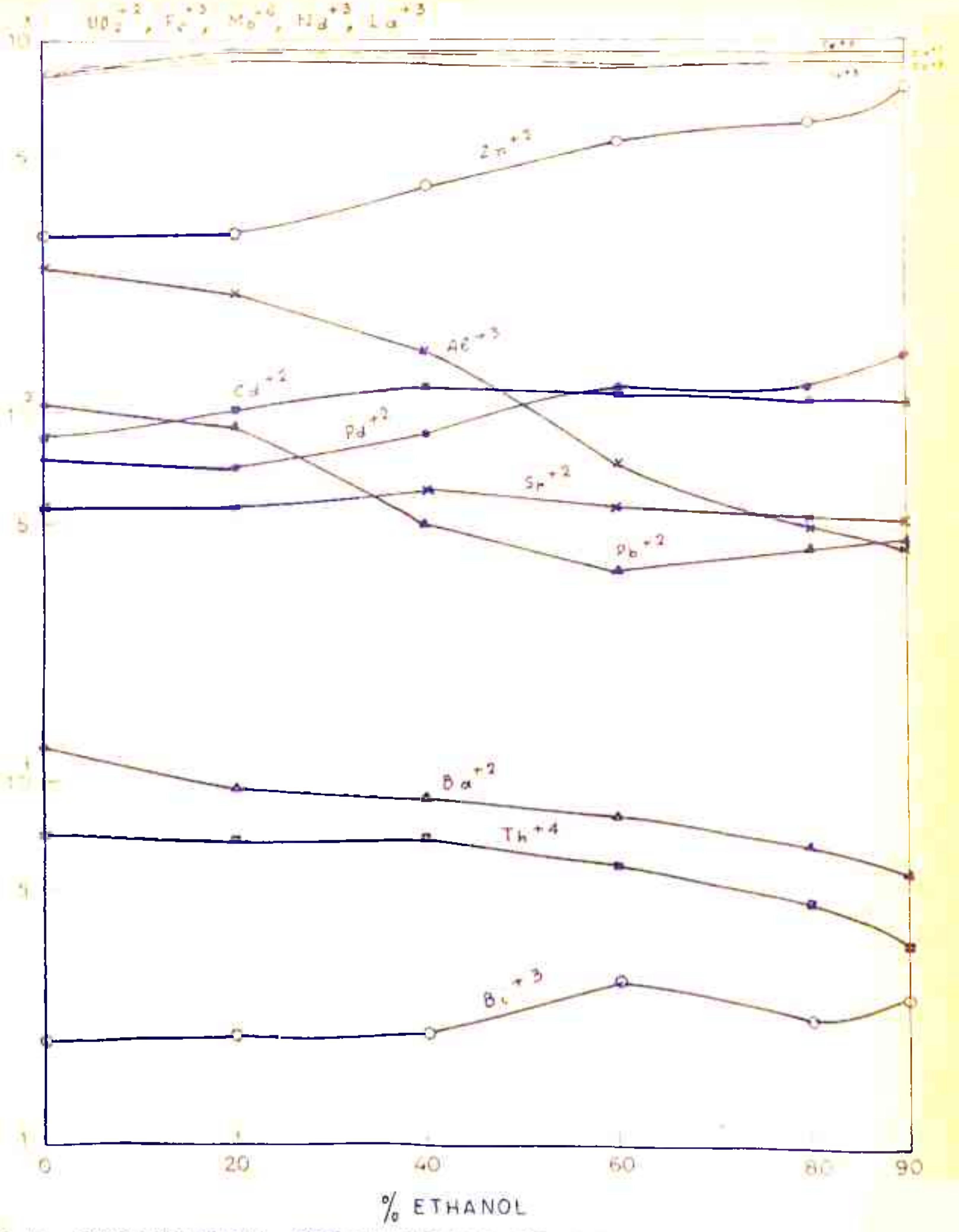
FIG. 5 DISTRIBUTION COEFFICIENTS OF METAL IONS IN AQUEOUS TETRAHYDROFURAN (REF. TABL. 5)



. 6 DISTRIBUTION COEFFICIENTS OF METAL IONS IN AQUEOUS ACETIC ACID (REF. TABLE 6)



G. 7 DISTRIBUTION COEFFICIENTS OF METAL IONS IN AQUEOUS METHANOL (REF. TABLE 7)



G.8 DISTRIBUTION COEFFICIENTS OF METAL IONS IN AQUEOUS ETHANOL (REF. TABLE 8)

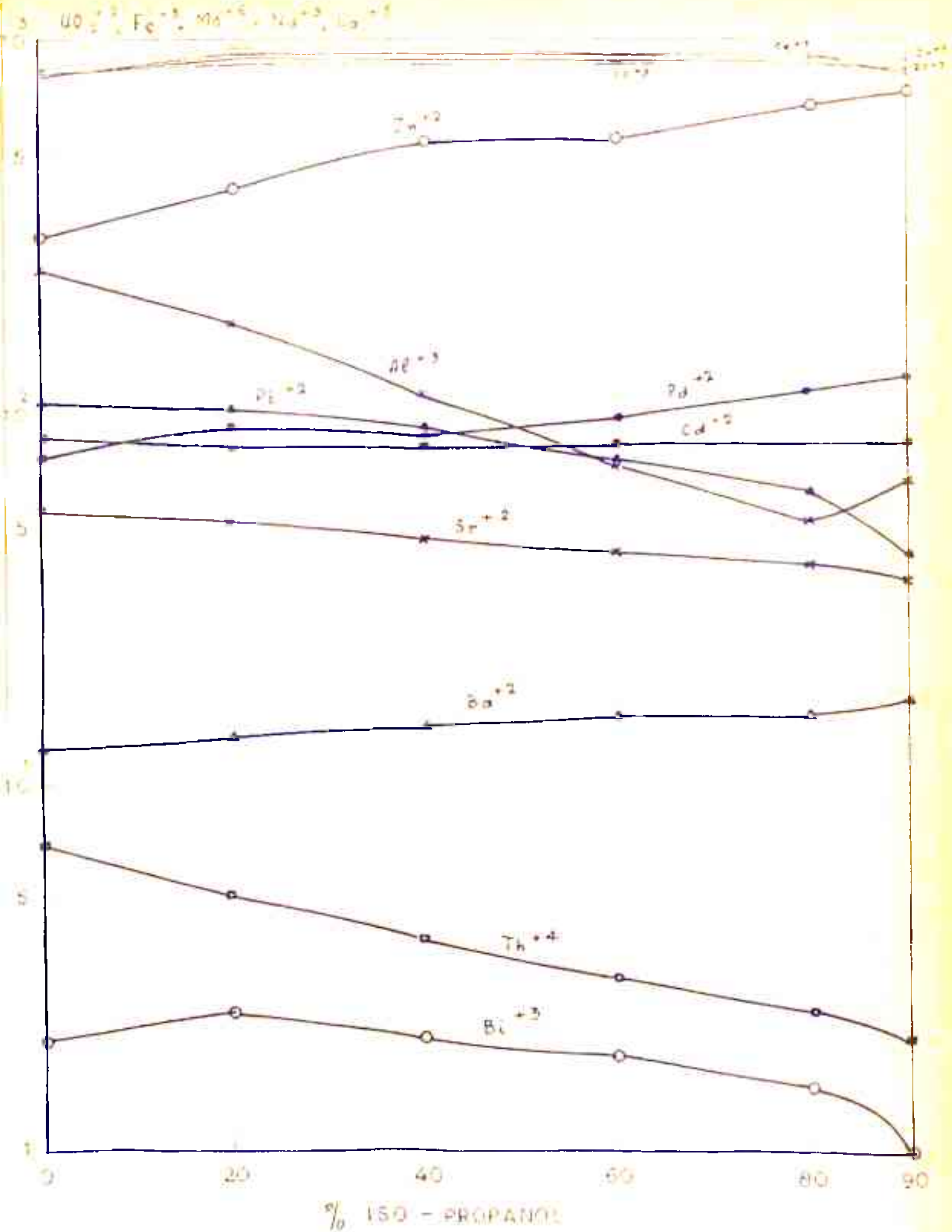
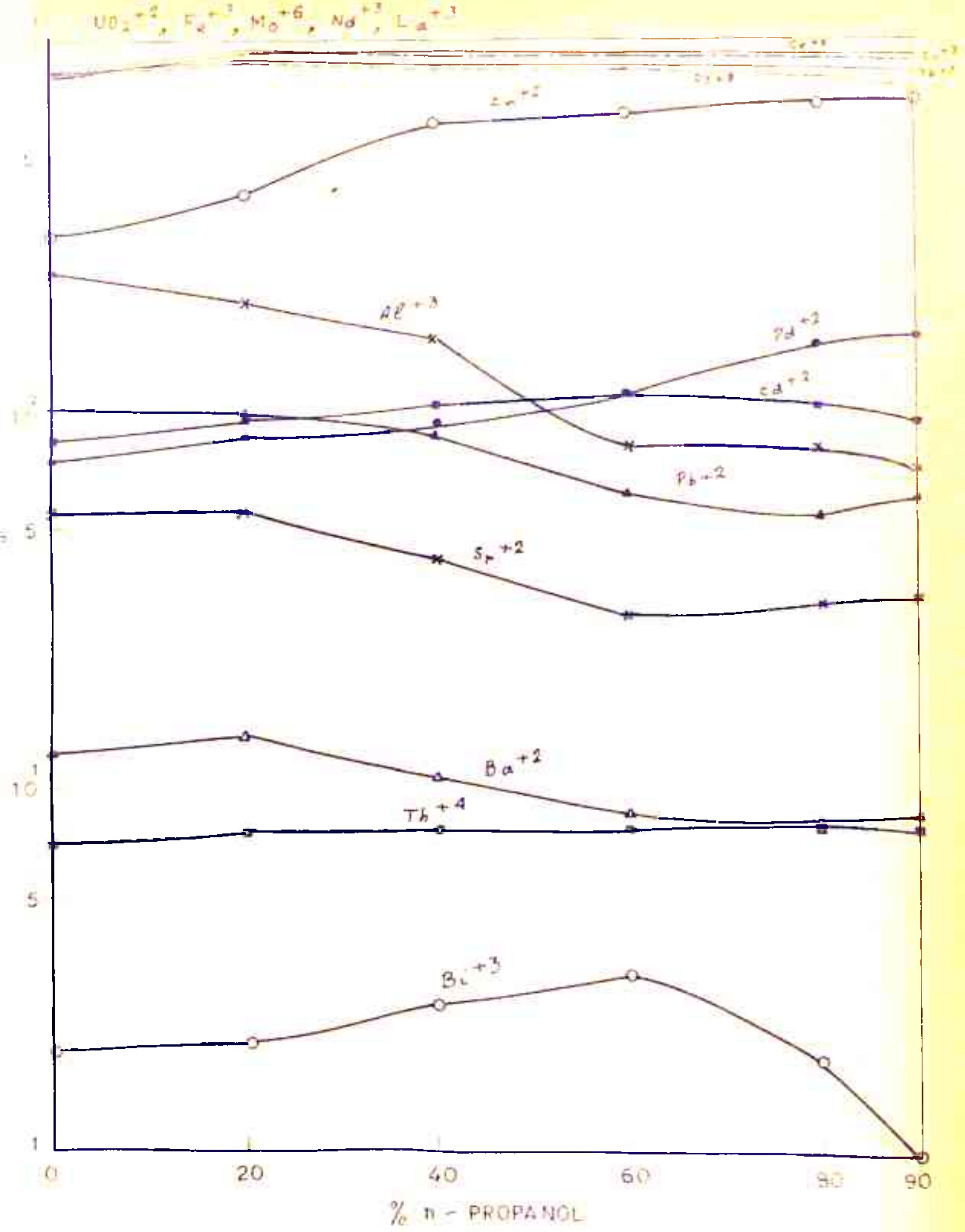
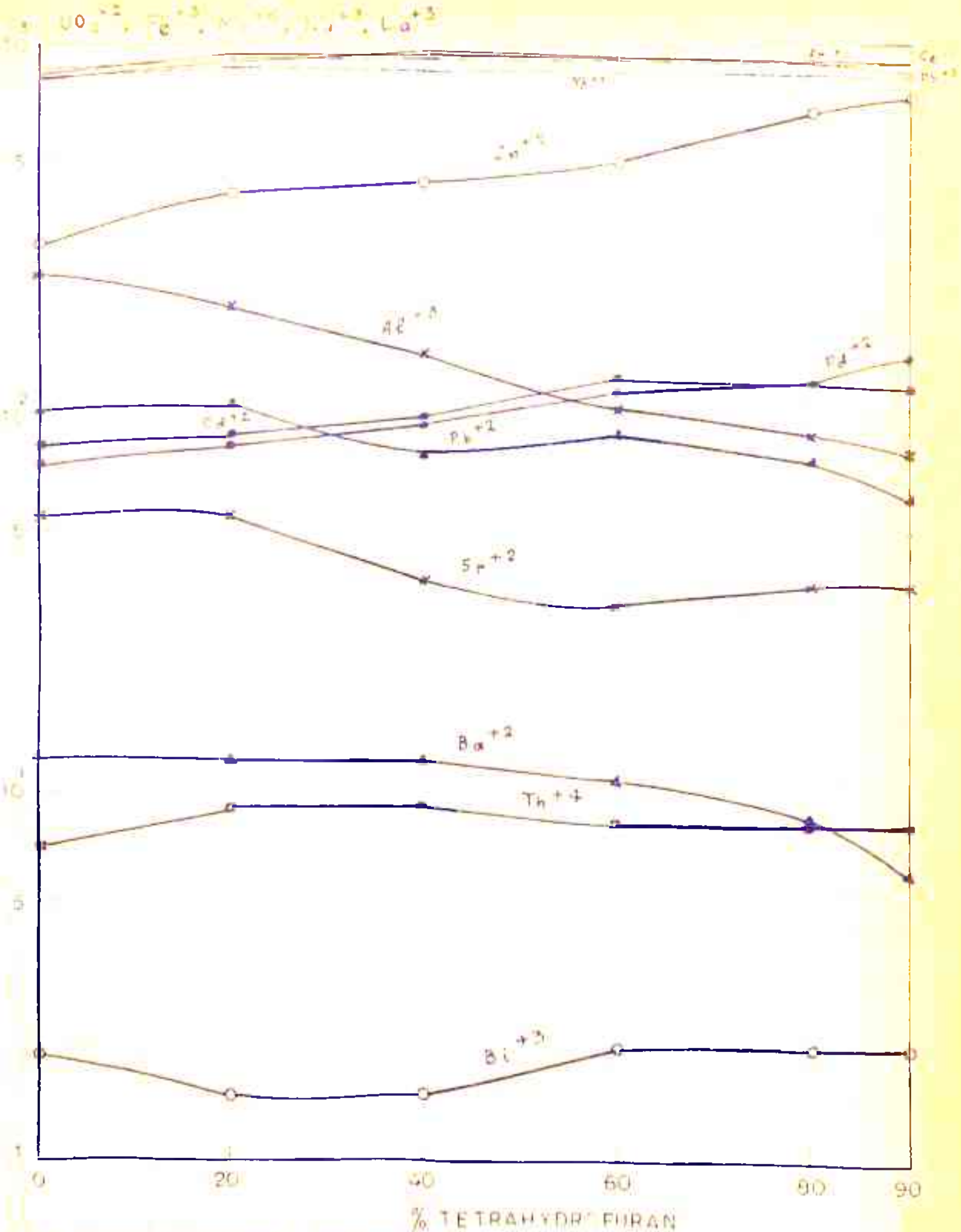


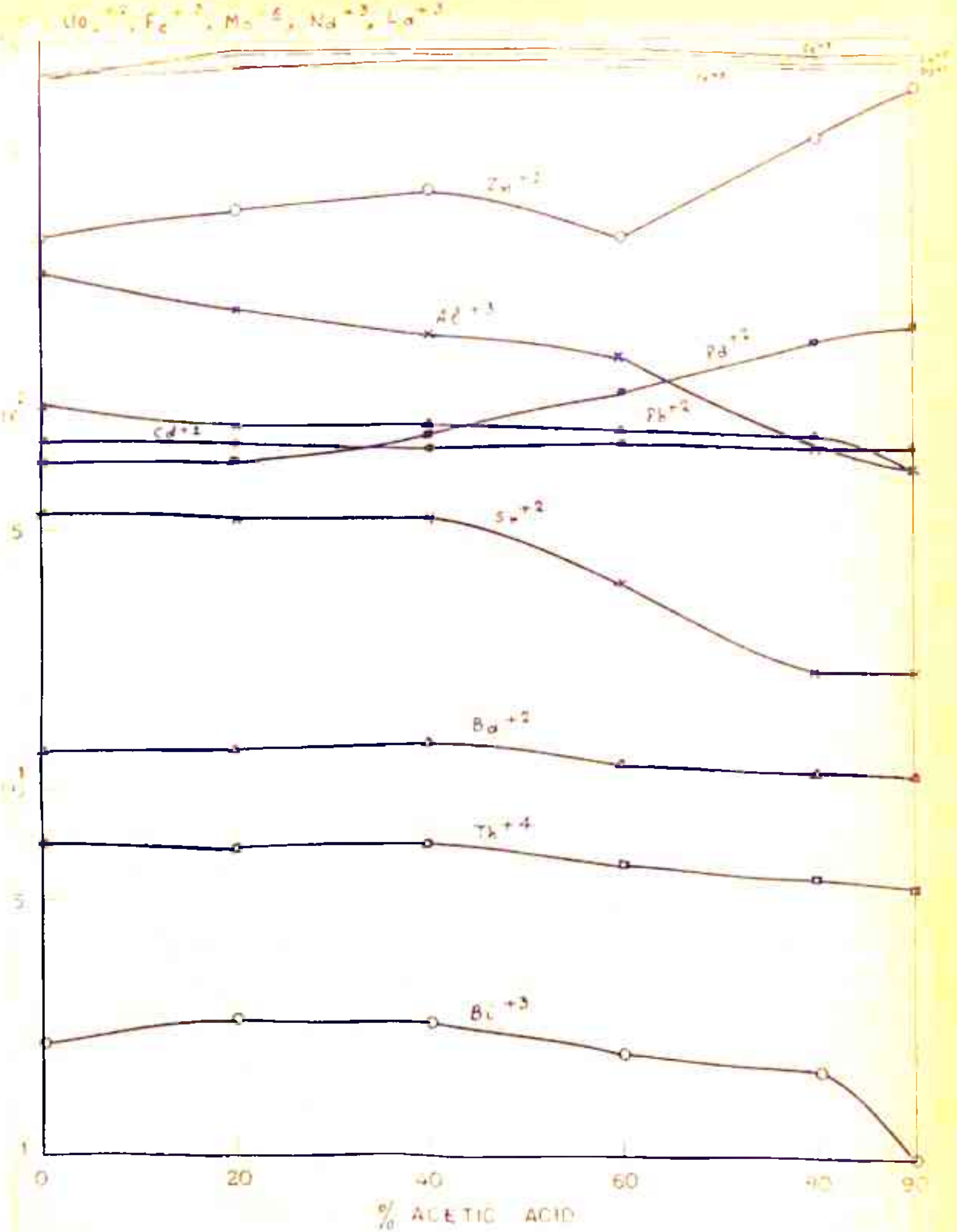
FIG. 9 DISTRIBUTION COEFFICIENTS OF METAL IONS IN AQUEOUS ISO-PROPANOL (REF. TABLE 9)



IG. 10 DISTRIBUTION COEFFICIENTS OF METAL IONS IN AQUEOUS n – PROPANOL (REF. TABLE 10)



G. II DISTRIBUTION COEFFICIENTS OF METAL IONS IN AQUEOUS TETRAHYDROFURAN (REF. TABLE II)



IG.12 DISTRIBUTION COEFFICIENTS OF METAL IONS IN AQUEOUS ACETIC ACID (REF. TABLE 12)

DISCUSSION

HYDROCHLORIC ACID MEDIUM:

In Methanol:

It appears from the Table 1 that UO_2^{+2}, Fe^{+3}, Zn^{+2}, Mo^{+6} and Zr^{+4} can be separated from all other ions used in the experiment. Th^{+4}, Bi^{+3} and Ba^{+2} can also be separated from all other ions. From the Figure 1 it appears that UO_2^{+2}, Th^{+4} and all other ions can be separated from the lanthanides ions like La^{+3}, Nd^{+3}, Ce^{+3}, Dy^{+3} and Yb^{+3}. Only ion that interferes with the rare-earth is Al^{+3} at 60% methanolic concentration. Thus this data can be utilised in the separation of UO_2^{+2}, Th^{+4} and rare-earths where three different Kd values give three distinct adsorption capacity on the resin.

In Ethanol:

It appears from the Table 2 and Figure 2 that UO_2^{+2}, Fe^{+3}, Mo^{+6}, Zr^{+4} can be separated from all other ions. Th^{+4} can be separated from the rare-earths and UO_2^{+2} ions but there are interferences by Ba^{+2} and Bi^{+3} at different concentrations of ethanol. Lanthanum can also be separated from Nd^{+3}, Dy^{+3} and Yb^{+3}. Aluminum ion interferes with a number of ions i.e., La^{+3}, Ce^{+3}, Nd^{+3}, Dy^{+3}, Yb^{+3}, Pd^{+2}, Sr^{+2} and Cd^{+2}. This system can be used for separation of UO_2^{+2}, La^{+3}, Th^{+4} and Pb^{+2} from each other as well as from the lanthanides Nd^{+3}, Ce^{+3}, Dy^{+3} and Yb^{+3}.

In Iso-Propanol:

Figure 3 shows that UO_2^{+2}, Fe^{+3}, Zn^{+2}, Mo^{+6} and Zr^{+4} can be separated from all other ions. Pb^{+2} can also be separated from all other ions. The number of interferences by different ions increase in this case. Al^{+3} and Pd^{+2} interfere with the rare-earth ions used in the experiment, also Al^{+3}, Pd^{+2}, Sr^{+2} and Cd^{+2} interfere with each other at different concentrations. However, in the absence of Al^{+3} and Pd^{+2}, actinide and lanthanide ions used in this experiment can be separated from each other.

In n-Propanol:

It appears from Table 4 and Fig.4 that UO_2^{+2} , Fe^{+3}, Zn^{+2}, Zr^{+4} and Mo^{+6} can be separated from all other ions. Pb^{+2} and Ba^{+2} can be separated from each other as well as from other ions except Th^{+4} which shows interference. Al^{+3} also interferes with the rare-earth ions. In addition to these interferences Pd^{+2}, Al^{+3}, Cd^{+2} and Sr^{+2} are interfering with each other. If Al^{+3} is absent, the rare-earth ions can be separated from UO_2^{+2} and Th^{+4} ions. However, the Kd values of rare-earth ions are so near to each other that a clean separation from each other is not possible.

In Tetrahydrofuran:

Figure 5 shows that UO_2^{+2}, Fe^{+3}, Zn^{+2}, Mo^{+6} and Zr^{+4} can be separated from all other ions. Th^{+4}, Pb^{+2} can be separated from all other ions except Ba^{+2} and Bi^{+3} which are interfering. Interference by Al^{+3}, Pd^{+2}, Cd^{+2} and Sr^{+2} is also observed where one or other of these ions show interference among them. The Kd values of rare-earth ions are so nearer to each other that it is not possible to separate them. Al^{+3} interferes with the rare-earth ions.

In Acetic Acid:

It is evident from the Table 6 that UO_2^{+2}, Fe^{+3} , Zn^{+2},MO^{+6} and Zr^{+4} can be separated from all other ions. Al^{+3} is interfering with the rare-earth ions. The interferences are observed with Al^{+3}, Pd^{+2} and Sr^{+2}. Similarly Ba^{+2} and Bi^{+3} show interference with thorium. The rare-earth ions have so close values that they are clustering around in a narrow Kd region. UO_2^{+2}, Th^{+4} and the rare-earths can be separated from each other provided Bi^{+3} and Ba^{+2} are not present there.

NITRIC ACID MEDIUM:

In Methanol:

It is observed from the Table 7 that UO_2^{+2}, Zn^{+2}, Fe^{+3}, La^{+3}, Nd^{+3} and Mo^{+6} can be separated from all other ions. Bi^{+3}, Th^{+4} and Ba^{+2} can be separated from each other as well as from other ions. Similarly Zn^{+2} can be separated from all other ions. There is an interference observed (Fig.7) with Pb^{+2}, Cd^{+2}, Pd^{+2}, Sr^{+2} and Al^{+3}, but these ions do not interfere with other ions. The rare-earth ions like Ce^{+3}, Dy^{+3}, Yb^{+3} as well as Zr^{+4} have so close Kd values that they are clustering around. However, they can be separated from other ions.

In Ethanol:

It is evident from the Table 8 that UO_2^{+2}, Fe^{+3}, Zn^{+2},

Mo^{+6}, La^{+3} and Nd^{+3} can be separated from all other ions. Ce^{+3}, Zr^{+4}, Dy^{+3} and Yb^{+3} have Kd values quite near to each other. Zn^{+2}, Ba^{+2}, Th^{+4} and Bi^{+3} can also be separated from all other ions. Interferences are observed between Pd^{+2}, Pb^{+2}, Sr^{+2} and Al^{+3} (Fig.8). Thus a number of ions can be separated from each other.

In Iso-propanol:

UO_2^{+2}, Fe^{+3}, Zn^{+2}, Mo^{+6}, La^{+3} and Nd^{+3} can be separated from all other ions. It is clear from Figure 9 that Zr^{+4}, Ce^{+3}, Dy^{+3} and Yb^{+3} have Kd values nearer to each other, but they can be separated from all other ions. Zn^{+2}, Ba^{+2}, Th^{+4} and Bi^{+3} can be separated from each other as well as from other ions. Al^{+3}, Pb^{+2}, Cd^{+2} and Pd^{+2} ions show interference with each other.

In n-propanol:

It appears from Table 10 that UO_2^{+2}, Fe^{+3}, Zn^{+2}, Mo^{+6}, La^{+3} and Nd^{+3} can be separated from all other ions. Bi^{+3}, Th^{+4}, Ba^{+2}, Sr^{+2} and Zn^{+2} can be separated from other ions as well as from each other. Figure 10 shows interference among Pd^{+2}, Cd^{+2}, Al^{+3} and Pb^{+2}. At the lower concentration there is more difference in the Kd values of Sr^{+2}, Th^{+4}, Ba^{+2} and Bi^{+3}. Rare-earth ions except La^{+3} and Nd^{+3} are clustering around and it is not possible to separate them from each other.

In Tetrahydrofuran:

In this case the same set of ions namely UO_2^{+2}, Fe^{+3}, Zn^{+2}, La^{+3} and Nd^{+3} can be separated from all other ions. Zn^{+2}, Sr^{+2}, Th^{+4} and Bi^{+3} can be separated from each other as well as other ions, however, Ba^{+2} interferes with the separation of Th^{+4} at higher concentration. Al^{+3}, Pd^{+2}, Cd^{+2} and Pd^{+2} show interference with each other (Fig.11). Upto 20% concentration of tetrahydrofuran, Kd values of Zn^{+2}, Pd^{+2}, Cd^{+2}, Al^{+3}, Pb^{+2}, Sr^{+2}, Th^{+4}, Ba^{+2} and Bi^{+3} are different from each other.

In Acetic Acid:

UO_2^{+2}, Fe^{+3}, Zn^{+2}, Mo^{+6}, La^{+3} and Nd^{+3} can be separated from all other ions. Zn^{+2}, Sr^{+2}, Ba^{+2}, Th^{+4} and Bi^{+3} can also be separated from each other as well as from other ions. Pd^{+2}, Cd^{+2}, Pb^{+2} and Al^{+3} show interference (Fig.12) with each other at higher concentration. Ce^{+3}, Zr^{+4}, Dy^{+3}, and Yb^{+3} have Kd values quite nearer to each other up to 30% acetic acid. Zn^{+2}, Pd^{+2}, Pb^{+2}, Cd^{+2}, Al^{+3}, Sr^{+2}, Ba^{+2}, Th^{+4} and Bi^{+3} have quite distinct Kd values.

Table 13 gives the radiometric estimation of uranium and thorium. A method has been developed for the separation of uranyl, thorium and platinum ions. Thorium ions are separated by solvent extraction using primene JM-T. The activities in the standard as well as the extracted sample are the same (99.2%). Uranyl ions have been eluted from the resin by water or tartaric acid or citric acid. The uranium activity eluted from the column is 98%. Similarly platinum was estimated colorimetrically. The eluted sample gave almost the same amount of platinum as was present in the original mixture.

In the table 14 some data for the separation of UO_2^{+2}, Th^{+4} and platinum ions are given. When a mixture containing all these ions is passed through a column of Amberlite IRA-400 the chloride complexes of platinum and uranium were adsorbed over the resin bed and Th^{+4} ions passed out of it. It appears from the Table 14 that 98.5% Th^{+4} activity came down. Uranium was eluted from the column by washing with water and 99% activity came down. Even if about 1% activity of Th^{+4} is subtracted from this, 98% of uranyl ions were definitely eluted from the column. Platinum is removed with 3N nitric acid and colorimetrically the eluted portion gave same absorbance as the standard sample used in the mixture of ions.

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CHAPTER 3

THIN LAYER CHROMATOGRAPHY

INTRODUCTION:

The resolution of solute mixtures on a medium (support) or on a solid surface by selective fixation and liberation with the aid of a fluid streaming in a definite direction is called chromatography. Another definition is given by Gordon, Martin and Synge[1], according to whom it is the technical procedure of analysis by percolation of fluids, with aid of which the mixture is introduced into a porous rigid material, which brings about the separation of the constituents, irrespective of the nature of physico-chemical changes that may take place. Strain[2] defines chromatography as an analytical technique for resolution of the solution in which separation is brought about by the differential migration in a porous medium and the migration is caused by the flow of the solvent.

The paper chromatography was the first step in the development of chromatography. In paper chromatography filter paper is used as an inert support of the aqueous stationary phase[3] in which the ions or molecules move with the solvent chiefly due to the capillary action in the filter paper medium. The movement of the solute in the filter paper is due to their diffusibilities which is generally different for different substances. This technique has been widely applied for the separation of the mixtures of organic compounds and to some extent for inorganic compounds too. In paper chromatography the filter paper serves as a porous medium for the migration of the solute, i.e., the process of the partition takes place on the filter paper. In this case the medium acts as a stationary phase through which the mobile phase passes and the solute migrates in the different portions of the medium. The stationary phase consists of water-cellulose complex[4] and adsorption takes place on it. The mobile phase travels over the filter paper setting an equilibrium between the water content of the complex and the mobile solvent. The partition of equilibrium depends upon the affinity towards the water-cellulose complex and the extent of miscibility with water and obviously the affinity for water increases when the solute is less captured by the complex. The solute molecules also having hydrophillic character either compete for position in water-cellulose complex or get attached to the water molecules already present in the complex. The distribution of the solute between the water-cellulose complex and the mobile phase depends upon the ease with which it enters either into the complex or moves along with the solvents. As this distribution differs from molecules to molecules and ions to ions, it is possible to separate them with the aid of filter paper and this is the basic principle on which the paper chromatography is based.

The second major development in this field was the introduction of gas chromatography. Later on the technical simplicity of paper chromatography and the speed of gas chromatography were combined together and this led to the development of the thin-layer chromatography (TLC). Izmailov and Shraiber[5] in 1938 reported that certain substances could be separated on thin layers of adsorbents on glass plates. The use of the thin layer of unbound adsorbent in predicting the best solvents for column chromatography was made by Crowe[6] in 1941. Williams[7] took two horizontal glass plates and the plate at the top had a small hole to introduce the sample and the developer. In 1949 Meinhard and Hall[8] used starch as a binding agent to hold the layer in proper place. In a number of publications between 1951-1957 Krichner, Miller and coworkers[9] investigated several adsorbents and binding agents. They also designed equipment[10] and studied the separation of terpenoids. These workers used very narrow plates with silicic acid-starch layer. Reitsema[11] used bigger plates and Mottier and Potterat[12] analysed food dyes over alumina and they separated amino acids by this technique. The work of other workers in this field before 1956 is reviewed by Demole[13]. The slow development in this technique took place because the equipment and chemicals were not easily available. Stahl[14] prepared standard size glass plates and standard adsorbent (silica gel - plaster of paris) and he named the technique thin layer chromatography. The technique developed very rapidly and again the work up to 1960 is reviewed by Demole[15].

Silica gel, alumina, Kieselguhr and cellulose are the most commonly used adsorbents in the thin layer chromatography. Other common substances used in this technique are polyamide powders, modified cellulose, calcium sulphate, polyethylene, magnesol, hydroxyl - apatite, sephadex, zinc carbonate and various mixtures of these. Waldi, Schnackerz and Munter[16] gave a comparative account of most widely used adsorbents and it was found that silica gel has the highest capacity to separate largest quantity of the mixture. Silica gel is acidic in nature and it can act in both adsorption and partition chromatography depending upon the solvents systems. Silica gel G contains a binder where G stands for gypsum.

The minimum thickness of the adsorbents is about 0.15 mm[14]. Honegger[17] reported that the best results could be obtained between 1 to 3 mm of the thickness of the adsorbents. Better results were obtained by Ritter and Meyer[18] using 1 mm thick layers. The thin layers prepared on glass plates were classified into three categories popularly known as the Kirchner type, the Stahl type and the spray type. In the Kirchner type apparatus the reservoir is kept stationary and a thin film is deposited over a glass plate which slowly passes under it. In Stahl type the spreading gadget keeps the plate stationary and the reservoir containing the slurry is moved slowly. The advantage of this type of apparatus is that the layer of the desired thickness can be prepared. In the spray type device the final thickness is unknown.

In the preparation of plates for thin layer chromatography the slurry is spread over the plate. The plates are activated by heating at the temperature 100-110°C for different periods of time. The time varies between one to several hours. Samples are applied to thin layers and the plates are placed in a solvent mixture. The migration caused by the metal ion is measured in terms of Rf values which were first introduced by Martin and Synge[19]. Mathematically the Rf value is expressed as the ratio of the rate of the movement of the solute and the rate of the movement of the solvents.

$$R_f = \frac{\text{Rate of the movement of the solute}}{\text{Rate of the movement of the solvent}}$$

Martin and Synge related the Rf values with the partition coefficient between the two phases by employing the concept of theoretical plates. Williams[7] has dealt Rf values considering all theoretical aspects in a purely methematical way. A new term R_m has also been introduced by Bate, Smith and Westall[20] which is nothing but $(\log \frac{1}{R_f} - 1)$ and it is proportional to the free energy of a moving molecule from one phase to the other.

Although the foundation of TLC as an analytical technique was laid down as early as 1938 but its development took place in the early 1950's. Upto 1958 it was used in the separation of organic substances. Since 1958 this method has been applied to numerous problems in analytical chemistry. A number of reviews in English[21], French[22], German[23-25] and Spanish[26] are available. A number of text-books are also available on this subject. The following books are of most value, which contain more or less detailed description of a number of separations as well as a thorough coverage of experimental methods and theory:

1. Thin Film Chromatography by E.V. Truter, Clever-Hume, Lond., 1963.
2. Thin Layer Chromatography by James N. Bobbitt, Reinhold Publishing Corporation, New York, 1964.
3. Laboratory Hand Book of Chromatographic Methods by O. Mikes translation editor R.A. Chalmers, Chapter 4, D. Van. Nostrand Company Ltd., London, 1966.

In this method the adsorption layer and the solvent can be changed and therefore this technique is better than the paper chromatography. A mixture of several substances can be separated more rapidly and in smaller time in comparison to the paper chromatography. Therefore this technique is more useful. Paper chromatography has been used for the separation of a number of ions using both normal and reversed phase techniques. Various solvents and mixtures of solvents have been used for the paper chromatographic separation of Th^{+4} and UO_2^{+2} from other metal ions. Acetyl acetone, aceto acetic ester and antipyrine with n-butanol containing 1.5 M nitric acid have been used by Pollard[27] for the separation of twenty four metal ions. Uranium, thorium and rare-earth were separated by butanol HCl mixtures[28]. Other solvents used were: amyl alcohol-formic acid, ethyl acetate - acetic acid, cyclohexanol - hydrochloric acid, ethyl ether - acid mixtures. Hahofer and Hecht[29] used n-butanol - 1.5 nitric acid for uranium separations. Thorium ions were separated from uranium ions with different solvent mixtures of methanol, pyridine toluene, n-butanol-dioxane, chloroform-toluene[30]. Uranium was separated from a number of metals using acetone-acetic acid water and acetone-HCl-water mixtures[31]. For the separation of uranium, methyl ethyl ketone, acetyl acetone, acetic acid mixtures were taken[32]. Formic acid-alcohol system was chosen for separation of tin and antimony from numerous metal ions by Qureshi and Khan[33]. Two dimensional paper chromatography was used for the separation of uranium in presence of thorium using ethyl alcohol-HCl-water and tetrahydrofuran-HNO_3-water[34].

The paper chromatographic separations are of considerable importance in the field of radiochemistry because a number of ions using both normal and reversed phase techniques were separated. The identical informations in the area of thin layer chromatography is insufficient although this method is rapid and its separation capacity is higher than the paper chromatography. Therefore the present work was undertaken with an objective to improve upon some of the separations achieved on paper chromatography. Further an attempt has been made to find out an alternative system of solvents for better separation of some actinides and lanthanides.

EXPERIMENTAL:

All chemicals used in the present investigation were of A.R. grade. Silica gel G Stahl (E.Merck) was treated with 6 M HCl and the supernatant liquid was decanted and the silica gel was again washed with acid and finally three times with distilled water. It was finally washed with 250 ml of ethanol and 250 ml of benzene and was dried in an oven at 120°C. Glass plates (20 x 20 cm) were washed with detergent and wiped with cotton soaked with hexane and dried before use. Silica gel G was mixed with double the amount of conductivity water and the slurry was prepared. The plates were placed on the polythene base of the Stahl type apparatus and the slurry was spread over the glass plates. The thickness of layer were 3 mm throughout the course of investigation. Plates were kept stationary for at least twenty minutes and then layers were activated by heating at 100-110°C for one hour in an oven.

All metal ions used were 0.1 M in nitrate form prepared from rare-earth oxides which were obtained from Johnson Mathew and Company except cerium (III) nitrate. The samples were applied to the bound layer by touching the tip of a filled capillary to the adsorbents layer. The diameter of the spot did not exceed 0.5 cm and it was kept as small as possible. The samples were spotted about one inch from the end of the plate so that the solvent level will be at least one cm below the centre of the spot.

Various organic complexing agents were used with the solvent system but they were found unsuitable though they could be used for few metal ions other than thorium and uranium. These complexing agents are -

(1) Benzal acetone
(2) Benzophenone
(3) Salicylaldehyde
(4) Acetyl acetone
(5) Primary amines
(6) 8-hydroxy quinoline
(7) Dimethyl glyoxime

A few solvents used above with complexing agents are: pyridine, dioxane, mesityl oxide, methanol, ethanol, n-propanol, iso-propanol and n-butanol, iso-butanol, tert.-butanol, cyclohexane, benzene, toluene, chloroform, carbontetrachloride, ethyl ether, ethyl acetate and cyclohexanol.

The development was performed continuously in an ascending manner on near vertical plates in an air-tight container saturated with solvent vapour. The time of development was about three hours for the entire experiment. Results were reproducible under similar conditions at the same temperature.

The visualization of developed chromatogram was carried out in several ways. A 5% solution of potassium ferrocyanide produced brown colouration for uranyl ions and blue colouration for ferrous ions. For aluminium and silver ions, 8-hydroxy quinoline (ammonical solution) was used as a visualizer. Other metal ions were detected using 1% alcoholic solution of Alizarin Red S and finally developed in an atmosphere of ammonia. Hemotoxylin (0.2% ethanolic solution) was used as a visualizer for all other ions except uranyl ions and ferrous ions.

The solvent systems used in Tables 1-4 consist of 80 ml dioxane, 20 ml acid of concentration, 0.1N, 0.5N, 1.5N and 2.5N (HCl, H_2SO_4, HNO_3 and $C_2H_4O_2$) and 2 g m-nitrobenzoic acid. A number of experiments were performed to ascertain the amount of m-nitrobenzoic acid. It was found that 2 g of m-nitrobenzoic acid was sufficient. Therefore 2 g of this compound was taken for all the experiments. The composition of the solvent systems in the Table 5 is given below:

A : 60 ml t.-butanol+30 ml ethanol+30 ml $4NHNO_3$
B : 50 ml t.-butanol+40 ml ethanol+30 ml $2NHNO_3$
C : 40 ml t.-butanol+50 ml ethanol+30 ml $1NHNO_3$
D : 30 ml t.-butanol+60 ml ethanol+30 ml $0.2NHNO_3$

The systems in the Tables 6,7, and 8 were the same except nitric acid was replaced by hydrochloric acid, sulphuric acid and acetic acid. In the Table 9, 90 ml ethanol and 10 ml $4NHNO_3$ was taken. In the Table 10, nitric acid was replaced by hydrochloric acid. In the Tables 11, 90 ml iso-butanol and 10 ml $4NHNO_3$ and in the Table 12, 90 ml iso-butanol and 10 ml 4N HCl were taken. The Rf values are recorded in the Tables 1-12.

TABLE 1: R_f values of metal ions with dioxane solvent in nitric acid medium at room temperature.

Sl. No.	Metal ions	Nitric acid			
		0.1N	0.5N	1.5N	2.5N
1	Fe^{+3}	0.59	0.55	0.46	0.45
2	UO_2^{+2}	0.99	0.94	0.88	0.82
3	Al^{+3}	0.47	0.39	0.33	0.30
4	Th^{+4}	0.91	0.76	0.70	0.46
5	Cr^{+3}	-	-	-	-
6	Zr^{+4}	0.66	0.56	0.44	0.40
7	Ca^{+2}	-	-	-	-
8	La^{+3}	0.65	0.57	0.44	0.38
9	Ce^{+3}	0.66	0.57	0.44	0.42
10	Pr^{+3}	0.66	0.56	0.43	0.41
11	Nd^{+3}	0.71	0.61	0.52	0.41
12	Sm^{+3}	0.69	0.56	0.49	0.41
13	Eu^{+3}	0.99	0.88	0.70	0.42
14	Gd^{+3}	0.68	0.57	0.46	0.43
15	Er^{+3}	0.61	0.53	0.46	0.41
16	Yb^{+3}	0.57	0.49	0.40	0.29
17	Lu^{+3}	0.66	0.52	0.43	0.41
18	Y^{+3}	0.64	0.56	0.45	0.41

TABLE 2: Rf values of metal ions with dioxane solvent in hydrochloric acid at room temperature.

Sl. No.	Metal ions	Hydrochloric acid			
		0.1N	0.5N	1.5N	2.5N
1	Fe^{+3}	0.98	0.88	0.81	0.80
2	UO_2^{+2}	0.92	0.86	0.79	0.79
3	Al^{+3}	0.39	0.34	0.31	0.26
4	Th^{+4}	0.29	0.31	0.36	0.42
5	Cr^{+3}	0.38	0.32	0.30	0.21
6	Zr^{+4}	0.30	0.26	0.21	0.20
7	Ca^{+2}	0.31	0.23	0.21	0.20
8	La^{+3}	0.25	0.29	0.32	0.31
9	Ce^{+3}	0.24	0.28	0.31	0.37
10	Pr^{+3}	0.37	0.34	0.30	0.29
11	Nd^{+3}	0.38	0.31	0.27	0.29
12	Sm^{+3}	0.26	0.28	0.30	0.24
13	Eu^{+3}	0.31	0.34	0.36	0.31
14	Gd^{+3}	0.31	0.36	0.39	0.42
15	Er^{+3}	0.33	0.29	0.31	0.39
16	Yb^{+3}	0.34	0.36	0.38	0.39
17	Lu^{+3}	0.26	0.29	0.31	0.24
18	Y^{+3}	0.35	0.38	0.39	0.40

TABLE 3: Rf values of metal ions with dioxane solvent in sulphuric acid at room temperature.

Sl. No.	Metal ions	Sulphuric acid			
		0.1N	0.5N	1.5N	2.5N
1	Fe^{+3}	0.49	0.52	0.48	0.19
2	UO_2^{+2}	0.86	0.80	0.84	0.86
3	Al^{+3}	0.54	0.56	0.59	0.64
4	Th^{+4}	0.64	0.68	0.71	0.22
5	Cr^{+3}	-	-	-	-
6	Zr^{+4}	0.49	0.53	0.56	0.43
7	Ca^{+2}	-	-	-	-
8	La^{+3}	0.86	0.81	0.79	0.74
9	Ce^{+3}	0.48	0.51	0.61	0.79
10	Pr^{+3}	0.49	0.52	0.64	0.78
11	Nd^{+3}	0.46	0.48	0.53	0.78
12	Sm^{+3}	0.44	0.48	0.56	0.78
13	Eu^{+3}	0.49	0.52	0.54	0.39
14	Gd^{+3}	0.54	0.58	0.66	0.79
15	Er^{+3}	0.46	0.49	0.54	0.58
16	Yb^{+3}	0.44	0.46	0.49	0.31
17	Lu^{+3}	0.44	0.46	0.49	0.28
18	Y^{+3}	0.46	0.49	0.52	0.36

TABLE 4: Rf values of metal ions with dioxane solvent in acetic acid medium at room temperature.

Sl. No.	Metal ions	Acetic acid			
		0.1N	0.5N	1.5N	2.5N
1	Fe^{+3}	0.99	0.98	0.95	0.78
2	UO_2^{+2}	0.69	0.74	0.82	0.80
3	Al^{+3}	0.95	0.94	0.92	0.89
4	Th^{+4}	0.41	0.44	0.46	0.47
5	Cr^{+3}	-	-	-	-
6	Zr^{+4}	0.66	0.69	0.71	0.70
7	Ca^{+2}	0.39	0.29	0.24	0.23
8	La^{+3}	0.41	0.40	0.38	0.37
9	Ce^{+3}	0.39	0.46	0.56	0.40
10	Pr^{+3}	0.39	0.41	0.46	0.52
11	Nd^{+3}	0.41	0.47	0.52	0.42
12	Sm^{+3}	0.42	0.39	0.38	0.36
13	Eu^{+3}	0.39	0.37	0.39	0.39
14	Gd^{+3}	0.36	0.38	0.40	0.38
15	Er^{+3}	0.42	0.50	0.58	0.44
16	Yb^{+3}	0.44	0.46	0.51	0.56
17	Lu^{+3}	0.29	0.31	0.30	0.24
18	Y^{+3}	0.46	0.52	0.58	0.46

TABLE 5: Rf values of metal ions with ter.-Butanol-Ethanol-HNO_3 at room temperature

Sl. No.	Metal ions	4N A	2N B	1N C	0.2N D
1	UO_2^{+2}	0.94	0.84	0.80	0.78
2	Th^{+4}	0.98	0.86	0.84	0.82
3	La^{+3}	0.88	0.90	0.92	0.86
4	Sm^{+3}	0.97	0.86	0.95	0.96
5	Zr^{+4}	0.96	0.92	0.94	0.84
6	Nd^{+3}	0.93	0.91	0.90	0.86
7	Lu^{+3}	0.94	0.95	0.93	0.92
8	Yb^{+3}	0.99	0.96	0.93	0.94
9	Gd^{+3}	0.97	0.98	0.96	0.88
10	Er^{+3}	0.95	0.91	0.83	0.93
11	Ce^{+3}	0.91	0.89	0.86	0.84
12	Pr^{+3}	0.88	0.79	0.86	0.88
13	Ni^{+2}	0.91	0.86	0.83	0.88
14	Co^{+2}	0.94	0.84	0.89	0.82
15	Mn^{+2}	0.93	0.84	0.93	0.87
16	Cr^{+3}	0.89	0.87	0.86	0.84
17	Fe^{+3}	0.87	0.81	0.86	0.91
18	Al^{+3}	0.88	0.89	0.97	0.81
19	Ag^{+1}	0.95	0.86	0.88	0.91
20	Pb^{+2}	0.86	0.85	0.87	0.89
21	Bi^{+3}	0.95	0.89	0.92	0.89
22	Cd^{+2}	0.92	0.94	0.91	0.83
23	Cu^{+2}	0.94	0.87	0.83	0.87
24	Hg^{+2}	0.93	0.97	0.88	0.96

TABLE 6: Rf values of metal ions with t.-Butanol-Ethanol-HCl at room temperature.

Sl. No.	Metal ions	4N A	2N B	1N C	0.2N D
1	UO_2^{+2}	0.86	0.88	0.84	0.82
2	Th^{+4}	0.87	0.80	0.93	0.88
3	La^{+3}	0.97	0.89	0.92	0.90
4	Sm^{+3}	0.86	0.83	0.94	0.88
5	Zr^{+4}	0.90	0.88	0.89	0.91
6	Nd^{+3}	0.83	0.79	0.86	0.85
7	Lu^{+3}	0.86	0.79	0.89	0.82
8	Yb^{+3}	0.89	0.83	0.90	0.87
9	Gd^{+3}	0.89	0.86	0.74	0.78
10	Er^{+3}	0.88	0.93	0.82	0.80
11	Ce^{+3}	0.76	0.86	0.82	0.72
12	Pr^{+3}	0.79	0.82	0.83	0.74
13	Ni^{+2}	0.88	0.79	0.87	0.83
14	Co^{+2}	0.91	0.86	0.79	0.87
15	Mn^{+2}	0.87	0.77	0.82	0.80
16	Cr^{+3}	0.82	0.82	0.81	0.81
17	Fe^{+3}	0.79	0.80	0.78	0.76
18	Al^{+3}	0.60	0.75	0.89	0.90
19	Ag^{+1}	0.84	0.80	0.86	0.79
20	Pb^{+2}	0.85	0.83	0.76	0.75
21	Bi^{+3}	0.89	0.91	0.92	0.84
22	Cd^{+2}	0.86	0.81	0.80	0.80
23	Cu^{+2}	0.83	0.82	0.80	0.80
24	Hg^{+2}	0.85	0.81	0.84	0.82

TABLE 7: Rf values of metal ions with t.-Butanol-Ethanol-H_2SO_4 at room temperature.

Sl. No.	Metal ions	4N A	2N B	1N C	0.2N D
1	UO_2^{+2}	0.70	0.91	0.88	0.90
2	Th^{+4}	0.72	0.85	0.83	0.92
3	La^{+3}	0.89	0.88	0.87	0.89
4	Sm^{+3}	0.81	0.85	0.87	0.88
5	Zr^{+4}	0.93	0.94	0.95	0.94
6	Nd^{+3}	0.86	0.91	0.90	0.91
7	Lu^{+3}	0.87	0.91	0.92	0.91
8	Yb^{+3}	0.93	0.88	0.92	0.91
9	Gd^{+3}	0.89	0.86	0.88	0.88
10	Er^{+3}	0.82	0.81	0.80	0.84
11	Ce^{+3}	0.79	0.81	0.83	0.82
12	Pr^{+3}	0.88	0.92	0.91	0.90
13	Ni^{+2}	0.84	0.86	0.87	0.86
14	Co^{+2}	0.89	0.88	0.87	0.83
15	Mn^{+2}	0.90	0.82	0.84	0.82
16	Cr^{+3}	0.91	0.91	0.91	0.91
17	Fe^{+3}	0.80	0.86	0.85	0.85
18	Al^{+3}	0.82	0.84	0.85	0.86

TABLE 8: Rf values of metal ions with t.-Butanol-Ethanol-Acetic Acid at room temperature

Sl. No.	Metal ions	4N A	2N B	1N C	0.2N D
1	UO_2^{+2}	0.56	0.68	0.79	0.69
2	Th^{+4}	0.18	0.13	0.17	0.10
3	La^{+3}	0.79	0.76	0.82	0.81
4	Sm^{+3}	0.52	0.62	0.15	0.10
5	Zr^{+4}	0.40	0.54	0.42	0.52
6	Nd^{+3}	0.41	0.36	0.45	0.35
7	Lu^{+3}	0.92	0.84	0.83	0.79
8	Yb^{+3}	0.88	0.88	0.94	0.82
9	Gd^{+3}	0.73	0.79	0.42	0.66
10	Er^{+3}	0.78	0.74	0.51	0.76
11	Ce^{+3}	0.28	0.60	0.62	0.39
12	Pr^{+3}	0.25	0.52	0.56	0.40

TABLE 9: Rf values of metal ions with Ethanol-HNO_3 at room temperature.

Sl. No.	Metal ions	4N HNO_3
1	Fe^{+3}	0.73
2	UO_2^{+2}	0.92
3	Al^{+3}	0.74
4	Tb^{+4}	0.62
5	Cr^{+3}	0.25
6	Zr^{+4}	0.16
7	La^{+3}	0.66
8	Sm^{+3}	0.66
9	Ce^{+3}	0.66
10	Nd^{+3}	0.70
11	Er^{+3}	0.68
12	Y^{+3}	0.68
13	Gd^{+3}	0.70
14	Pr^{+3}	0.66
15	Yb^{+3}	0.68
16	Lu^{+3}	0.70
17	Eu^{+3}	0.62
18	Ca^{+2}	0.58

TABLE 10: Rf values of metal ions with Ethanol-HCl at room temperature.

Sl. No.	Metal ions	4N HCl
1	Fe^{+3}	0.89
2	UO_2^{+2}	0.82
3	Al^{+3}	0.75
4	Th^{+4}	0.49
5	Cr^{+3}	-
6	Zr^{+4}	0.39
7	La^{+3}	0.46
8	Sm^{+3}	0.46
9	Ce^{+3}	0.51
10	Nd^{+3}	0.55
11	Er^{+3}	0.55
12	Y^{+3}	0.51
13	Gd^{+3}	0.51
14	Pr^{+3}	0.51
15	Yb^{+3}	0.50
16	Lu^{+3}	0.49
17	Eu^{+3}	0.32
18	Ca^{+2}	0.21

TABLE 11: Rf values of metal ions with Iso-butanol-HNO_3 at room temperature.

Sl. No.	Metal ions	4N HNO_3
1	Fe^{+3}	0.81
2	UO_2^{+2}	0.92
3	Al^{+3}	0.82
4	Th^{+4}	0.79
5	Cr^{+3}	0.76
6	Zr^{+4}	0.41
7	La^{+3}	0.70
8	Sm^{+3}	0.68
9	Ce^{+3}	0.70
10	Nd^{+3}	0.67
11	Er^{+3}	0.72
12	Y^{+3}	0.70
13	Gd^{+3}	0.71
14	Pr^{+3}	0.72
15	Yb^{+3}	0.69
16	Lu^{+3}	0.72
17	Eu^{+3}	0.71
18	Ca^{+2}	0.29

TABLE 12: Rf values of metal ions with Iso-butanol-HCl at room temperature.

Sl. No.	Metal ions	4N HCl
1	Fe^{+3}	0.62
2	UO_2^{+2}	0.32
3	Al^{+3}	0.80
4	Th^{+4}	0.12
5	Cr^{+3}	0.60
6	Zr^{+4}	0.29
7	La^{+3}	0.14
8	Sm^{+3}	0.14
9	Ce^{+3}	0.13
10	Nd^{+3}	0.14
11	Er^{+3}	0.15
12	Y^{+3}	0.13
13	Gd^{+3}	0.13
14	Pr^{+3}	0.13
15	Yb^{+3}	0.14
16	Lu^{+3}	0.13
17	Eu^{+3}	0.11
18	Ca^{+2}	-

DISCUSSION:

A perusal of the data recorded in the Table 1 shows that UO_2^{+2} and Th^{+4} ions can be separated from the lanthanides using 2.5N nitric acid with dioxane at room temperature. These ions can also be separated from Fe^{+3}, Al^{+3}, Zr^{+4} at this concentration. However the rare-earths ions have Rf values quite similar or near to each other. Uranyl and Th^{+4} ions can also be separated from the lanthanides at 0.5N HNO_3. But the separation of Fe^{+3} is not better than that used with 2.5N HNO_3. The separation of the rare-earths shows identical characteristics discussed with 2.5N HNO_3. A comparison of the Rf values with 0.5N and 2.5N nitric acid shows that a better separation of uranyl and thorium ions can be achieved by using 0.5N nitric acid and dioxane mixture. The observations recorded in the Table 2 show that uranyl and Th^{+4} ions can be separated from all other rare-earths using 0.1N HCl concentration. It has been observed that uranyl ions separation can be achieved with all other concentration of hydrochloric acid but some interferences have been observed in the separation of Th^{+4} ions, where some rare-earths have identical Rf values. The separation of uranyl ions and thorium ions can also be done from Fe^{+3}, Al^{+3}, Cr^{+3}, Zr^{+4} and Ca^{+2}. The Rf values of the lanthanides obtained in this experiment are either identical or are clustering together. The data presented in the Table 3 show that uranyl ions and Th^{+4} ions can be separated from lanthanides, Fe^{+3}, Al^{+3} and Zr^{+4} using either 1.5N or 2.5N sulphuric acid and dioxane. If 1.5N sulphuric acid is used, a number of rare-earths can also be separated although exceptions have to be made for those having Rf values identical with each other. It appears from the Table 4 that separation of uranyl and thorium ions from lanthanides, Fe^{+3} and Al^{+3} is possible using either 0.5N or 2.5N acetic acid. The better separation is achieved using 0.5N acetic acid where the lanthanides can also be separated from each other.

An examination of the Table 5 shows that uranyl and Th^{+4} ions can be separated from lanthanides and some other metal ions listed there. The solvent system for this separation is a mixture of t.-butanol, ethanol and 1N nitric acid. This separation is also possible with 0.2N nitric acid but cobalt ions have identical Rf values to thorium ions. The selectivity of these twenty four ions is based upon the fact that all of these ions are present in fission-products of uranium and thorium and their separation always poses a challenge in the radio-chemistry. Although the separation is not better than those discussed with reference to the Tables 1-4, but this system is definitely of analytical interest because twenty-two ions can be separated from thorium and uranium. In this case the rare-earths ions show the similar nature as observed with the cases discussed earlier. It is concluded from the Rf values recorded in the Table 6 that the solvent system t.-butanol-ethanol-1N HCl can be used for the separation of uranyl and thorium ions from other twenty-one ions including rare-earths ions. Here Hg^{+2} ions interface in the separation with the uranyl ions. In this solvent system 4N, 2N and 0.2N hydrochloric acid does not serve any useful analytical purpose. A number of rare-earths ions can also be separated in this case but some of them cannot be separated because they have same Rf values. It can be found out from the Table 7 that uranyl and Th^{+4} ions can be separated from sixteen other metal ions including lanthanides using t.-butanol-ethanol-4N sulphuric acid. All other concentrations of sulphuric acid do not give useful separation. It can be seen from the Table 8 that uranyl and Th^{+4} ions can be separated from ten other lanthanides using t.-butanol-ethanol and acetic acid (1N, 2N or 4N) but in this case a number of ions do not develop fairly well and therefore their Rf values are not recorded in the Table 8. Acetic acid poses the limitation as an analytical solvent system for the separation of some actinides and lanthanides because the number of such ions have been reduced to 50%.

A perusal of Tables 9 and 10 shows that ethanol and 4N HNO_3 or 4N HCl can be used in the separation of UO_2^{+2} from Th^{+4} and other ions including some lanthanides. However the separation of Th^{+4} ions is not possible with some lanthanides. The solvent system iso-butanol-4N HNO_3 (Table 11) can be used for the separation of UO_2^{+2} and Th^{+4} ions from sixteen other ions including some lanthanides. If in this solvent system nitric acid is replaced by hydrochloric acid of identical strength separations are possible but the Rf values are so nearer to each other that it is not of much practical use.

The temperature has an effect on the Rf values. Some experiments were performed at higher temperature and it was observed that Rf values decrease with the increase of temperature. Hence all the experiments were performed at room temperature.

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CHAPTER 4

SOLVENT EXTRACTION

INTRODUCTION

Tri-butyl phosphate, TBP, has been studied much more extensively than any of the other organophosphorous extractants and, indeed, probably more than any other extractant. Its dielectric constant is about 8[1] and electrolytes are essentially unionised in pure TBP or in dilute solutions of TBP[2]. There is an evidence that electrolytes may ionise in hydrated TBP or in concentrated solutions of TBP[3,4]. This compound is non-volatile at the room temperature and remains liquid between -80°C - 289°C[5]. It is very highly viscous and its solubility in water is 0.4 gm per litre at the room temperature. Its density is quite close to that of water. Therefore it is diluted by heptane, benzene, kerosene, carbontetrachloride and n-butyl ether. The best diluting agents for TBP are aromatic and aliphatic hydrocarbons[6-12]. The distribution coefficients decrease with an increase in the temperature[13-21].

TBP forms a monohydrate with water in dilute solutions of TBP in organic solvents. If the concentration of TBP is greater than 0.1M other species may be present such as H_2O2TBP. IR spectra of the system TBP-water has been interpreted as indicating weak hydrogen bonding between the phosphoryl groups and water molecules[22,23]. Whitney and Diamond[24] reported that $TBP.H_2O$ is present upto 0.1M, while Bullock and Tuck[25] found the system to be quite complicated. They suggest the formation of $(TBP)_2.H_2O$, $(TBP)_3.2H_2O$, and

$(TBP)_{n+1}.nH_2O$. Olander and Benedict[26] view the dissolving of water in TBP as a mass transfer process involving no complexation. The elements which are well extracted include gold(III), uranium(IV & VI), neptunium (IV & VI), thorium zirconium, hafnium, cerium (IV) and others depending upon the conditions used. Ishimori and Watanabe[27] has given distribution coefficients for extraction of metal nitrates of a number of ions by hundred per cent TBP. Some of these metal nitrates extracted are: $LiNO_3.2TBP$[28], $NaNO_3.3TBP$[29], $Cu(NO_3)_2.3TBP.H_2O$[30]. All the lanthanides form anhydrous trisolvates[31]. Similarly Ce(III), iron (III) also form trisolvates. Tetravalent metals probably extract as disolvates of TBP, although other solvates have been reported. Peppard[32] found that solvation number of thorium, zirconium and scandium varies with nitric acid concentration. The hexavalent actinides extracts as disolvates. The formation of $UO_2(NO_3)_2.2TBP$ has been confirmed by many workers[33-39]. Salt effects, solvents effects, temperature effects and competing anion effects for the extraction of uranium by TBP has also been studied. When TBP is saturated with uranium (VI) nitrate, the composition of the complex remains the same. In presence of a high concentration of nitric acid and TBP the formation of $HUO_2(NO_3)_3.2TBP$[40] was detected. Infra red spectra have been interpreted as indicating that lithium, magnesium, nickel(II), iron(III), and chromium(VI) nitrates are hydrated in TBP while thorium and uranium (VI) nitrates are anhydrous[22].

A complex of the composition HNO_3.TBP with nitric acid and TBP is formed and it is anhydrous[41-50]. The amount of nitric acid extracted is greater than that expected from the above complex. On this basis additional complexes such as $2HNO_3$.TBP, $3HNO_3$.TBP, $4HNO_3$.TBP and $2HNO_3$.TBP.H_2O, $3HNO_3$.TBP.H_2O are reported[51]. In the species HNO_3.TBP, the nitric acid molecule is bonded to the phosphoryl oxygen for species such as $3HNO_3$.TBP. There is disagreement as to whether two additional nitric acid molecules are bonded to the oxygen in the alkoxy groups or to the nitrate oxygen. The TBP in an organic diluent extracts nitric acid, the water content of the organic phase decreases until the acid concentration in the organic phase equals to that of TBP. The excess amount of nitric acid extracted in TBP increases the water content of the organic phase. This is due to the formation of 1:1 complex and then hydration of that complex and of the nitric acid extracted in excess of 1:1 complex.

Since the extraction of uranyl nitrate and nitric acid was done extensively by TBP, it was planned to extract uranyl perchlorate and thorium tetrachloride in TBP. The extraction of actinides was done with phosphine oxides and substituted phosphime oxides, phosphinates, phosphonates and phosphates. As none of these compounds were available, uranyl perchlorate and thorium tetrachloride were used for solvent extraction.

Sulphoxides, like the phosphine oxides, were also used as solvent extractants since 1958. The reaction of complex formation by sulphoxides with organic substances was reported by Sterlnikova[52]. Aliphatic sulphoxides are used for estimation of mineral acids and uranium salts by solvent extraction techniques. Di-n-pentyl sulphoxides have also been used as extractants for thorium[53,54]. Cation-exchange behaviour of several metal ions in dimethyl sulphoxides-aqueous hydrochloric acid media has been studied by Birge[55] and anion exchange behaviour by Phipps[56]. Studies with cations in dimethyl sulphoxide by ion-exchange are reported by Tanener[57]. It was decided to investigate some of the solvent extraction properties of an aryl sulphoxide. Diphenyl sulphoxide was selected for this purpose and this work reports some results with DPSO.

EXPERIMENTAL AND DISCUSSION

Extraction of uranium and thorium with TBP:

Uranyl perchlorate was prepared by the method suggested by Sutton[58]. In this method one mole of UO_3 is dissolved in 2 moles of perchloric acid and the following reaction takes place:

$$UO_3 + 2HClO_4 = UO_2(ClO_4)_2 + H_2O$$

The concentration of uranyl perchlorate solution prepared in this manner was determined by a gravimetric method. The uranyl perchlorate was dried and burnt to U_3O_8. The heating of uranyl perchlorate can be done safely. The following solutions were taken for the investigation:

1. Uranyl perchlorate (0.5M)
2. Sodium perchlorate (4M)
3. Thorium tetrachloride (0.01M)
4. Tri-n-butyl phosphate, TBP, 30% in carbon tetrachloride
5. Perchloric acid (0.3M)
6. Hydrochloric acid, 0.1M to 4M.

A mixture containing 5 ml uranyl perchlorate, 5 ml thorium tetrachloride, 1 ml sodium perchlorate, 5 ml perchloric acid and 5 ml of hydrochloric acid of varying concentrations was taken and 4 ml water was mixed with 25 ml of 30% TBP solution in a separating funnel. The funnel was stoppered and shaken well in a mechanical shaker. The time interval for the mixing varied from 5 minutes to 1 hour and equilibrium was attained in one hour. The two layers were separated for the analysis. Uranium and thorium were extracted in the TBP solution. Thorium was removed from the organic phase using 10% sodium per-iodate solution. It requires three washing containing 3 M HCl to remove thorium. Thorium was estimated by thoron as a complexing agent[59]. Uranium was determined in the aqueous phase by PAR[60]. Uranium in the organic phase was determined by first stripping with the solution of sodium carbonate followed by the use of sodium peroxide. Thorium in the aqueous phase was determined using thoron. The solutions were diluted before estimation so that the amount of thorium was about 8 micro-gram/ml and uranium was 6 micro-gm/ml. The distribution coefficients were determined for uranium and thorium ions, and are given in Table 1.

TABLE 1: Extraction of uranium and thorium from hydrochloric acid solution by TBP in carbon tetrachloride

Molarity of HCl (M)	Distribution Coefficients	
	U(VI)	Th(IV)
0.1	110	6.0
0.2	124	6.5
0.5	140	7.1
0.7	160	7.4
1.0	170	7.8
1.5	192	8.0
2.0	206	8.5
2.5	220	8.9
3.0	260	9.5
4.0	262	9.5

It appears from the Table 1 that the distribution coefficient increases with the increase of concentration, of HCl, but finally at 3M hydrochloric acid concentration, it attains a steady value. Therefore, this concentration of acid was selected for the solvent extraction.

In another set of experiments the amount of sodium perchlorate was increased stepwise upto 5 ml and the amount of water was decreased simultaneously and extraction was carried out keeping other constituents the same except HCl at 3M. The results of these measurements are given in Table 2.

TABLE 2: Effect of sodium perchlorate on the extraction of uranium and thorium.

Sodium perchlorate added in ml.	Distribution coefficients	
	U(VI)	Th(IV)
1.0	260	9.5
2.0	280	10.4
3.0	282	10.5
4.0	284	10.5
5.0	285	10.6

It appears from the Table 2 that distribution coefficients attain a steady-state at 2 ml of sodium perchlorate. Hence 2 ml of sodium perchlorate was selected for the extraction of thorium and uranium.

In another experiments perchloric acid was varied from 1 to 8 and the distribution coefficients are given in Table 3.

TABLE 3: Effect of perchloric acid on the extraction of uranium and thorium.

Perchloric acid in ml	Distribution coefficients	
	U(VI)	Th(IV)
1.0	230	8.8
2.0	236	9.0
3.0	245	9.5
4.0	265	10.0
5.0	280	10.4
6.0	284	10.5
7.0	288	10.6
8.0	290	10.6

It appears from the Table 3 that 5 ml of perchloric acid is sufficient to extract uranium and thorium.

It is concluded from the observations that optimum conditions for the extraction of uranium and thorium are as follows:

1.	Uranyl perchlorate	5 ml (0.5M)
2.	Perchloric acid	5 ml (0.3M)
3.	Sodium perchlorate	2 ml (4.0M)
4.	Hydrochloric acid	5 ml (3M)
5.	Thorium tetrachloride	5 ml (.01M)
6.	Water	3 ml

Extraction of thorium with DPSO:

Five ml (0.04M) thorium tetrachloride aqueous solution 5 ml (0.08M) diphenyl sulphoxide in carbon tetrachloride and 2 ml hydrochloric acid of varying concentrations between 0.2M - 2M were mixed together in a separating funnel and the equilibrium was attained in 15 minutes. The lower layer containing extracted thorium was separated and the amount of thorium left over was estimated as an oxalate,[61] The colorimetric estimation of thorium as thoron was not found useful in this investigation because the concentration was very high and therefore it was easy to estimate thorium as an oxalate. This method has also its limitation because thorium oxalate dissolves in hydrochloric acid at a higher concentration. Therefore the concentration of HCl was kept near 1M. The results are given in the Table 4.

TABLE 4: Extraction of thorium from hydrochloric acid solution by DPSO in carbon tetrachloride.

Molarity of acid (M)	Distribution coefficients
0.4	0.165
0.6	0.208
0.8	0.255
1.0	0.288
1.2	0.260
1.4	0.238
1.6	0.232
2.0	0.225

The values given in the Table 4 are plotted using distribution coefficient and acid concentration. It appears from the figure1 that maximum extraction can take place at 1M HCl.

The concentration of DPSO was changed between 0.02 M - 0.2M . 5 Ml of DPSO, 5 ml 0.04M thorium tetrachloride and 2 ml 1M HCl were mixed together and the efficiency of extraction was studied. The results are given in the Table 5.

A graph is plotted between the distribution coefficient and concentration of DPSO (Fig.2). It appears that maximum extraction of DPSO takes place at 0.08M.

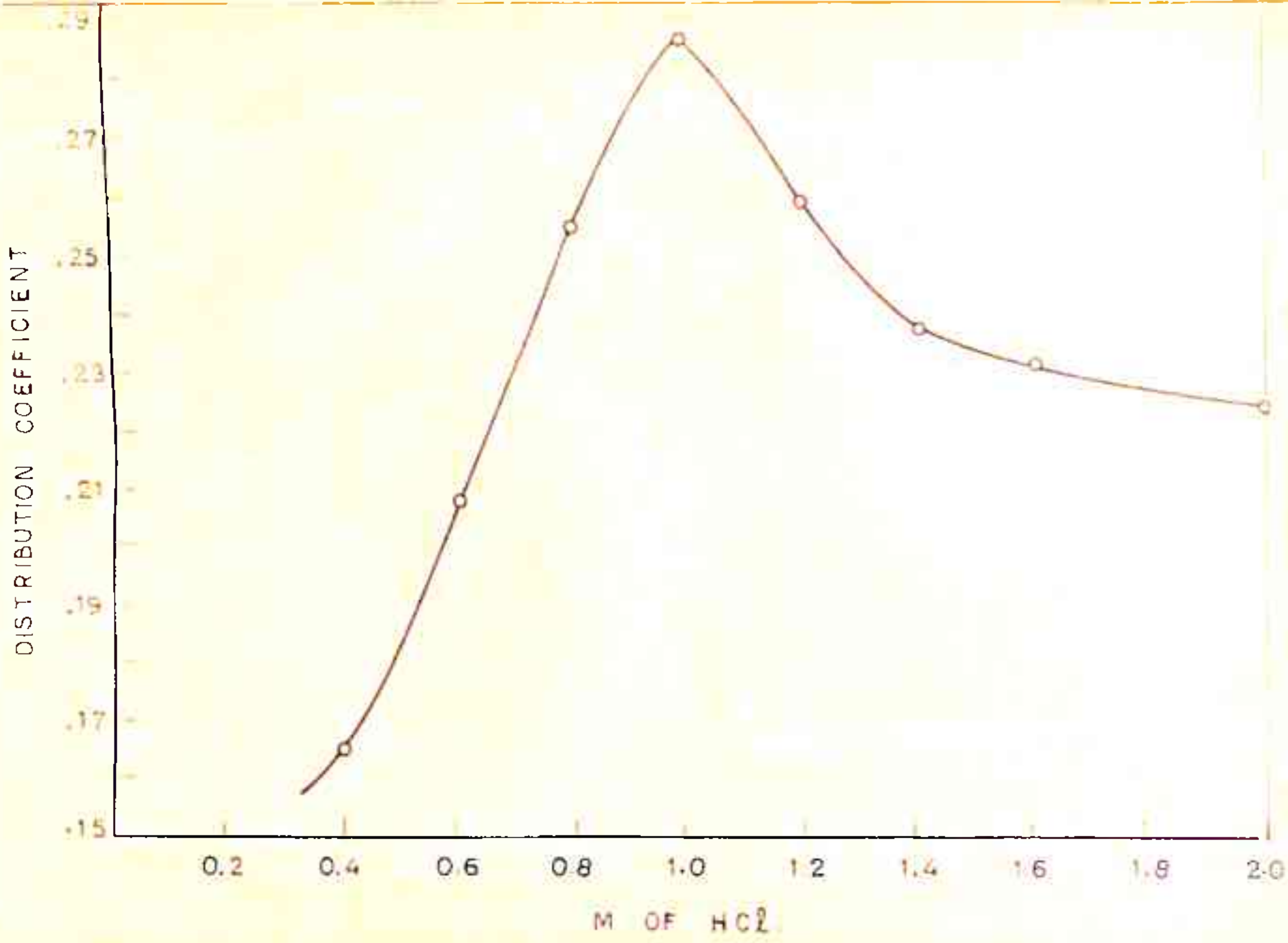

FIG. I EXTRACTION OF THORIUM ON ACID CONCENTRATIONS WITH DPSO

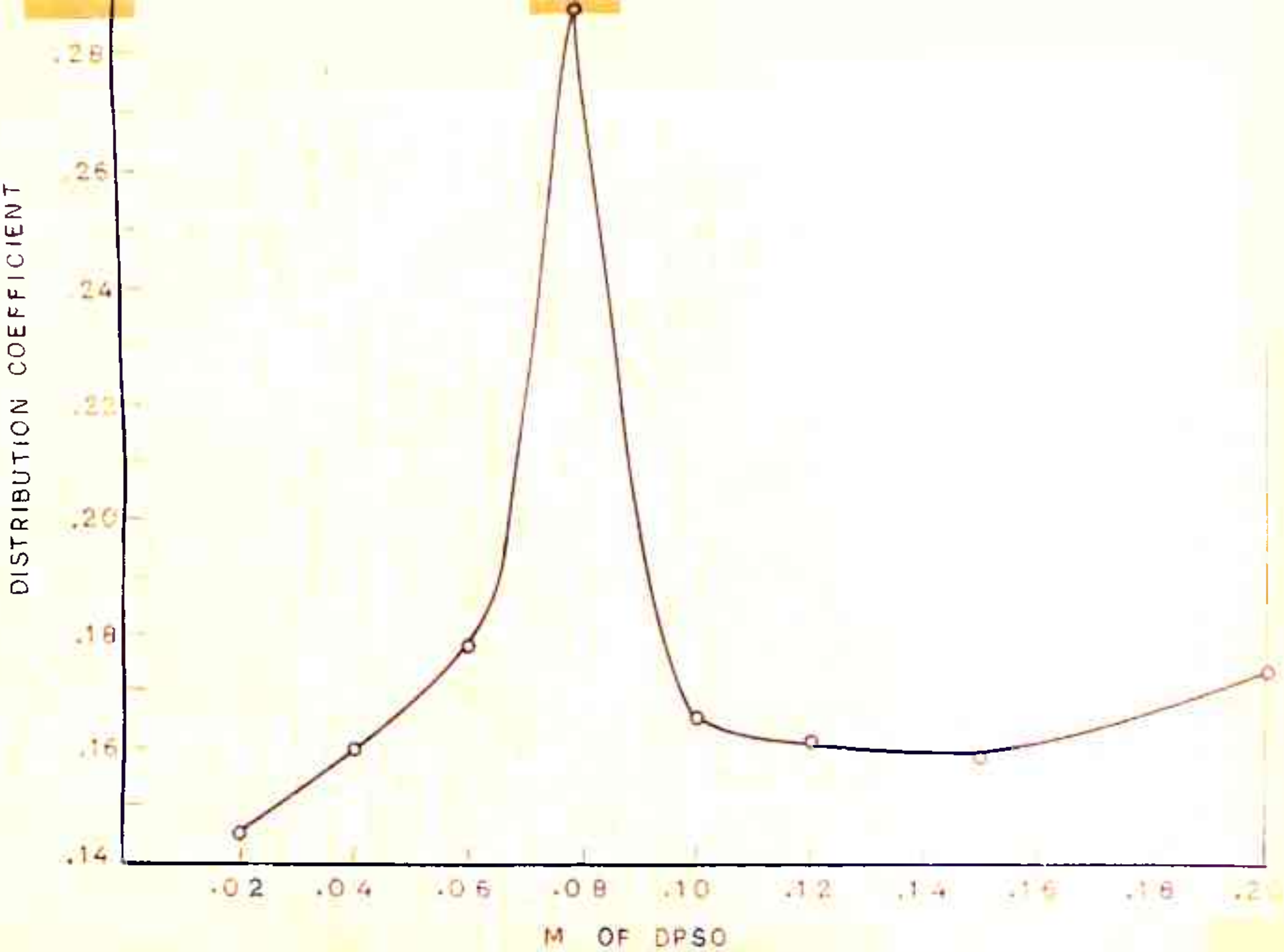

FIG. 2 EXTRACTION OF THORIUM WITH DPSO

TABLE 5: Effect of DPSO concentration on extraction of thorium in hydrochloric acid solution.

Molarity of DPSO (M)	Distribution coefficient
0.02	0.145
0.04	0.160
0.06	0.178
0.08	0.288
0.10	0.165
0.12	0.162
0.15	0.159
0.20	0.174

Blank experiments were also performed to find out the amount of hydrochloric acid being extracted by DPSO. The results are given in Table 6, and a graph is plotted in Fig.3 between the acid concentration and amount of HCl extracted.

TABLE 6: Extraction of hydrochloric acid with DPSO.

Molarity of hydrochloric acid (M)	mg of HCl extracted
0.2	1.5
0.4	3.8
0.6	6.4
0.8	8.6
1.0	11.0
1.2	13.3
1.4	15.7

It gives a straight line. It is concluded that almost a small amount of hydrochloric acid is extracted. The effect of chloride ions on the extraction of thorium was also studied. Two ml 1M HCl, 5 ml 0.04M thorium tetrachloride and 5 ml 0.08M DPSO and 2 ml 1M-5M sodium chloride were mixed together. The results are given in the Table 7.

TABLE 7: Effect of chloride ion concentration on the extraction of thorium by DPSO.

Molarity of NaCl (M)	Distribution coefficient
1.0	0.215
2.0	0.190
3.5	0.260
4.0	0.285
4.5	0.280
5.0	0.276

The data are plotted in Fig.4. It shows that maximum extraction takes place when the concentration of sodium chloride is 4M.

From these observations it is concluded that the condition for the extraction of thorium with DPSO are as follows:

2 ml 1M HCl

5 ml 0.04M thorium tetrachloride

5 ml 0.08M diphenyl sulphoxide

2 ml 4M sodium chloride.

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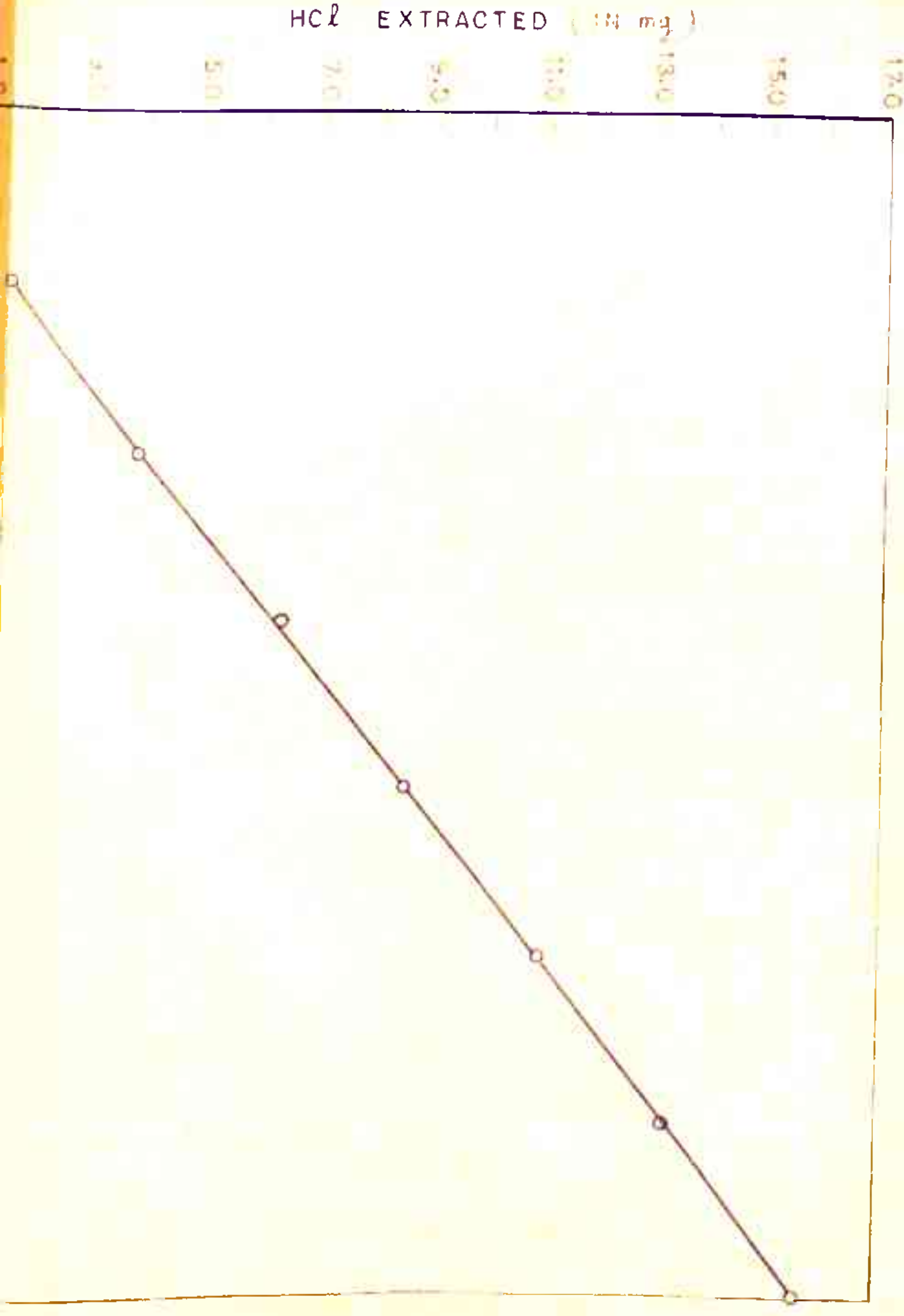
HCℓ EXTRACTED (IN mg)
3.0
5.0
7.0
9.0
11.0
13.0
15.0
17.0

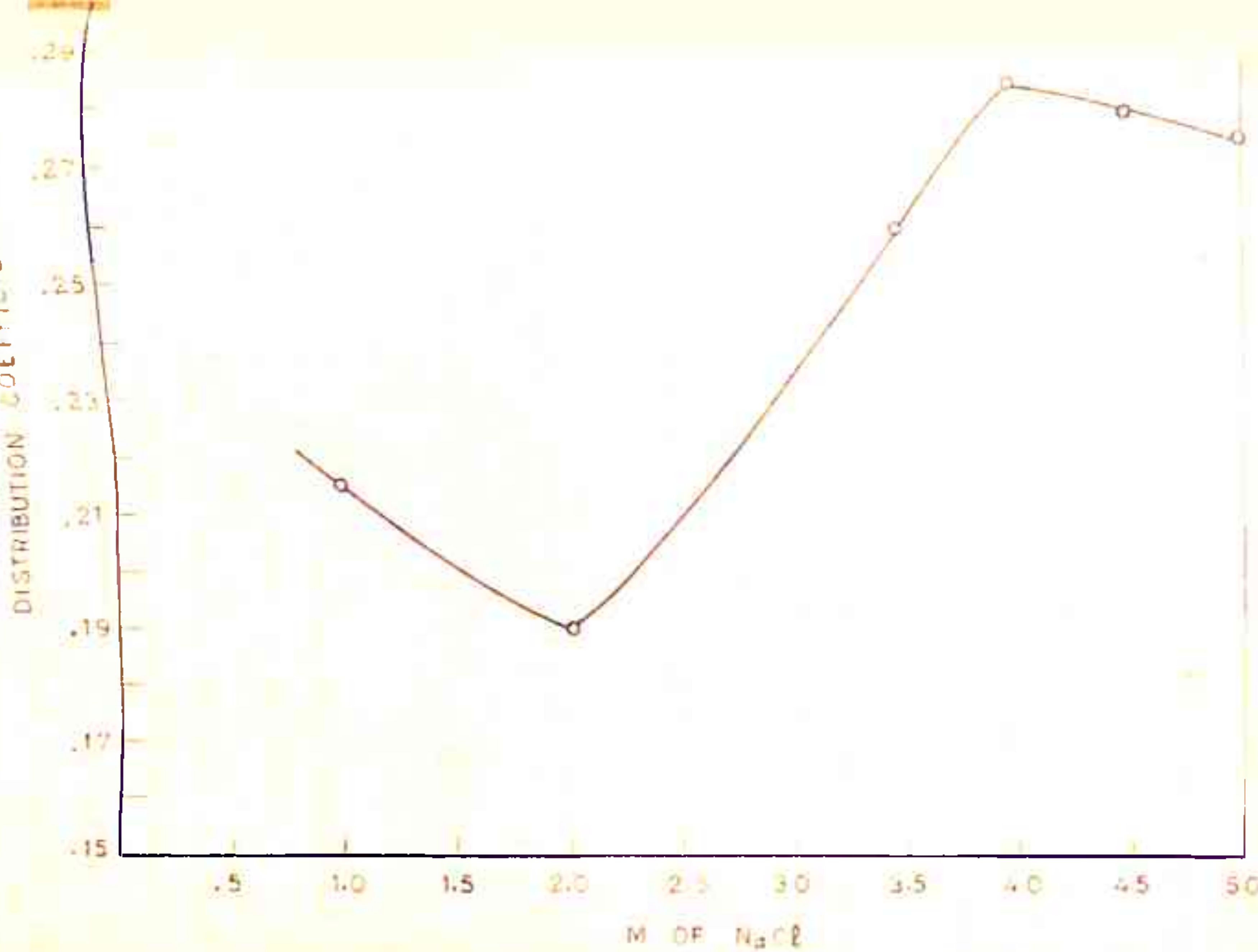

FIG. 4 EFFECT OF CHLORIDE IONS CONCENTRATION ON THE EXTRACTION OF OF THORIUM WITH DPSO.

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CHAPTER 5

HETEROGENEOUS EXCHANGE REACTIONS

INTRODUCTION

The precipitation techniques are one of the most commonly used classical method of analytical chemistry. Radioisotopes present in traces are separated using either a carrier or exchanging them at a solid surface. A solid phase in contact with an aqueous phase adsorbs atoms at the interface. Once such a heterogeneous exchange takes place on the surface, it is followed by recrystallisation and self diffusion process in the interior of the solid phase. In a heterogeneous exchange reactions where solid-fluid exchange is involved, diffusion process is slow and the distribution of isotope becomes heterogeneous.

Two kinds of adsorption process, namely, primary and secondary adsorption take place at the boundary between the solid and the solution. The primary adsorption is associated with the formation of a monomolecular layer at the surface of the crystal lattice. The secondary adsorption takes place at the boundary between the monomolecular layer and the solution. When a nascent or previously prepared precipitate is mixed with a radioactive element present in the form of a cation or anion containing identical ions or ions isomorphous to them, primary adsorption takes place. All the ions having a charge of opposite sign to that of the charge of the monomolecular layer take part in the secondary exchange adsorption. It depends to a very large extent on the valency of the ions. The secondary exchange adsorption depends on the charge of the surface of the precipitate, on the solubility of the adsorbed compound of the radio-element and the magnitude of the surface area of the precipitate.

In connection with the determination of the metal contaminant first of all zinc and mercury in hydrogenating analysis by destructive activation analysis aroused the idea of a systematic study of the possibilities of the separation and determination of traces of metal ions by heterogeneous isotopic exchange or speaking more cautiously by retention on metal sulphides precipitates. The process of adsorption of tracers on a precipitate and subsequent interactions are called heterogeneous exchange reactions. In the heterogeneous exchange process the radioactive isotopes and non-isotopic carriers may be removed by incorporation of the tracer into the crystal lattice of the precipitate and by adsorption on the surface. The process has been divided into four groups by Hahn[1]. These are: (i) isomorphous replacement, (ii) adsorption, (iii) anomalous mixed crystal formation, (iv) internal adsorption. If the tracer is incorporated by isomorphous replacement, the Berthelot-Nernst distribution law can be applied, provided the distribution is homogeneous. The homogeneous distribution coefficient (D) is given by Henderson and Kracek[2] by the following expression:

$$\left(\frac{\text{Tracer}}{\text{Carrier}}\right)_{\text{Solid}} = D\left(\frac{\text{Tracer}}{\text{Carrier}}\right)_{\text{Solution}}$$

If the tracer is distributed in the precipitate in a heterogeneous manner, logarithmic distribution law of Doerner and Hoskins[3] is applicable. Let x and y be the amount of tracer and carrier, then since the amounts dx and dy of tracer and carrier deposited in a given crystal layer are proportional to their respective concentrations,

$$\frac{dx}{dy} = \lambda \frac{(a-x)/V}{(b-y)/V}$$

where V is the volume of the mother liquor, λ is a constant characteristic of the system and is called the logarithmic distribution coefficient. Integration gives:

$$\log \frac{a}{a-x} = \lambda \log \frac{b}{b-y}$$

or $$\log\left(\frac{\text{Total tracer}}{\text{Tracer in solution}}\right) = \lambda \log\left(\frac{\text{Total carrier}}{\text{Carrier in solution}}\right)$$

If the value of D or λ is greater than unity, the precipitate is present with a large amount of tracer metal. The tracer is carried more efficiently, the greater is the value of D and λ. The numerical values of D and λ should essentially be the same and characteristic constant for a given precipitation system. Coprecipitation via adsorption can take place efficiently on a solid surface even though the tracer and carrier ions are sufficiently similar. The efficiency of the process depends upon the surface area of the precipitate, presence of oppositely charged lattice ions, insolubility of the compound or complex formed by the tracer ion with oppositely charged lattice ion and prolonged standing of the precipitate in contact with the tracer.

The formation of a anomalous mixed crystal formation or internal adsorption takes place when a tracer is coprecipitated with carrier, though the carrier compounds do not form isomorphous mixed crystals. In this process the tracer is incorporated into the crystal lattice of the precipitate. When tracer is adsorbed on the surface of a growing crystal, it is stopped by subsequently formed layer resulting in the internal adsorption. This process is characterised by the variation in the values of the distribution coefficient obtained under similar conditions and separation by carrying in the presence of an excess of the lattice-ion, whose charge is of the same sign as the tracer or by the presence of other highly charged ions of the same sign. A distinction is drawn between anomalous mixed crystal formation and internal adsorption by radio autographs. In the former process a continuous distribution of the tracer and in the latter process discontinuity in the distribution of tracer in the crystal is observed.

Although the removal of tracer by coprecipitation is quite sufficient in a sizable fraction of tracer, which can be removed from the solution by deposition on precipitates, the tracer is rapidly adsorbed either by exchanging with the counter ion or with lattice ion on the surface of the crystal. Fajan[4], Hahn[5], Paneth and coworkers[6] formulated the rules, that an ion in an aqueous solution is rapidly adsorbed if the latter has a large surface area and the ion combine with the oppositely charged lattice ion to form a compound that is dissolved or dissociated with very great difficulty. In a well formed crystals there is no diffusion of ions and therefore exchange at the surface is rapid but in the interior it is slow. If some ions are present in the solution that can fit into the crystal lattice and are not isotopic with the lattice ion for the position in the surface and will thus be adsorbed slowly. They will be incorporated as the crystallisation process proceeds. This isomosphous replacement process is influenced by high concentration of the lattice ions of the same charge as the tracer. A large surface area, a long contact time, a high temperature and a high acid concentration is necessary for it.

Various procedures have been developed to isolate quantitatively chemically and radiochemically pure thorium and uranium. These methods are based on adsorption and coprecipitation which is now commonly called heterogenous exchange reaction. A freshly formed or aged precipitate is capable to exchange ions on its surface, the exchange is affected by the charge of the precipitate, charge on the ions of the precipitate, the solubility of the compound formed from the exchanged ions, temperature order of the addition of reagents, speed of precipitate formation and the digestion process. Rapid radiochemical separations have been achieved by heterogenous exchange reaction and coprecipitation technique. This technique has been especially useful in the separation of fission product of uranium and thorium. A very well known example is the separation of ^{102}Te from ^{102}Mo[7] where the former is the daughter of the latter. For several years it was believed that the isotopic exchange between ions in aqueous solutions and ions in the precipitate occurs very quickly but later on the process becomes slow and it takes long time to complete. The rapid exchange of ions is supposed to take place between the ions in the solution and ions at the surface layer of the solid. Kolthoff and coworkers[8-12] used a number of insoluble lead salts to investigate a large series of exchange reactions. They have demonstrated that recrystallisation is important with freshly prepared precipitate. The solution-solid exchange has been successfully investigated for metallic selenium and poly selenide ions in alkaline solutions[13] and solid silver sulphide ions in aqueous solutions. Exchange between Ag^+ ions and freshly prepared AgBr was complete in 24 minutes[15]. Fast exchange in AgCl/Cl and AgBr/Br has also been demonstrated[16]. The fast exchange with halides was utilised in the removal of traces of radio-active silver from solutions by treatment with precipitated AgCl[17]. A number of radiochemical procedures[18-21] have been described where heterogeneous isotopic processes have been used for separation. It has also been demonstrated that not only the surface layer takes part in the adsorption but inner layer may also take part in this process. The thorium isotope, UX_1, has been successfully removed from the solution or uranyl nitrate hexahydrate by shaking with charcoal[22]. A number of insoluble compounds of thorium and their use for the removal of the trace amount of thorium from solutions have been reported. Barium sulphate has been used as a carrier to separate tetravalent actinides and trivalent lanthanides for the ter- and hexavalent states. The separation of thorium from uranium, rare earths, and some other elements has been successfully done on lead iodate and bismuth iodate precipitates[23]. The heterogeneous reactions described above which involve separation of own and related ions by rapid exchange reaction on the surface layer of precipitate provide very rapid and clean separation. Precipitation reactions in radiochemistry are of special interest in preparative analytical chemistry. The separation seems to be rapid where the ionic reactions are of the same order as a tracer itself.

Heterogeneous isotopic exchange with precipitate has been more extensively used for quantitative separation or determination. In the course of activation analysis only lately, the isotopic exchange of solid silver sulphide with its ions in solution has been studied by Peschanski[24] by means of ^{110}Ag and ^{35}S. The isotopic exchange between radio-silver and silver halide has first been recommended for quantitative determination by Langar, Sunderman and Meinke[25]. They allowed to react the solution containing radioactive silver ion with AgCl precipitated on a platinum wire. Rai, Nethaway and Wahl[26] have thoroughly studied the conditions under which ^{140}Ba, ^{90}Sr, ^{114}Sn ions are quantitatively retained from aqueous solutions on $BaSO_4$, $SrCO_3$ and Sn(IV) or Sn(II) sulphide precipitates, according to their assumptions by isotopic exchange. Hama, Guchi, Onuma, Watanabe and Kuroda[27] utilised the exchange reaction of Sr between the precipitated sulphate and salt solution for separating carrier free ^{90}Sr and ^{90}Y. Qureshi, Shahid and Hasany[28] used isotopic exchange with $SrSO_4$ or oxalate for the radiochemical separation of antimony. In the course of the determination of Sn in Ni, Csajka[29] adsorbed the radionuclide ^{125m}Sn on the dioxide precipitate after dissolving the activated sample. Girardi, Pietra and Sabbione[30] studied the retention of different radio ions on twelve precipitates of ionic character mainly oxides and phosphates and on ion exchange resins with special regard to radiochemical possibilities of separation. Gimesi, Banyai, Csajka and Szabadhazy[31] used a number of radionuclides namely ^{203}Hg and ^{65}Zn ions which were retained over HgS and ZnS respectively and thus Hg^{++} and Zn^{++} ions were separated rapidly and determined in the presence of a number of interfering ions.

Separation of a number of radioisotopes using metallic sulphides has been reported. These are: ^{210}Bi by CuS ^{143}Ce and ^{95}Zr by Bi_2S_3, ^{64}Cu by Bi_2S_3, ^{45}Ca by CdS and ^{210}Pb by CuS and ^{227}Ac by Bi_2S_3. Very little work has been reported for the separation on the precipitates of sulphides. Only coprecipitation in an alkaline medium has been studied with alkali insoluble sulphides. There are two ways in which coprecipitation with sulphides takes place, firstly one of the sulphide is acidic and other is basic and secondly elements form sparingly soluble sulphides.

A perusal of the literature presented here demonstrates that some of the fission products from uranium and thorium can be successfully separated from uranium or thorium on precipitates containing a metal ion. Insoluble precipitates of these metals specially sulphides promise a rapid separation. Since lead and bismuth sulphides have already been utilized in the separation[32], it was thought worthwhile to use other sulphides for this investigation. Separation of uranium, thorium and tin over a precipitate of Sn(IV) sulphide and that of uranium, thorium and antomony over the precipitate of Sb_2S_3 have been carried out. These investigations ranged from the tracer concentration to the macro amount of thorium and uranium.

EXPERIMENTAL:

^{238}U is a long lived parent of (4n+2) disintegration series and it grows ^{234}Th in it. Fig. 1 gives the decay scheme. ^{234}Th gives UX_2 and about 0.4% decays to produce UZ. The β-particles emitted by this isotope are very soft and they cannot be detected efficiently. However, its daughter protactinium gives hard betas which have been used for measuring the activity of ^{234}Th. The half life of protactinium, the daughter element is very short in comparison to the half life of the parent ^{234}Th. Therefore a period of

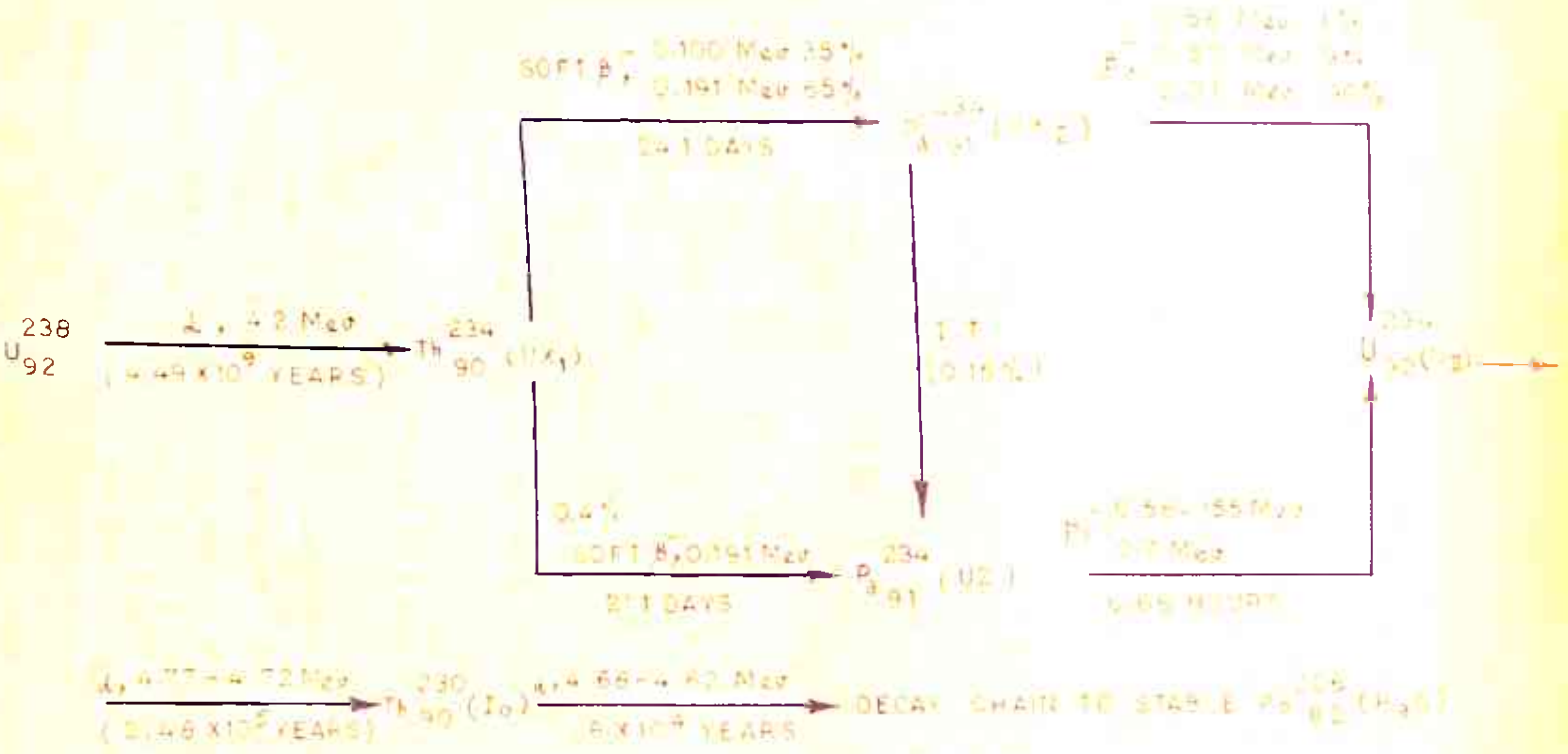


FIG. I A PART OF DECAY SCHEME OF U^{238}_{92}

three half lives of the daughter is allowed to establish a steady-state. The quantity of protactinium in secular equilibrium is controlled by the amount of thorium present. The rate of the decay for ^{234}Th follows the first order law -

$$-\frac{dN_1}{dt} = \lambda N_1$$

$$N_1 = N_1^{o} e^{-\lambda_1 t}$$

where N_1 is the number of parent atoms at a time t and N_1^{o} is equal to initial number of parent atoms. The daughter is formed at the rate at which the parent decays $(\lambda_1 N_1)$ and itself decays at the rate $\lambda_2 N_2$. Thus,

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2$$

or

$$\frac{dN_2}{dt} + \lambda_2 N_2 = \lambda_1 N_1^{o} e^{-\lambda_1 t}$$

Using standard methods of differential equation it can be solved to give a solution for N_2 as a function of time t,

$$N_2 = \frac{\lambda 1}{\lambda_2 - \lambda_1} N_1^{o} (e^{-\lambda_1 t} - e^{-\lambda 2 t}) + N_2^{o} e^{-\lambda 2 t}$$

The last term gives the contribution at any time from daughter atom present initially and drops out when initial sample contains only parent atoms. For the case where parent is long lived than the daughter $(\lambda_1 < \lambda_2)$, a steady-state is reached after a certain time and the ratio of disintegration rate of parent and daughter becomes a constant.

$$N_2 = \frac{\lambda_1}{\lambda_2-\lambda_1} N_1^0 e^{-\lambda_1 t}$$

and because $N_1 = N_1^0 e^{-\lambda_1 t}$ the above equation approximates to

$$\frac{N_2}{N_1} = \frac{\lambda_1}{\lambda_2-\lambda_1}$$

or $N_1 \; {}_1 = N_2(\lambda_2-\lambda_1)$

for the case where $\lambda_1 \ll \lambda_2$, it takes the form

$$\frac{N_2}{N_1} = \frac{\lambda_1}{\lambda_2}$$

or $\lambda_1 N_1 = \lambda_2 N_2$

This equation indicates that at steady-state condition the rate of disappearance of daughter atom is equal to the rate of the disappearance of parent atom. The life of ^{238}U is very long, the decay chain is specially blocked for that isotope shorter than those of geological magnitude.

Extraction of ^{234}Th

^{234}Th is separated from ^{238}U using the technique of complex formation and solvent extraction. A 10% aqueous solution of uranyl nitrate hexahydrate was treated with freshly prepared saturated solution of ammonium carbonate until the yellow coloured precipitate, which is first formed, redissolved. The final pH of the solution was adjusted between 8 to 8.5 by adding either ammonium carbonate or nitric acid as required. The solution was transferred to a separating funnel and 2 ml of 6% freshly prepared aqueous cupferron and 10 ml of chloroform were added. The mixture was shaken to extract thorium complex into lower layer of chloroform. This was runoff into container and the extraction procedure was repeated 3 to 4 times. The combined chloroform extract was washed with 20 ml of distilled water and 1 ml of cupferron reagent at pH between 8.0 - 8.5 adjusted as before. The solution was transferred to a separating funnel and the lower layer was runoff into a container. To the chloroform extract 10 ml $3MHNO_3$ combined with few ml of saturated bromine was added, which decomposed the UX_1 cupferrate. This allowed extraction of all organic material and bromine into chloroform layer. The aqueous phase was washed twice with chloroform and was evaporated. The reactions involved are given below:

$$UO_2^{+2} + CO_3^{-2} \longrightarrow UO_2CO_3$$

$$UO_2CO_3 + 2CO_3^{-2} \longrightarrow \left[UO_2(CO_3)_3\right]^{-4}$$

$$4C_6H_5\text{-}N(NO)O.NH_4 + Th^4 \longrightarrow \left[C_6H_5\text{-}N(NO)O\right]_4 Th + 4NH_4^+$$

Identification of ^{234}Th:

^{234}Th isolated from ^{238}U by the above procedure was identified by measuring its half life and the maximum range of β-particles which were found to be absorbed on aluminium absorbers of increasing thickness positioned above the source.

The count rates were recorded for each thickness for paralysis time and background for every isolated ^{234}Th sample. The graph between count rate and absorber thickness was plotted and by Feather's analysis the value of maximum range was found out in the usual manner. Feather's analyser is given in Fig.2 and another graph plotted between range fraction R and thickness (mg/cm^2) is given in Fig.3. The range estimated by Feather's analysis is 1215 mg/cm^2. The maximum β-range is calculated from the equation -

$$\begin{aligned} E_{max} &= 1.85R + 0.245 \\ &= 1.85 \times 1.215 + 0.245 \\ &= 2.49275 \text{ Mev} \end{aligned}$$

Thus the maximum energy for β-radiation calculated by Feather's analysis is 2.49275 Mev. The actual energy is 2.51 Mev. Hence the percentage error is only 0.8% and is quite agreeable in radiochemical analysis and it fully characterizes the isotope ^{234}Th.

Greiger Muller Counter:

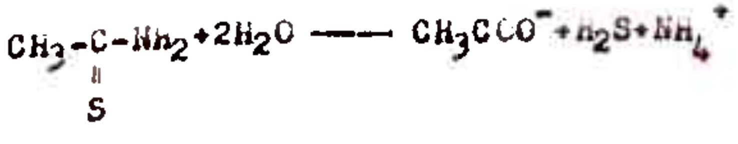
Model DS325 G.M. counter manufactured by B.A.R.C. was used for the counting. It has a high speed reliable scaler, combining stability of operation and short resolving time along with scaler and operates in the voltage region of 900-1400 volts. Plateau was observed in the region 1250 to 1350 volts and for all counting 1300 volts was selected.

Preparation of precipitate bed of Sn(IV) sulphide:

A stock solution of 0.025 M containing $SnCl_4 \cdot 5H_2O$ was taken in 0.6 MHCl. The solution was heated to 60°C and maintained at this temperature for 2.5 hours during which time gaseous hydrogen sulphide was passed through it with stirring. Then heating was stopped and the gas introduction continued for a further period of half an hour. The slurry was stored for four days in stoppered flasks, then filtered on a G-4 sintered glass filter and precipitate was washed with 0.6 MHCl saturated with H_2S and then with carbon disulphide and benzene to dissolve sulphur possibly precipitated. Then it was dried at 110°C for on hour.

Preparation of antimony sulphide bed:

A stock solution of 0.025 M $Sb_2(SO_4)_3$ was prepared in 0.6 MHCl. Varying amounts of samples were withdrawn and about 1 ml 5% solution of thioacetamide was mixed. The mixture was kept in a boiling water bath and complete precipitation was ensured. The gradual evolution of H_2S through the reaction



$$CH_3-\underset{\underset{S}{\|}}{C}-NH_2+2H_2O \longrightarrow CH_3COO^-+H_2S+NH_4^+$$

gives crystalline sulphide precipitate, which settled down easily on standing. The precipitate appears quite homogeneous due to the slow evolution of H_2S inside the solution. A filter paper was placed on the perforated glass sheet of the sintered glass funnel and a known amount of the precipitate was placed on the filter paper and the filtration was carried out under suction. The precipitate was transferred in such a way that it settled down uniformly and no cracks were observed. It was washed with CS_2 and benzene to remove sulphur.

To determine the amount of the metal retained over the precipitate the activity of the precipitate was measured after the exchange and it was compared to that of the standard. Care is taken that thickness of precipitated layer should be small so that error in counting due to self absorption may be avoided.

A number of samples containing 0.5 ml ^{234}Th were dried over aluminium planchets and were counted for the standard. The same amount of the tracer solution was dropped over the precipitates containing varying amounts of Sb_2S_3 and SnS_2 while suction was being applied. The contact time between the precipitate and effluent was of the order of about 2 seconds. The effluents were collected, dried and counted. The precipitates were dried, mounted on aluminium planchets and counted.

Solutions of uranyl nitrate hexahydrate and thorium nitrate each 0.01 M were prepared. 2.5 ml of each were withdrawn separately and dropped over the precipitate having the maximum thickness recorded in Tables 3 and 4. The amount of uranium and thorium in the effluent were estimated spectrophotometrically, using PAR and thoron as complexing agents.

Solid ammonium carbonate was added to complex the uranium. Thorium was precipitated as hydroxide by adding ammonium hydroxide and was dissolved in hot aqua-regia. The pH was maintained at 0.5 and (O-Arsono-phenyl-Azo)-2 naphthol 3:6 disulphonic acid (thoron) was used as a colorimetric reagent. Model 139 UV spectrophotometer (Hitachi Perkin-Elmer) was used at the wavelength 550 nm.

A series of solutions containing uranium and PAR, (4-(2-pyridyl-azo)-resorcin) was adjusted at pH 11 by addition of NaOH and colorimetric determination was carried out at 550 nm.

The data recorded in the Tables 3 and 4 show that the maximum retention of activity of ^{234}Th on different precipitate beds is about 99%. Therefore this thickness was chosen for further studies. In order to find out the effect of large amount of thorium and uranyl ion on adsorption, solution of thorium nitrate and uranyl nitrate were poured over. The precipitate and effluent were estimated from the standard curves (Fig. 4.3) and the results are given in Table 5. It appears from the Table 5 that the entire uranyl nitrate or thorium nitrate is retained over the precipitate. To observe the effect of isotopic carrier thorium, 2.5 ml (0.01M) thorium nitrate was taken and its activity was determined. Later on it was mixed with ^{234}Th (0.5 ml) tracer and the mixture was poured over the precipitated bed. The rate of passing out of the solution mixture through the precipitate was 0.5 ml per minute. The activity in the precipitate and effluent was determined. The activity of thorium nitrate was subtracted and the results are given in the Table 6.

It has been found out earlier that UNH is completely retained over the precipitated bed. However a solution of uranyl nitrate hexahydrate containing 50 mg/ml in 0.6 NHCl saturated with H_2S was used in the usual manner and the bed of the precipitate containing UNH was washed with 0.6 NHCl containing H_2S and the activity was determined. The results are given in the Table 7.

Since these results are not consistent, it was thought necessary to separate UO_2^{+2} ions from Sb. The precipitate of Sb_2S_3 containing UO_2^{+2} ions was dissolved in 5 ml of 1 NHCl and boiled over a water bath to expel H_2S. The solution was diluted with HCl so that its strength became 0.6 N. H_2S was bubbled for 2 minutes and the slurry was boiled over a water bath until it settled down. The precipitate was centrifuged and the liquid was collected. The precipitate was washed with 15 ml (0.6 NHCl) containing H_2S. The bulk was boiled for 5 minutes over a water bath and the precipitate was centrifuged and the liquid was collected. All collected liquids were evaporated and counted for the activity of UO_2^{+2} which agreed within 1% from the original value.

For the separation of thorium and Sb_2S_3 same procedure was adopted and it was found that ^{234}Th is separated.

For this purpose the precipitate of Sb_2S_3 was prepared by dissolving 20 gm of $SbCl_3$, 20 gm of tartaric acid and

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For the separation of thorium and Sb_2S_3 same procedure was adopted and it was found that ^{234}Th is separated.

For this purpose the precipitate of Sb_2S_3 was prepared by dissolving 20 gm of $SbCl_3$, 20 gm of tartaric acid and

200 ml of conc. HCl and it was dissolved in one litre of distilled water. The solution was heated just to boil and its temperature was maintained at 60-75°C for 2.5 hours during which time gaseous H_2S was passed through it with stirring. Then again 800 ml of distilled water was added. The temperature was maintained by heating and H_2S was passed for half an hour at 60°C. The heating was stopped and H_2S was passed for a further period of half an hour. The slurry was kept such for a day and then filtered. The precipitate was washed with enough distilled water and then dried at 100°C for 3 hours. The precipitate was grinded in an agate mortar and then collected. 5 ml of active solution in 4% HCl was passed through a suitably pretreated precipitate by suction, then 10 ml 4% HCl solution was passed. The filtrate was made up to 20 ml in a volumetric flask and the activity of a 10 ml aliquot was measured.

Isotopic exchange of ^{120m}Sb on Sb_2S_3 precipitate in 4% HCl was studied and the results are given in Table 8.

TABLE 1:

Background counts = 200/4 mts.; Operating voltage = 1300 V

Sl. No.	Thickness of Al absorber in mg/cm^2	Counts/ 4 mts.	Counts after deducting background
1	0.0	9859	9659
2	2.7	9826	9626
3	5.4	9330	9130
4	13.5	9299	9099
5	27.0	8712	8512
6	40.5	7870	7670
7	84.5	6625	6425
8	219.0	3229	3029
9	243.0	2865	2665
10	324.0	1741	1541
11	432.0	978	778
12	540.0	584	384
13	709.0	346	146
14	864.0	300	100

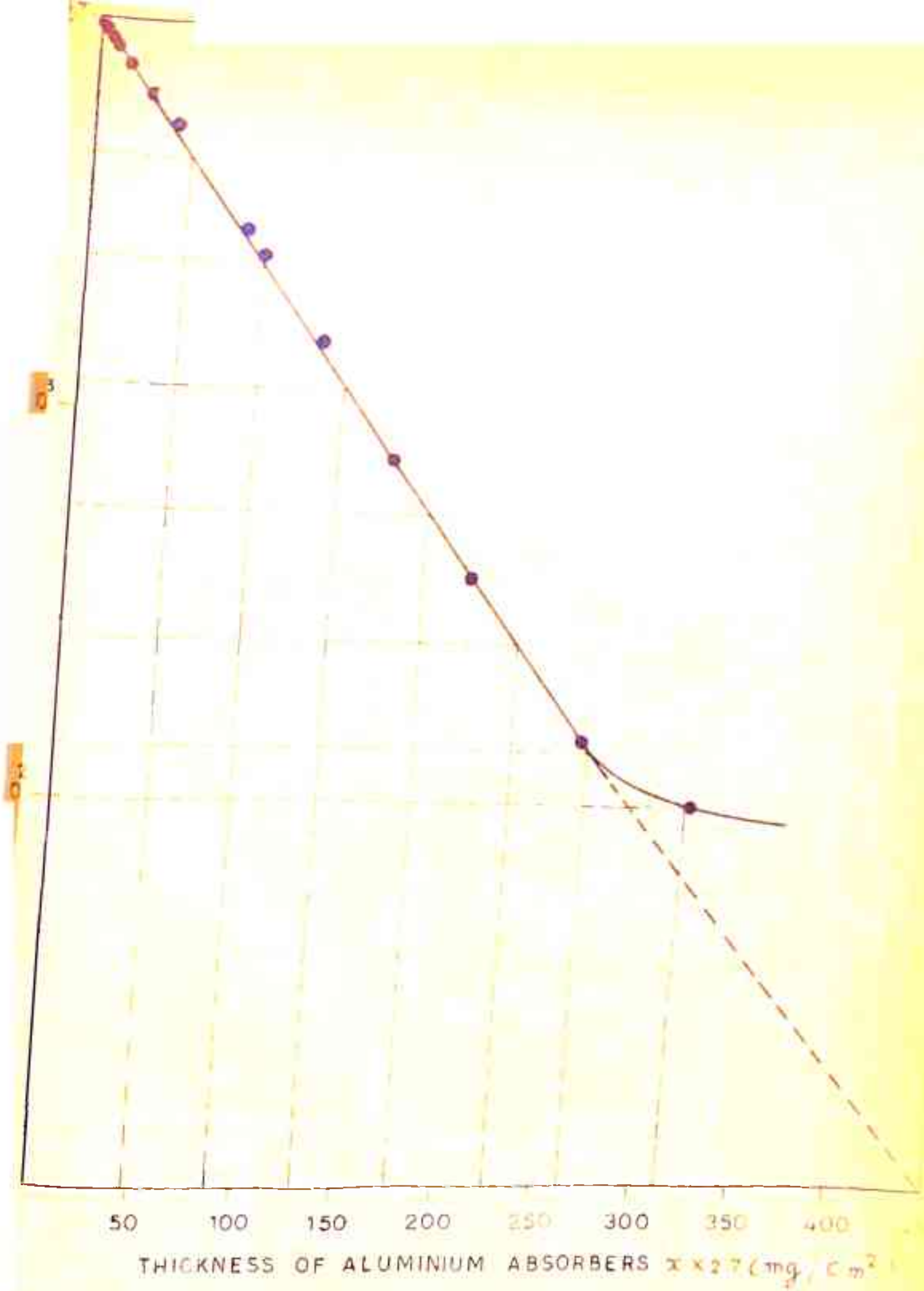


FIG. 2 APPLICATION OF FEATHER ANALYSER TO ABSORPTION CURVE OF β - EMITTER ^{234}Th

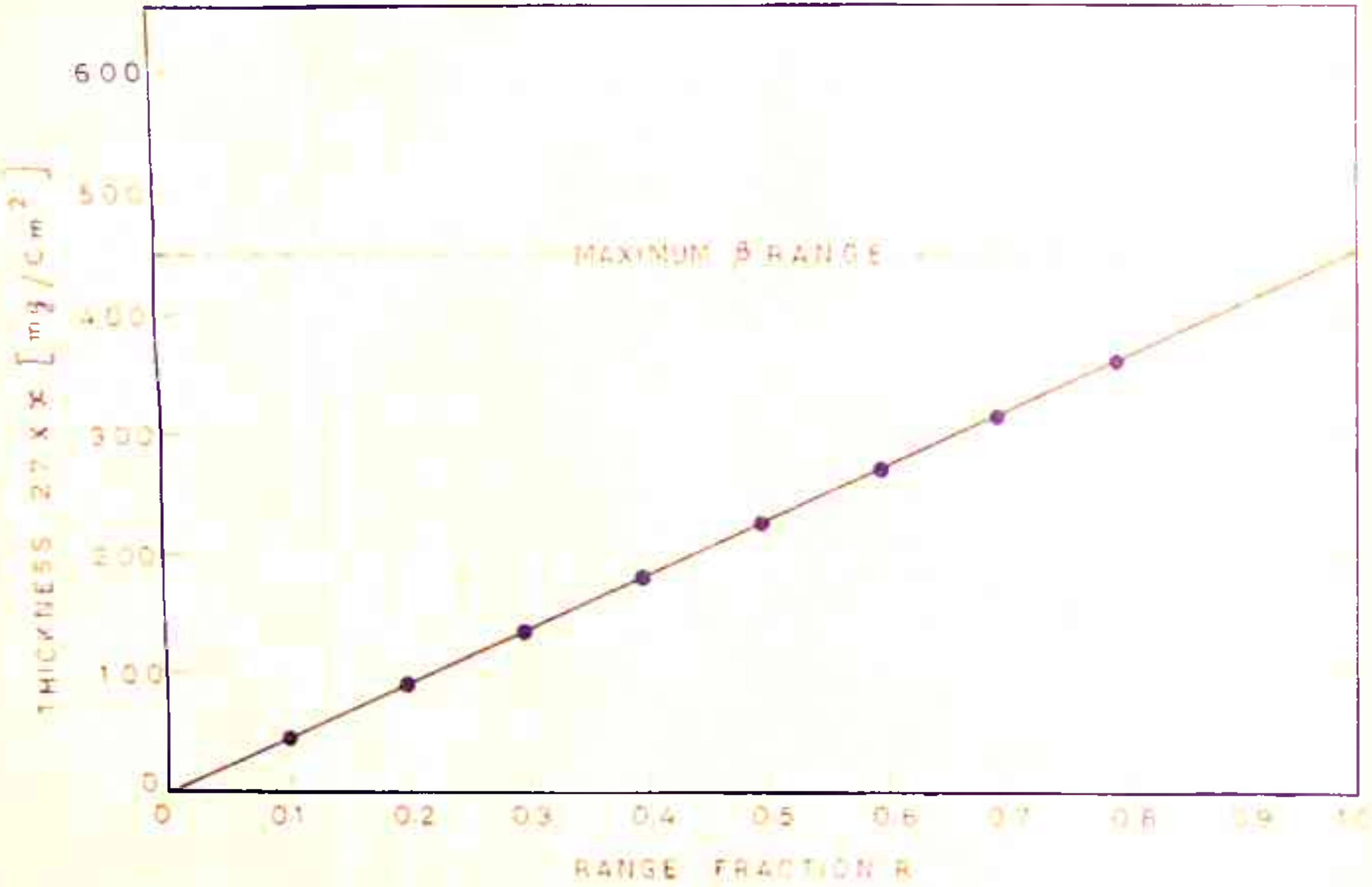


FIG. 3 DETERMINATION OF FEATHER RANGE

TABLE 3:

Sl. No.	Amount of $SnCl_4.5H_2O$ (0.025M) in ml precipitated as SnS_2	% ^{234}Th activity on precipitate	% ^{234}Th activity in the effluent
1	1	18.4	80.9
2	2	26.3	73.4
3	4	34.8	65.1
4	6	59.0	41.0
5	8	72.2	27.4
6	10	81.8	18.1
7	12	85.9	14.1
8	14	90.2	9.6
9	16	94.2	5.6
10	18	99.1	0.8

TABLE 4:

Sl. No.	Amount of $Sb_2(SO_4)_3$ (0.025M) in ml precipitated as Sb_2S_3	% ^{234}Th activity on the precipitate	% ^{234}Th activity in the effluent
1	1	24.8	74.2
2	2	40.0	59.8
3	4	74.5	25.1
4	6	85.9	14.1
5	8	93.5	6.2
6	10	96.6	3.4
7	12	99.5	0.5

TABLE 5: Colorimetric estimation of UNH and TNH

Precipitated bed	Reagent	Absorbance for effluent	Amount in ppm
SnS_2	UNH	1.5	13.68
SnS_2	TNH	0.43	41.60
Sb_2S_3	UNH	1.7	16.30
Sb_2S_3	TNH	0.46	45.50

Table 6: Effect of isotopic carrier on ^{234}Th

Precipitate bed	% activity on the precipitate	% activity in the effluent
SnS_2	86.1	13.8
Sb_2S_3	86.0	13.9

TABLE 7: $UO_2^{\cdot\cdot}$ over SnS_2

% unadsorbed $UO_2^{\cdot\cdot}$	% washed down $UO_2^{\cdot\cdot}$
65.50	21.60
55.80	32.30
67.40	30.20
65.00	26.40

<u>TABLE 8</u>: Isotopic exchange of ^{120m}Sb on Sb_2S_3 precipitate in 4% HCl.

Sl. No.	Weight of Sb_2S_3 precipitate in mg	% activity retained
1	100	90.0
2	200	93.0
3	300	95.0
4	400	98.0
5	500	98.0

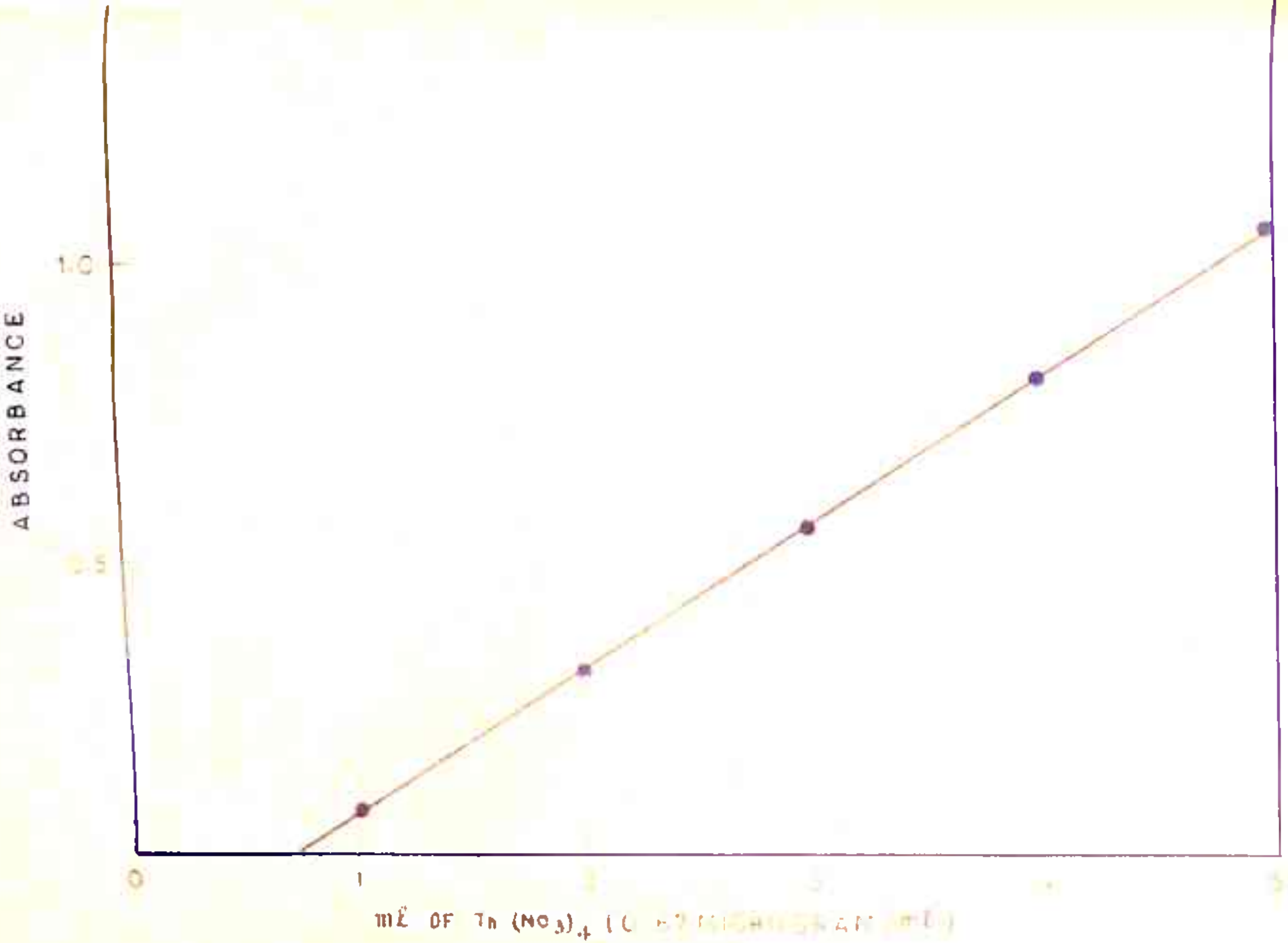


FIG. 4 STANDARD CURVE FOR ESTIMATION OF THORIUM - THORON COMPLEX

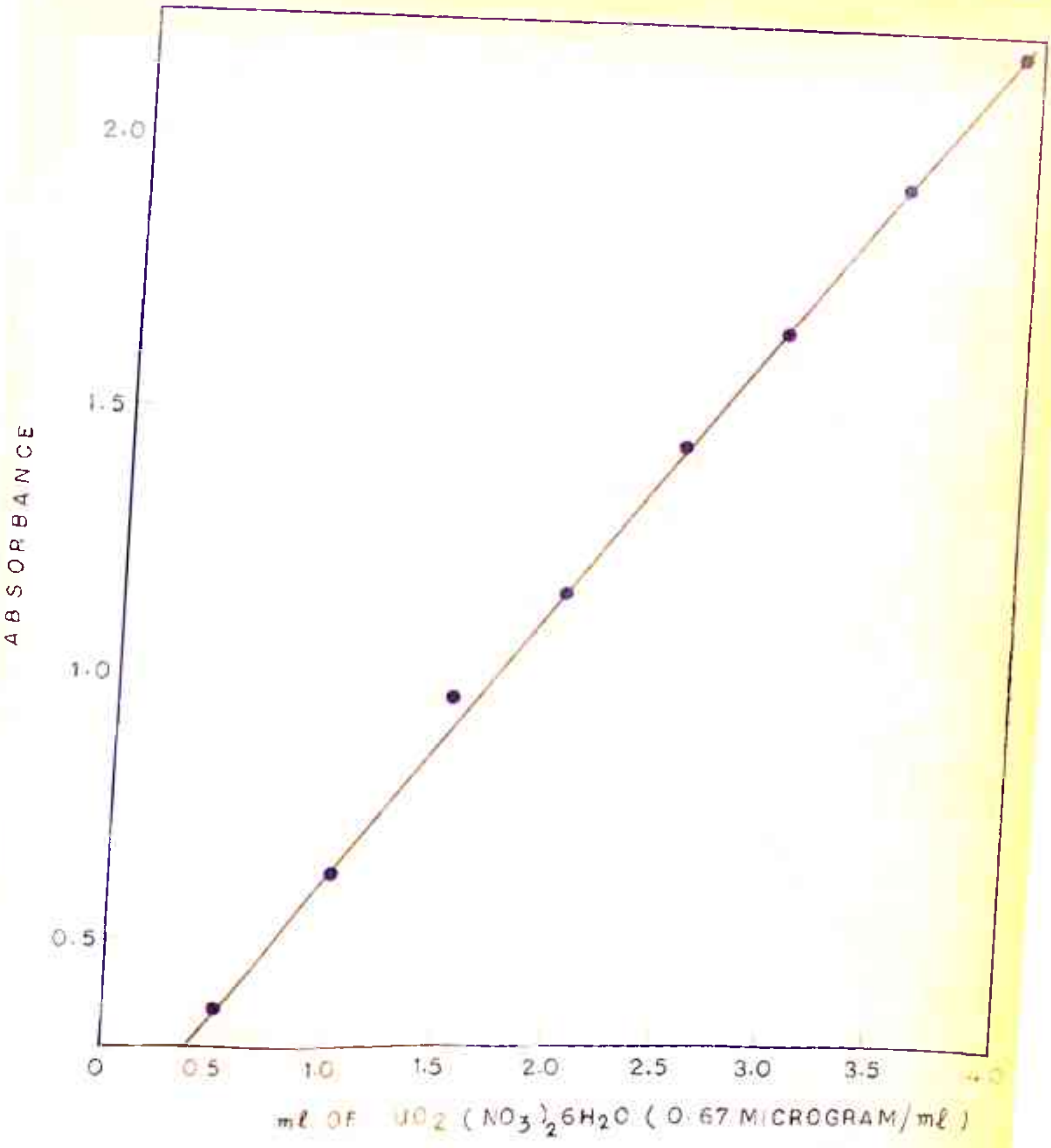
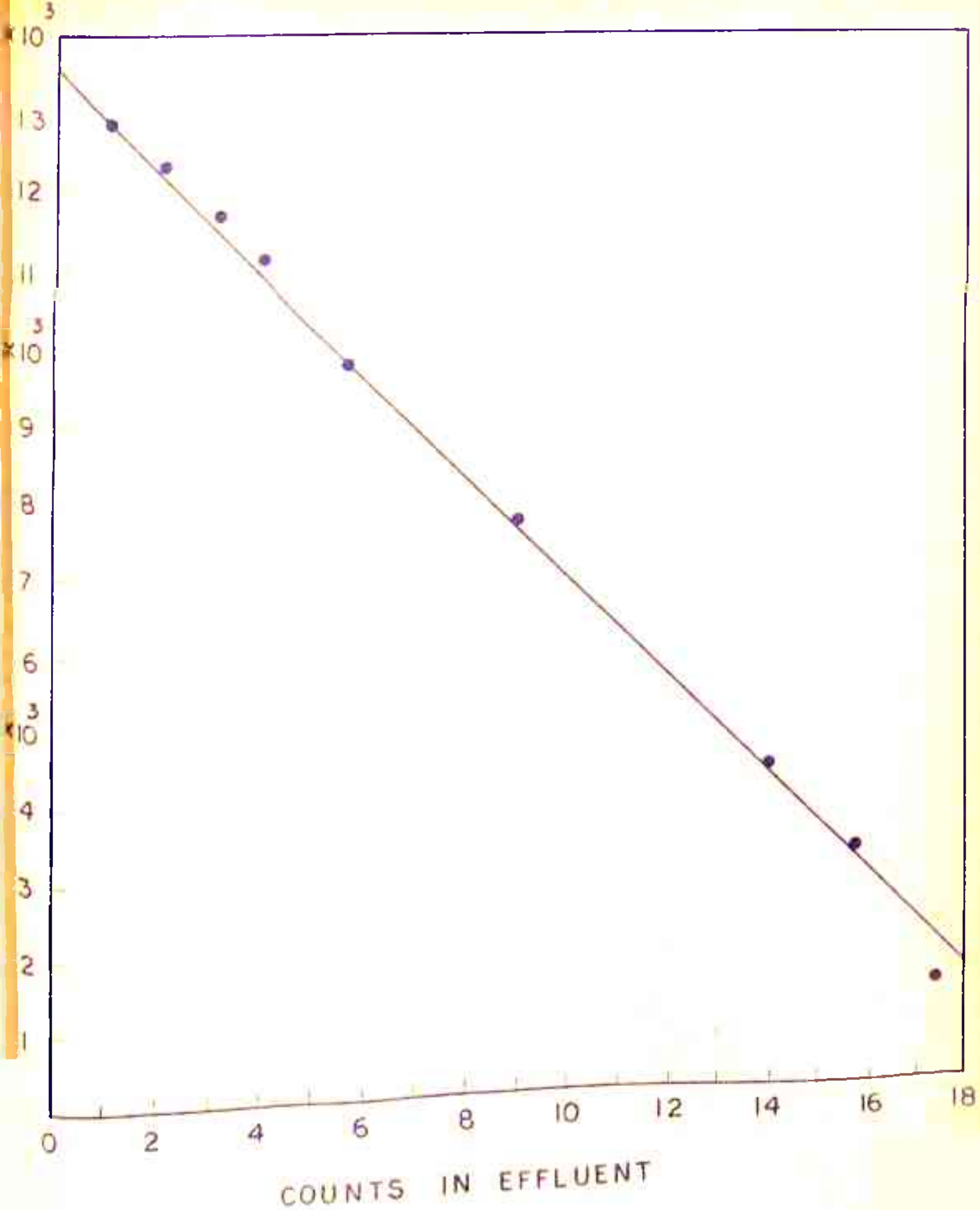


FIG. 5 STANDARD CURVE FOR ESTIMATION OF UNH AS URANYL-PAR COMPLEX.



×10³
13
12
11
×10³
9
8
7
6
×10³
4
3
2
1
0
2
4
6
8
10
12
14
16
18
COUNTS IN EFFLUENT

FIG. 6

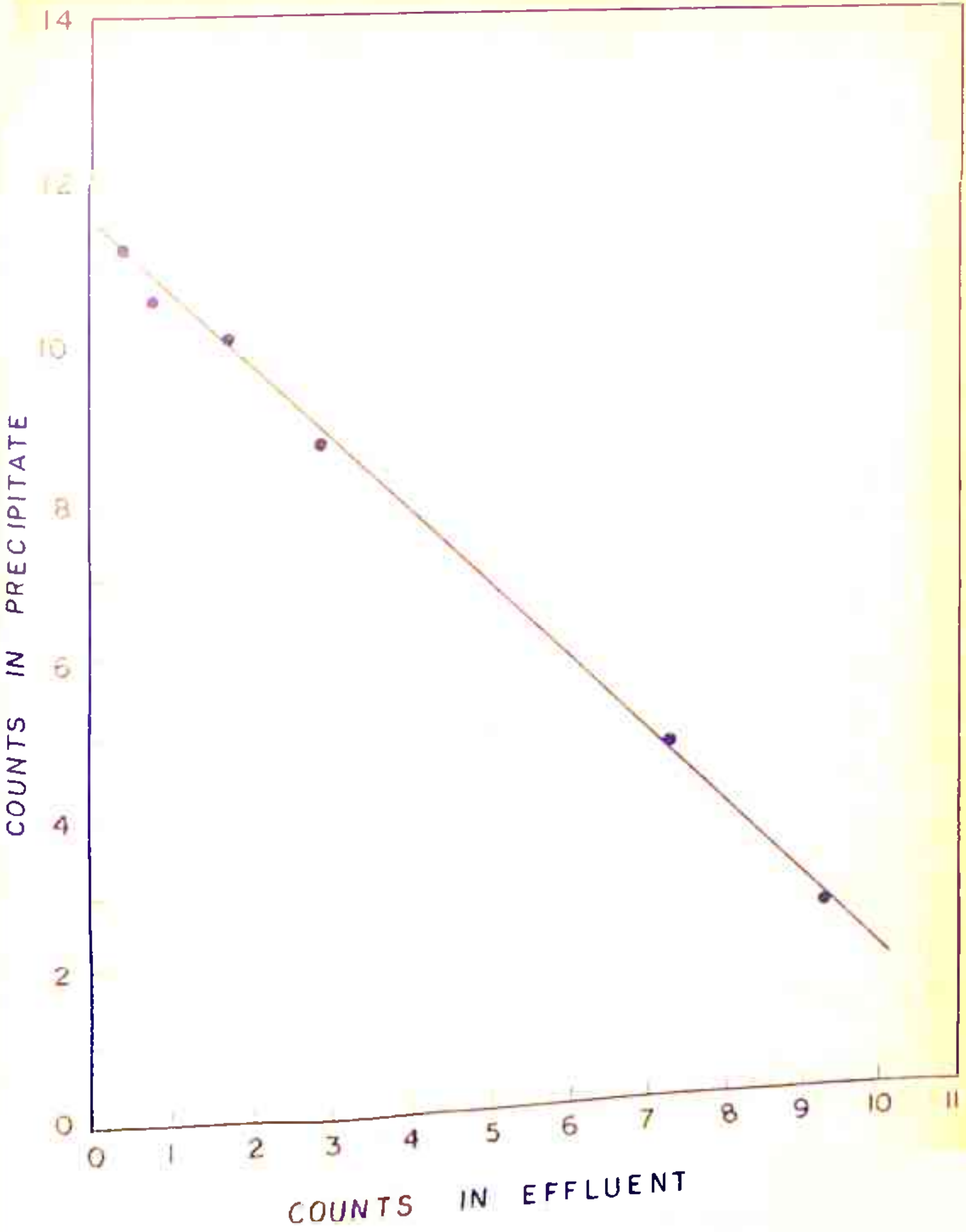

14
12
10
8
6
4
2
0
COUNTS IN PRECIPITATE
0
1
2
3
4
5
6
7
8
9
10
11
COUNTS IN EFFLUENT

FIG. 7

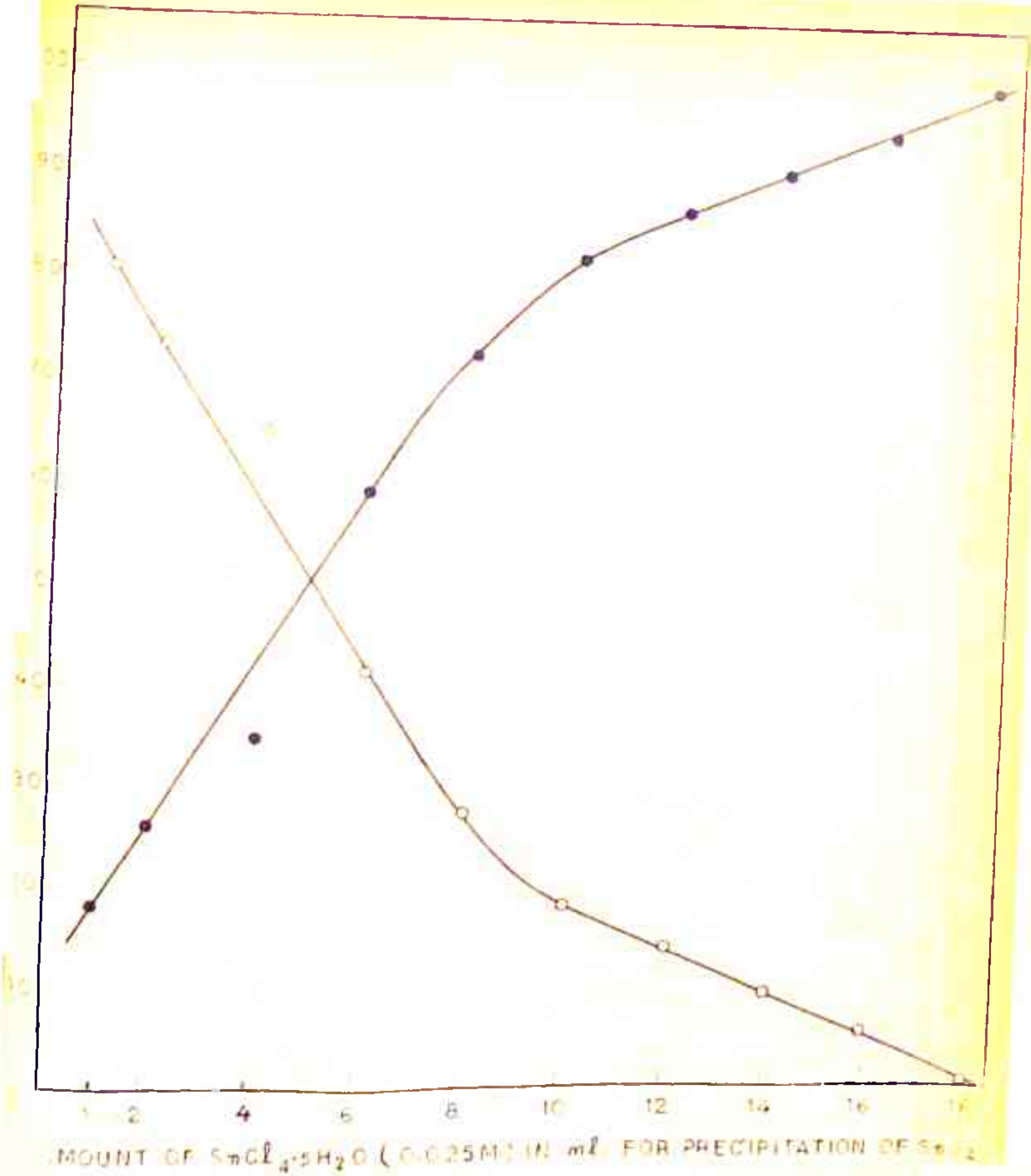
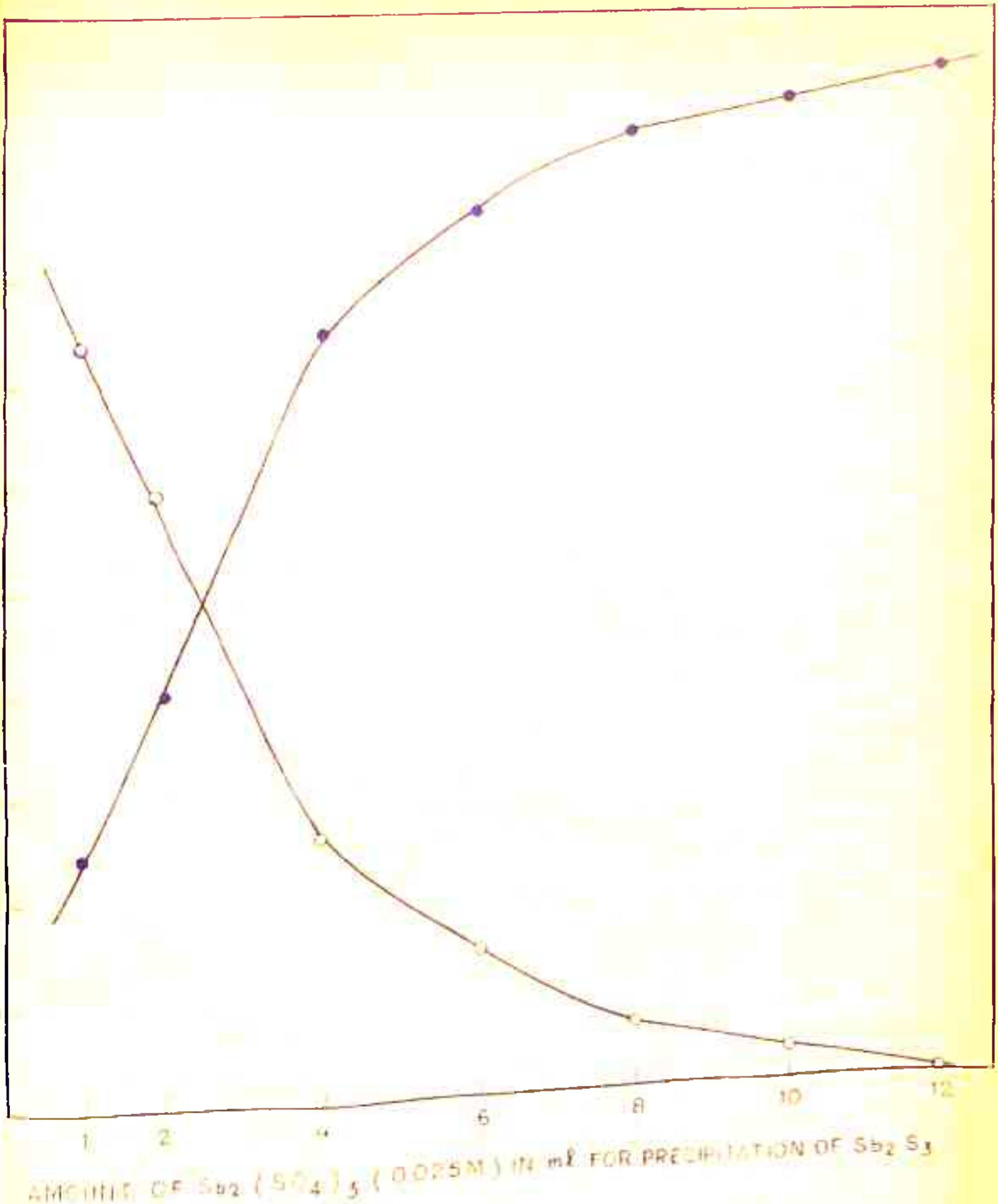


FIG. 8 PERCENT ACTIVITY ON THE PRECIPITATE (●) AND IN THE EFFLUENT (○) ON TIN SULPHIDE



IG. 9 PERCENT ACTIVITY ON THE PRECIPITATE (●) ON ANTIMONY SULPHIDE AND IN THE EFFLUENT (○)

DISCUSSION:

Wahl and coworkers[26,33] found that $^{113}Sn(IV)$ in 0.6M HCl containing 35 mg UO_2^{+2} ions and 10 mg $In(NO_3)_3$/ml could be separated even in the presence of 10^{-6} M tin carrier. Indium was separated from the precipitate by washing with 0.6M HCl saturated with H_2S. Therefore tin and thorium were separated and also thorium was separated from antimony and UO_2^{+2} ions over Sb_2S_3.

Carrier free ^{234}Th was taken and the exchange over the precipitate was determined. A plot of the concentration of thorium ions versus activity over the precipitate is linear in nature but it decreases gradually (Fig.6 and 7). The time of the contact between the solution and the precipitate is of the order of not more than 5 seconds. It can be concluded that at the initial stages ^{234}Th is retained by the process of adsorption in the presence of thorium ions, an exchange between the active and inactive thorium ions is observed. This demonstrates that isotopic exchange mechanism is operating here.

Further plots of the activity of ^{234}Th retained over the precipitate and the activity in the effluent (Fig.8 and 9) gave a linear relationship in the beginning indicating that heterogeneous distribution of thorium is taking place over the precipitate. It has already been pointed out that the rate of exchange decreases gradually. This shows that after the rapid exchange over the surface the inhomogeneous distribution of isotopes takes place and diffusion process replaces the heterogeneous exchange. The latter part of the curves in Fig.8 and 9 confirm that the exchange is taking place at a slower rate.

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CHAPTER 6

SUMMARY OF RESULTS

ION-EXCHANGE CHROMATOGRAPHY

Amberlite IRA-400 exchange resin has been selected and some twenty elements in a mixture of hydrochloric acid or nitric acid - and organic solvent media have been studied. A complete picture of adsorption characteristics and separation possibilities of elements in different organic solvents and acids were found out.

One gm of dried resin was taken and 1 ml hydrochloric acid, 18 ml methanol, ethanol, isopropanol, n-propanol, acetic acid or tetrahydrofuran and 5 mg metal ions/ml were mixed. In the other set of experiments hydrochloric acid was replaced by nitric acid. Equilibrium was attained in two hours and ions were estimated by EDTA, using indicator such as pyrocatechol violet, xylenol orange, hamotoxylin, eriochrome black T, solochrome black T and PAR. Kd values were determined and the following results were obtained.

Hydrochloric Acid Medium:

In Methanol:

UO_2^{+2}, Fe^{+3}, Zn^{+2}, Mo^{+6} and Zr^{+4} can be separated from all other ions used in the experiment. Th^{+4}, Bi^{+3} and Ba^{+2} can also be separated from all other ions. UO_2^{+2}, Th^{+4} and all other ions can be separated from the lanthanide ions like La^{+3}, Nd^{+3}, Ce^{+3}, Dy^{+3} and Yb^{+3}. Al^{+3} is the only ion that interferes with the rare-earths at 60% methanolic concentration.

In Ethanol:

UO_2^{+2}, Fe^{+3}, Mo^{+6} and Zr^{+4} can be separated from all other ions. Th^{+4} can be separated from rare-earths and UO_2^{+2} ions but there are interferences by Ba^{+2} and Bi^{+3} at different concentrations of ethanol. La^{+3} can also be separated from Nd^{+3}, Dy^{+3}, and Yb^{+3}. Al^{+3} interferes with a number of ions i.e, La^{+3}, Ce^{+3}, Nd^{+3}, Dy^{+3}, Yb^{+3}, Pd^{+3}, Sr^{+2} and Cd^{+2}. This system can be used for the separation of UO_2^{+2} , La^{+3}, Th^{+4} and Pb^{+2} from each other as well as from the lanthanides Nd^{+3}, Ce^{+3}, Dy^{+3} and Yb^{+3}.

In Isopropanol:

UO_2^{+2} , Fe^{+3}, Zn^{+2}, Mo^{+6} and Zr^{+4} can be separated from all other ions. Pb^{+2} can also be separated from other ions. The number of interferences by different ions increase in this case. Pb^{+2} and Al^{+3} interfere with the rare-earth ions. However, in the absence of Al^{+3} and Pd^{+2}, actinides and lanthanide ions can be separated from each other.

In n-Propanol:

UO_2^{+2}, Fe^{+3}, Zn^{+2}, Mo^{+6} and Zr^{+4} can be separated from all other ions. Pb^{+2}, and Bi^{+3} can be separated from each other as well as from other ions except Th^{+4} which shows interference. Al^{+3} also interferes with the rare-earths. In addition to these interferences Pd^{+2}, Al^{+3}, Cd^{+2} and Sr^{+2} are interfering with each other. If Al^{+3} is absent, rare-earths ion can be separated from UO_2^{+2} and Th^{+4}.

In Tetrahydrofuran:

UO_2^{+2}, Fe^{+3}, Zn^{+2}, Mo^{+6} and Zr^{+4} can be separated from all other ions. Th^{+4}, Pb^{+2} can be separated from all other ions, except Ba^{+2} and Bi^{+3} which are interfering. Interference by Al^{+3}, Pd^{+2}, Cd^{+2} and Sr^{+2} is also observed. Al^{+3} interferes with the rare-earths ions. The Kd values of rare-earths are so nearcer to each other that it is not possible to separate them from each other.

In Acetic Acid:

UO_2^{+2}, Fe^{+3}, Zn^{+2}, Mo^{+6} and Zr^{+4} can be separated from all other ions. Al^{+3} interferes with the rare-earths. Ba^{+2}, and Bi^{+3} show interference with thorium ions. The rare-earth ions have so close Kd values that they are clustering around in a narrow Kd region. The interferences are observed with Al^{+3}, Pd^{+2} and Sr^{+2}.

Nitric Acid Medium

In Methanol:

UO_2^{+2}, Zn^{+2}, Fe^{+3}, La^{+3}, Nd^{+3} and Mo^{+6} can be separated from all other ions. Pn^{+3}, Th^{+4} and Ba^{+2} can be separated from each other as well as from other ions. Similarly Zn^{+2} can be separated from all other ions. There is an interference with Pb^{+2}, Cd^{+2}, Pd^{+2},Sr^{+2} and Al^{+3}. The rareearths ions like Ce^{+3}, Dy^{+3}, Yb^{+3} as well as Zr^{+4} have so close Kd values that they are clustering around.

In Ethanol:

UO_2^{+2}, Fe^{+3}, Zn^{+2}, Mo^{+6} and Nd^{+3} can be separated from all other ions. Ce^{+3}, Zr^{+4}, Dy^{+3} and Yb^{+3} have Kd values quite nearer to each other. Zn^{+2}, Ba^{+2}, Th^{+4} and Bi^{+3} can also be separated from other ions. Pd^{+2}, Pb^{+2}, Sr^{+2} and Al^{+3} show interferences.

In Isopropanol:

UO_2^{+2}, Fe^{+3}, Zn^{+2}, Mo^{+6}, La^{+3} and Nd^{+3} can be separated from all other ions. Zr^{+4}, Ce^{+3}, Dy^{+3} and Yb^{+3} have Kd values nearer to each other but they can be separated from all other ions. Zn^{+2}, Ba^{+2}, Th^{+4} and Bi^{+3} can be separated from each other as well as from other ions. Al^{+3}, Pb^{+2}, Cd^{+2} and Pd^{+2} show interference with each other.

In n-Propanol:

UO_2^{+2}, Zn^{+2}, Mo^{+6}, La^{+3} and Nd^{+3} can be separated from all other ions. Bi^{+3}, Th^{+4}, Ba^{+2}, Sr^{+2} and Zn^{+2} can be separated from other ions as well as from each other. Pd^{+2}, Cd^{+2}, Al^{+3} and Pb^{+2} show interference with each other. Rare-earths ions except La^{+3} and Nd^{+3} are clustering around and it is not possible to separate them from each other.

In Tetrahydrofuran:

Uo_2^{+2}, Fe^{+3}, Zn^{+2}, La^{+3}, Mo^{+6} and Nd^{+3} can be separated from all other ions. Zn^{+2}, Th^{+4}, Sr^{+2} and Bi^{+3} can be separated from each other as well as from other ions, however Ba^{+2} interferes with the separation of Th^{+4}. Al^{+3}, Pd^{+2}, Cd^{+2} and Pb^{+2} show interference with each other.

In Acetic Acid:

UO_2^{+2}, Fe^{+3}, Zn^{+2}, Mo^{+6}, La^{+3} and Nd^{+3} can be separated from all other ions. Zn^{+2}, Sr^{+2}, Ba^{+2}, Th^{+4} and Bi^{+3} can also be separated from each other. Pd^{+2}, Cd^{+2}, Pb^{+2} and Al^{+3} show interference with each other at higher concentration , Ce^{+3}, Zn^{+4}, Dy^{+3} and Yb^{+3} have Kd values quite nearer to each other. Upto 30% acetic acid Zn^{+2}, Pd^{+2}, Pb^{+2}, Cd^{+2}, Al^{+3}, Sr^{+2}, Ba^{+2}, Th^{+4} and Bi^{+3} have quite distinct Kd values.

In another set of experiments platinum, thorium and uranium were separated over Amberlite IRA-400 using Primene JM-T. Metal ions at pH 1.8 and a 10% solution of Primene JM-T were mixed and after half an hour thorium was separated in the organic phase. UO_2^{+2} ions were eluted from the resin by water, tartaric acid or citric acid.

In another set of experiments a mixture of ions containing UO_2^{+2}, Th^{+4} and platinum is passed through the column. Here chloride complexes of uranium and platinum were adsorbed on the resin and thorium is passed out of it. Uranium was eluted by washing with water and platinum is removed with 3M nitric acid.

THIN LAYER CHROMATOGRAPHY

This method has been selected for the separation of a number of ions. Silica gel G, 3 mm thick was plated over glass plates with Stahl type apparatus and plates were activated by heating at 100-110°C for one hour. All metal ions were 0.1M in nitrate form. Each spot was about 0.5 cm and samples were spotted about one inch from the end of the plates. The development was performed continuously in an ascending manner on near vertical plates in an airtight container saturated with solvent vapours. Time of development was about 3 hours. A number of chemicals were used for visualization.

In one set of experiments the solvent system was made of 80 ml dioxane, 20 ml acid of concentration, 0.1N, 0.5N, 1.5N and 2.5N (HCl, HNO_3, H_2SO_4 and $C_2H_4O_2$) and 2 g of m-nitrobenzoic acid.

In another set of experiments the composition of solvent system is given below:

A : 60 ml t-butanol + 30 ml ethanol + 30 ml 4N HNO_3
B : 50 ml t-butanol + 40 ml ethanol + 30 ml 2N HNO_3
C : 40 ml t-butanol + 50 ml ethanol + 30 ml 1N HNO_3
D : 30 ml t-butanol + 60 ml ethanol + 30 ml 0.2N HNO_3

In another sets of experiments nitric acid was replaced by hydrochloric acid, sulphuric acid and acetic acid.

Besides the above mentioned solvent systems the following solvent systems were also studied:

A : 90 ml ethanol + 10 ml 4N HNO_3
B : 90 ml ethanol + 10 ml 4N HCl
C : 90 ml iso-butanol + 10 ml 4N HNO_3
D : 90 ml iso-butanol + 10 ml 4N HCl

Rf values were determined and the following conclusions were drawn:

UO_2^{+2} and Th^{+4} ions can be separated from the lanthanides using 2.5N HNO_3 with dioxane at room temperature. These ions can also be separated from Fe^{+3}, Al^{+3} and Zr^{+4} at this concentration, however the rare-earths ions have Rf values quite similar or nearer to each other. UO_2^{+2} and Th^{+4} ions can also be separated from the lanthanides at 0.5N HNO_3. But the separation of Fe^{+3} is not better than that used with 2.5N HNO_3. The separation of rare-earths shows identical characteristics discussed with 2.5N HNO_3. Better separation of UO_2^{+2} and Th^{+4} ions can be achieved by using 0.5N nitric acid and dioxane mixture. UO_2^{+2} and Th^{+4} ions can be separated from all rare-earths using 0.1N HCl. UO_2^{+2} ions separation can also be achieved with all other concentrations of HCl, but some interference is observed with Th^{+4} ions. The Rf values of lanthanides obtained in this system are either identical or are clustering together. UO_2^{+2} and Th^{+4} ions can be separated from lanthanides, Fe^{+3}, Al^{+3} and Zr^{+4} using either 1.5N or 2.5N sulphuric acid and dioxane. If 1.5N H_2SO_4 is used, a number of rare-earths can also be separated although exceptions have to be made for those having values identical to each other . The separation of UO_2^{+2} and Th^{+4} ions from Al^{+3}, Fe^{+3} and lanthanides is possible using either 0.5N or 2.5N acetic acid. The better separation is achieved using 0.5N acetic acid where rare-earths ions can also be separated from each other.

UO_2^{+2} and Th^{+4} ions can be separated from rare-earths ions and some other metal ions using a solvent system of t-butanol, ethanol and 1N nitric acid. This separation is also possible with 0.2N nitric acid but Co^{+2} interferes with Th^{+4} ions. Solvent system t-butanol-ethanol-1N HCl can be used for the separation of uranyl and thorium ions from other twenty one ions. Hg^{+2} interferes in the separation of UO_2^{+2} ions. In this solvent system 4N, 2N and 0.2N hydrochloric acid does not serve any useful analytical purpose. UO_2^{+2} and Th^{+4} ions can be separated from sixteen other metal ions including lanthanides using t-butanol-ethanol-4N H_2SO_4. UO_2^{+2} and Th^{+4} ions can be separated from ten other lanthanides using t-butanol-ethanol- and acetic acid (1N, 2N or 4N) but in this case a number of ions do not develop fairly well. Acetic acid poses a limitation as an analytical system for the separation of some lanthanides and actinides because a number of ions have been reduced to 50%.

Ethanol and 4N HNO_3 or 4N HCl can be used in the separation of UO_2^{+2} from Th^{+4} and other ions including some lanthanides. However, the separation of Th^{+4} is not possible with some rare-earths ions. The solvent system isobutanol-4HNO_3 can be used for the separation of uranium and thorium ions from sixteen other ions including some lanthanides. If in this system nitric acid is replaced by hydrochloric acid of identical strength, separations are possible but the Rf values are so nearer to each other that it is not of much practical use. The temperature has an effect on the Rf values. Rf values decrease with the increase of the temperature.

SOLVENT EXTRACTION

The following two analytical procedures were developed for the extraction of uranium and thorium. The optimum conditions for the extraction were fixed by investigating with varying amount of one chemical and fixing the composition of others.

A 30% solution of tri-n-butyl phosphate was prepared using carbon tetrachloride as a diluent. The following solutions were mixed together:

1. Uranyl perchlorate	5 ml (0.5M)
2. Perchloric acid	5 ml (0.3M)
3. Sodium perchlorate	2 ml (4M)
4. Hydrochloric acid	5 ml (3M)
5. Thorium tetrachloride	5 ml (0.01M)
6. Water	3 ml

25 ml of this mixture and 25 ml of 30% TBP solution were mixed in a separating funnel and the funnel was shaken in a mechanical shaker for one hour. Uranium and thorium were extracted in the TBP solution. Thorium was removed from the organic phase using 10% sodium periodate solution. Thorium was removed using 3 more washing with 3M HCl. Thorium

was estimated by thoron as a complexing agent and uranium was determined by PAR. Uranium in the organic phase was determined by first stripping with the solution of Na_2CO_3 followed by the use of sodium peroxide.

In another procedure thorium was extracted with diphenyl sulphoxide. The following solutions were mixed together:

1. 2 ml 1M HCl,
2. 5 ml 0.04M thorium tetrachloride
3. 5 ml 0.08M diphenyl sulphoxide in carbon tetrachloride
4. 2 ml 4M sodium chloride.

These solutions were mixed in a separating funnel and equilibrium was attained in 15 minutes. The lower layer containing extracted thorium was separated and the amount of thorium left over was estimated as an oxalate keeping the concentration of HCl near 1M.

HETEROGENEOUS EXCHANGE REACTIONS

^{234}Th a daughter of ^{238}U was separated from the parent using the techniques of complex formation and solvent extraction. This isotope was identified by measuring the half life and maximum range of β particles using Feather's analyser. A solution 0.025M $SnCl_4.5H_2O$ prepared in 0.6M HCl was precipitated as Sn(IV) sulphide and was filtered over the cone chimney apparatus. Similarly a solution of 0.025M $Sb_2(SO_4)_3$ was prepared in 0.6M HCl and was precipitated as sulphide. The precipitate was transferred in such a way that it settled down and no cracks were observed. The precipitates were washed with CS_2 and C_6H_6 to remove sulphur.

^{234}Th tracer was dropped over different amounts of sulphide while suction was being applied and the time of contact between the precipitate and the solution was of the order of about a few seconds. The activity over the precipitate and in the effluent was counted. A solution containing 2.5 ml each of uranyl nitrate hexahydrate and thorium nitrate of strength of 0.01M was dropped over the precipitate and uranium in the effluent was estimated by PAR and thorium by thoron respectively. About 99% ^{234}Th is retained on different precipitate beds. When a 18 ml $SnCl_4.5H_2O$ (0.025M) is precipitated as SnS_2 more than 99% of ^{234}Th activity is retained over it. Similarly 12 ml of $Sb_2(SO_4)_3$, (0.025M) precipitated as Sb_2S_3 retains 99.5% of ^{234}Th activity. The effect of isotopic carrier on the retention of ^{234}Th activity over the precipitate is that the retention becomes less. UO_2^{+2} ions are partially retained over SnS_2. However, if the precipitate bed is washed with 0.6N HCl containing H_2S, more than 90% uranyl ions activity comes donw. Similarly Sb_2S_3 precipitate weighing 400 mg retains 98% ^{120m}Sb activity. Since some uranyl ione are retained over the precipitate of Sb_2S_3, therefore it was separated. The precipitate of Sb_2S_3 containing uranyl ions was dissolved in 5 ml of 1N HCl and H_2S was boiled off. The solution was diluted with HCl to make it 0.6N. It was precipitated as sulphide and the precipitate was washed with 15 ml 0.6N HCl containing H_2S. The precipitate was centrifuged and all liquids portions were collected and evaporated to dryness. The total number of counts of this samples were of the order of about 10 activity of uranyl ions. Similarly the precipitate gave the activity of antimony. Thorium was separated from tin and antimony and was estimated.

A plot of the concentration of thorium ions versus activity over the precipitate is linear in nature, but it decreases gradually. Therefore, it is concluded that at the initial stages ^{234}Th is retained by the process of adsorption. An exchange between the active and inactive thorium ions has also been noted, which confirms the isotopic mechanisms in this process. Further plots of activity of ^{234}Th retained over the precipitates and the activity in the effluent gave a linear relationship indicating that heterogenous distribution of thorium is taking place over the precipitate. The rate of exchange decreases gradually. This shows that after the rapid exchange at the surface, the inhomogeneous distribution of isotope takes place and diffusion process replaces the heterogeneous exchange and the rate becomes slow.

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