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NUCLEAR MATERIALS*

SELECTED DATA ON ION EXCHANGE SEPARATIONS IN RADIOANALYTICAL CHEMISTRY

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SELECTED DATA ON
ION EXCHANGE SEPARATIONS IN RADIOANALYTICAL CHEMISTRY

Abstract-Ion exchange techniques play an important role in radiochemical separations. This report presents some ion exchange data selected from analytical and radiochemical journals. Ten charts of cation- and anion exchange distribution coefficients and nineteen diagrams of ion exchange chromatographic separations are included in the report.

In the past three decades, ion exchange has found wide applications in radioanalytical chemistry. Ion exchange techniques have proved to be an increasingly useful analytical tool for the simple and, in many cases, rapid separations, concentrations and purifications of radioactive species in quantities ranging from tracer to macro levels. Its most remarkable success was in the separation and identification of rare earth fission products and several synthetic transuranium elements.

The purpose of this report is to compile some data on ion exchange which are of great interest to radiochemists. It is not the aim of the present report to cover the broad subject of ion exchange because a number of excellent books and review papers have already described the fundamental principles of the ion exchange and its applications in analytical chemistry. In writing this report, emphasis is placed on the compilation of the ion exchange data which were published in the literature during the last two decades. However, some earlier work which is pertinent to recent progress is also included. No attempt has been made to include ion exchange data with inorganic ion exchangers and liquid ion exchangers.

This report is divided into two sections; (1) Charts of ion exchange distribution coefficients: (2) Ion exchange chromatographic separations. The first section contains information regarding ion exchange distribution coefficients of elements on ion exchange resins. The second section deals with selected procedures of ion-exchange chromatographic separations of radioanalytical importance.

Charts of ion exchange distribution coefficients

Adsorption behavior of a given solute on ion exchange resins is represented by the equilibrium distribution coefficient. The data on the distribution coefficients are very useful for analytical chemists, since they provide a basis for devising ion exchange separation schemes.

Two kinds of definitions of the distribution coefficient are used in the literature of ion exchange studies: i) volume distribution coefficient, $\mathcal{D}_v$ (amount of a solute adsorbed per milliliter resin bed/amount of a solute per milliliter of solution), and ii) weight distribution coefficient, $\mathcal{D}_g$ (amount of a solute adsorbed per gram dry resin/amount of a solute per milliliter of solution). $\mathcal{D}_v$ and $\mathcal{D}_g$ are related by the resin bed density and can be converted each other.

Since the pioneer work of Kraus and Nelson, substantial amounts of information have been accumulated regarding the disribution coefficients of a large number of elements. This section contains selected charts of cation- and anion distribution coefficients. The cation exchange data are presented in Figs. 1, 2, 3 and 4 for different cations in aqueous solutions of HCl, HBr, $HClO_4$ and HNO_3-tartaric acid, whereas the anion exchange data are given in Figs. 5, 6, 7, 8, 9 and 10 for a number of anions in aqueous solutions of HCl, HNO_3, HF acetic acid and HNO_3-tartaric acid as well as a solution of the mixture of HCl and acetone.

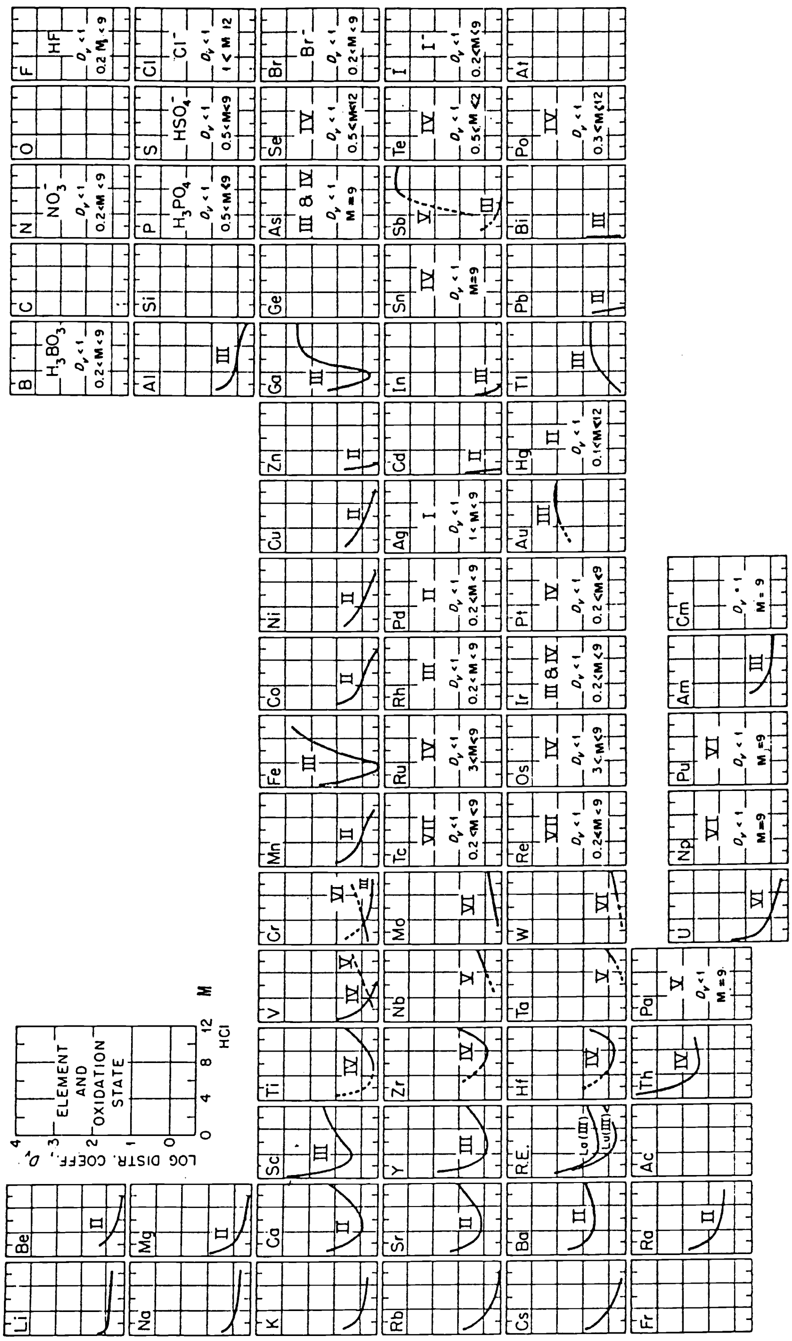

Fig. 1. Cation exchange distribution coefficients in HCl solutions.(Dowex 50-X4) (Ref.1)

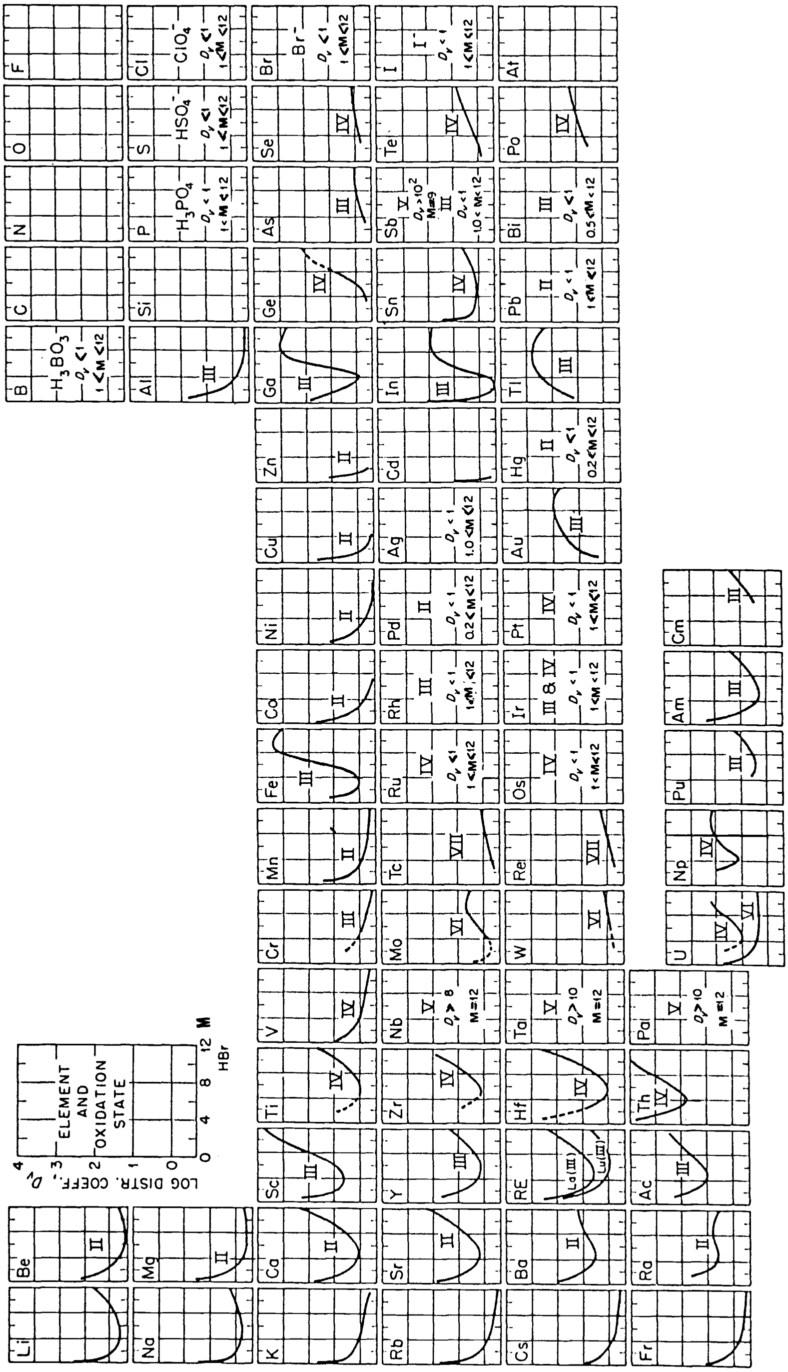

Fig. 2. Cation exchange distribution coefficients in HBr solutions. (Dowex 50-X4) (Ref. 2)

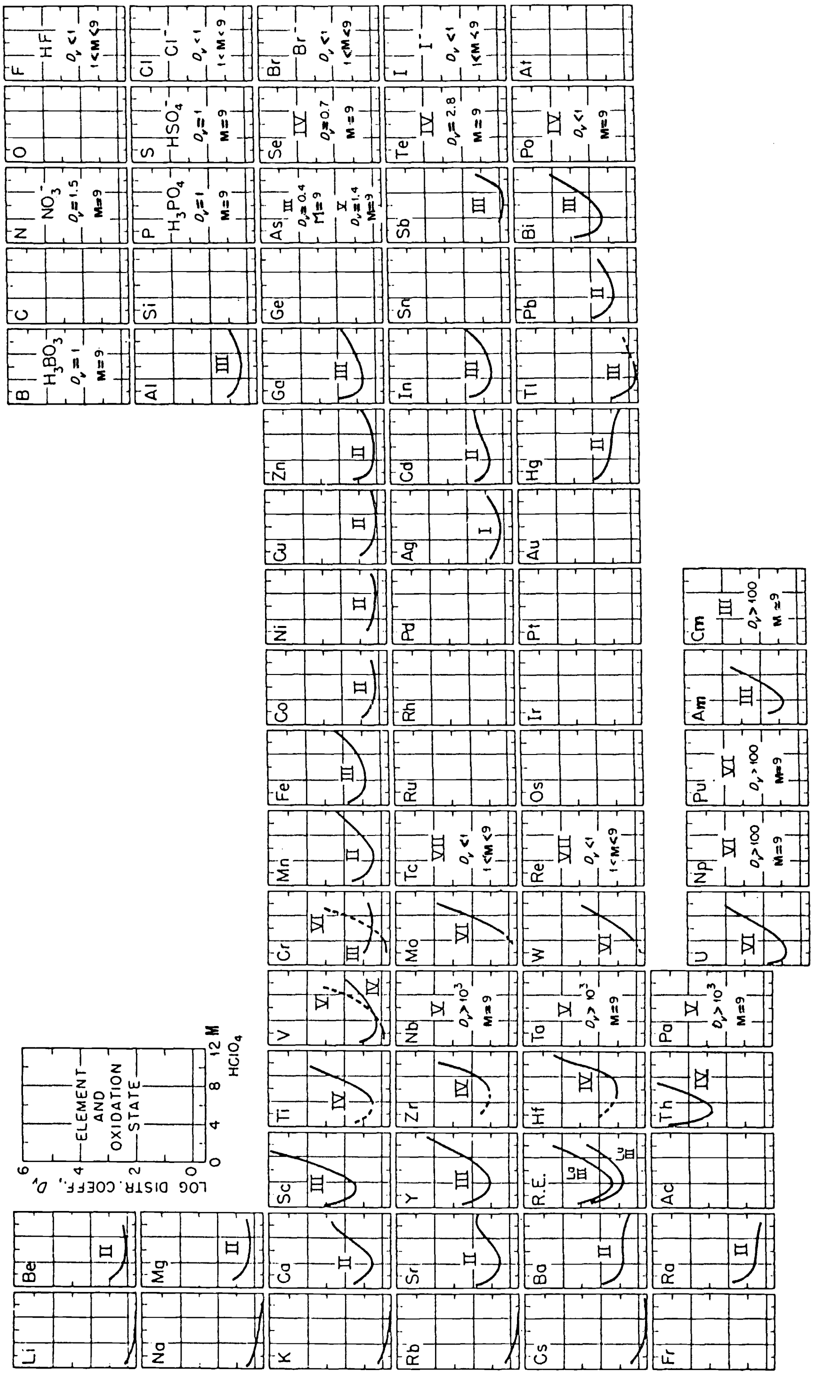

Fig. 3. Cation exchange distribution coefficients in $HClO_4$ solutions. (Dowex 50-X4)(Ref. 1)

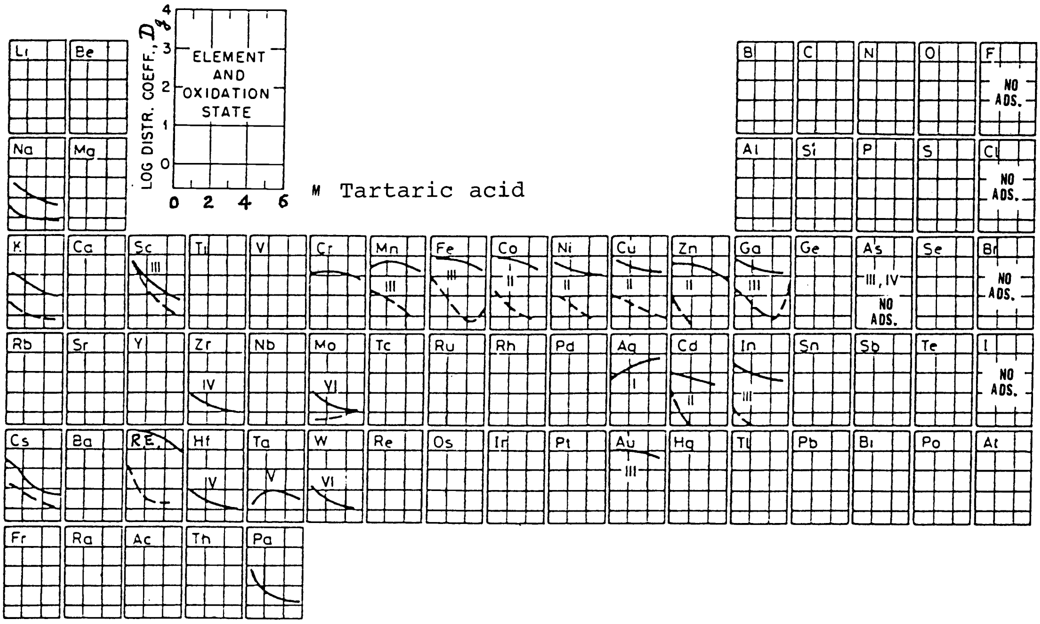

Fig.4. Cation exchange distribution coefficients in 0.3M HNO_3-Tartaric acid solutions.(Dowex 50-X8)(Ref. 7) (Broken lines represent the data in HCl solutions)

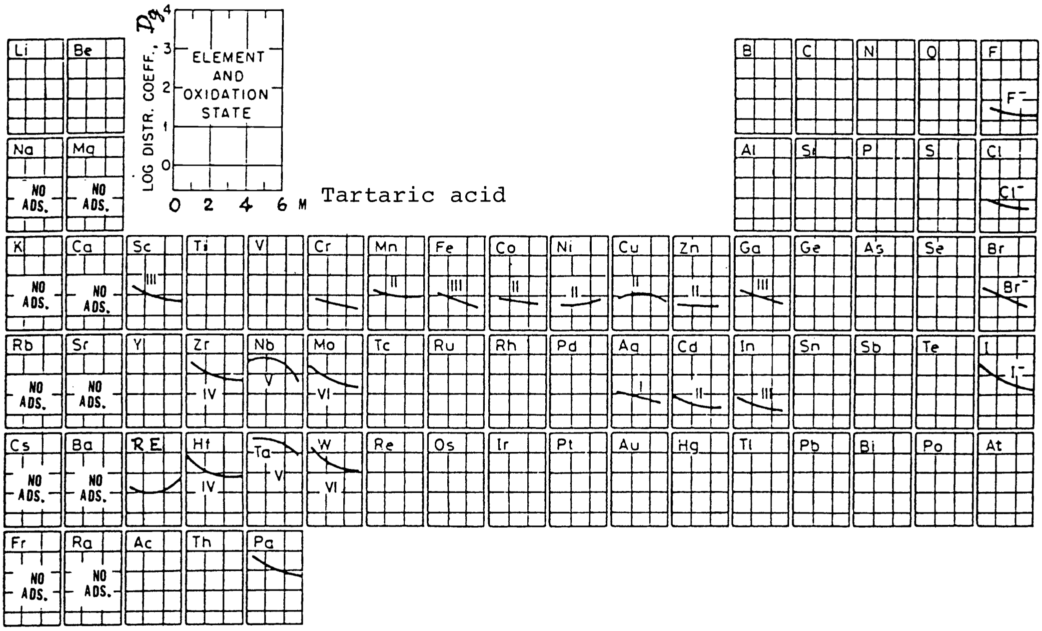

Fig. 5. Anion exchange distribution coefficients in 0.3M HNO_3 -Tartaric acid solutions.(Dowex 1-X8)(Ref. 7)

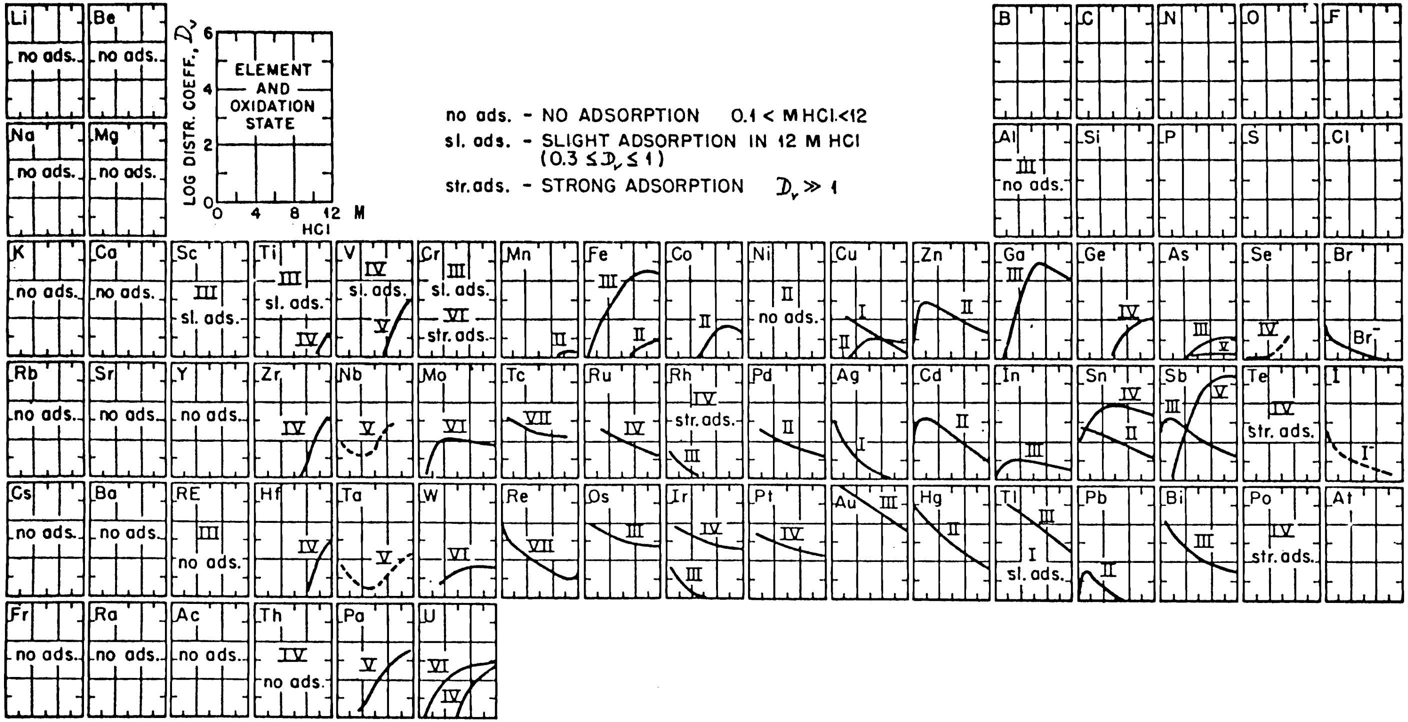

Fig. 6. Anion exchange distribution coefficients in HCl solutions. (Dowex 1-X10) (Ref. 3)

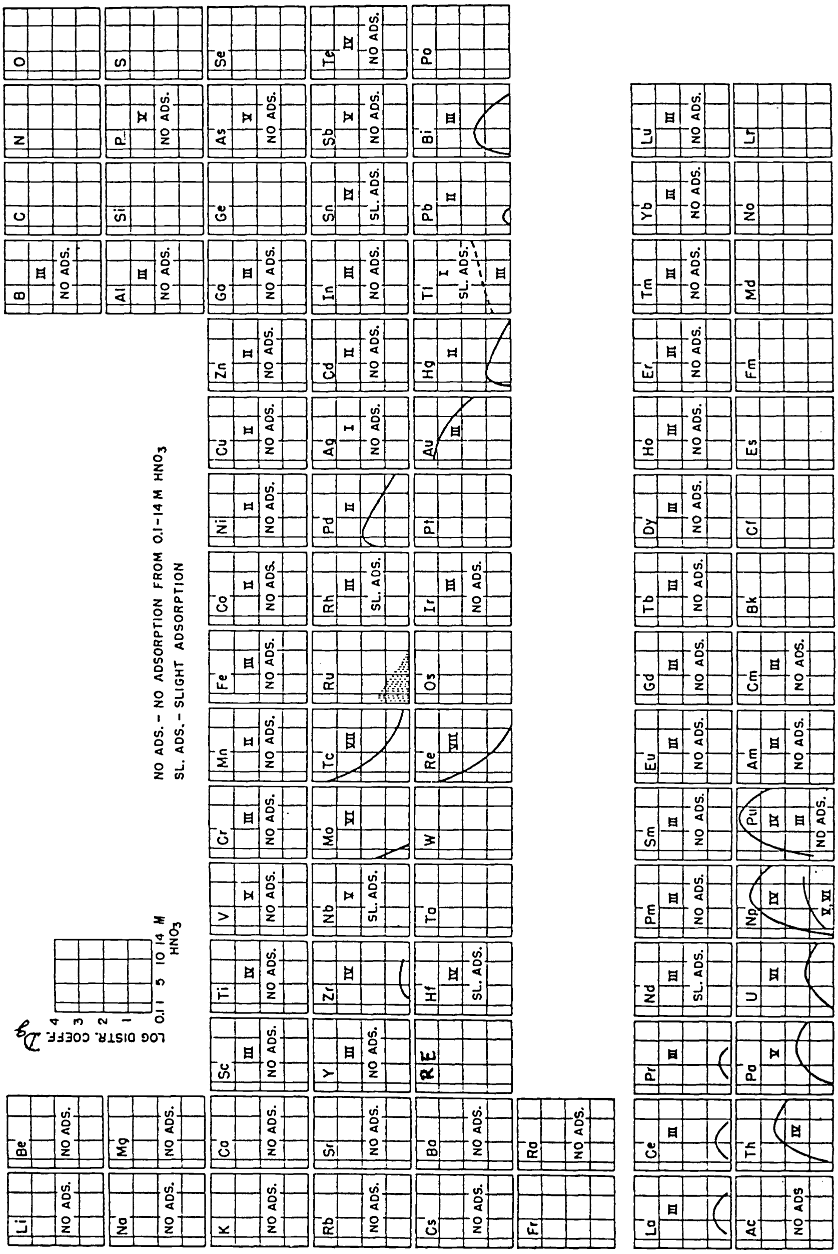

Fig. 7. Anion exchange distribution coefficients in HNO_3 solutions. (Dowex 1-X10) (Ref. 4)

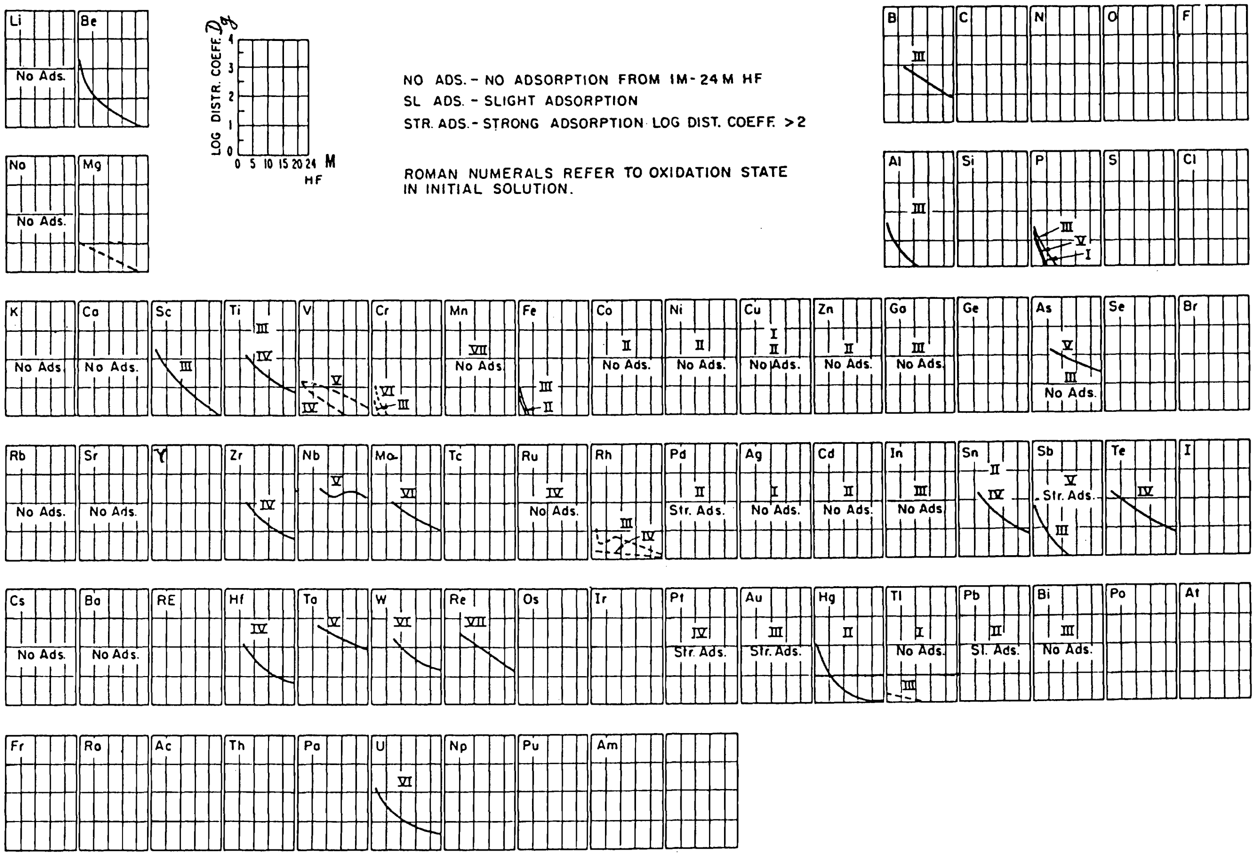

Fig. 8. Anion exchange distribution coefficients in HF solutions.(Dowex 1-X10) (Ref. 5)

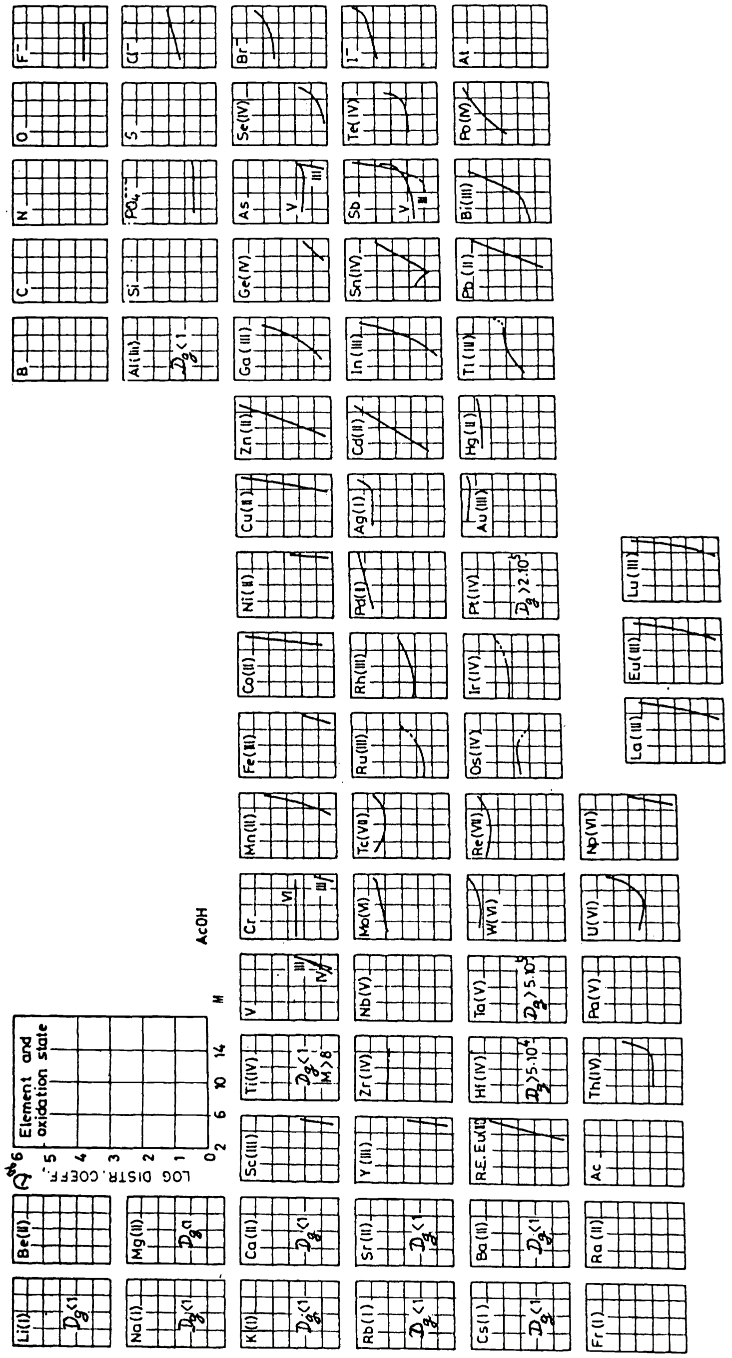

Fig. 9. Anion exchange distribution coefficients in acetic acid solutions. (Dowex 1-X8)(Ref. 6)

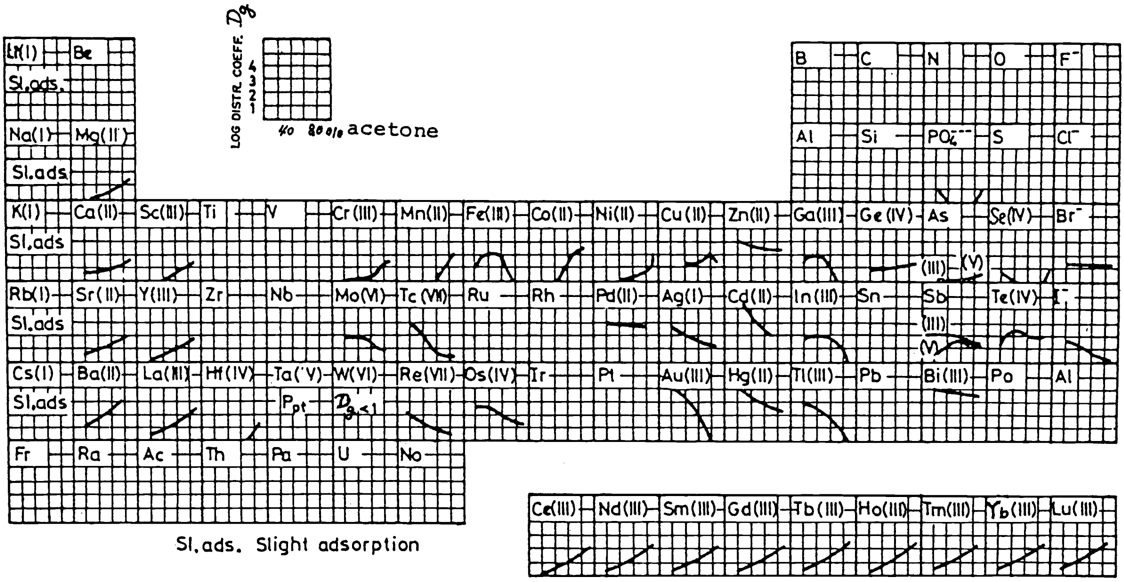

Fig. 10. Anion exchange distribution coefficients in HCl(1.2M)-water-acetone mixtures.(Dowex 1-X8) (Ref. 8)

Ion exchange chromatographic separations

Because of its high selectivity and wide applicability,ion exchange chromatography has been extensively utilized for the separation of elements.The method involves the adsorption of a mixture of ions on ion exchange resins followed by selective elution.In this section are presented selected elution diagrams which demonstrate the versatility of ion exchange chromatography in radioanalytical chemistry.

The efficiency of ion exchange separations depends on a number of experimental factors including:1)kind of resin and its form;2)grain size of resins;3)flow rate of eluting solutions;4)column dimension;5)kind of eluting agent;6)temperature;7)loading.A brief description of specific experimental conditions is shown with each figure of the elution diagram.

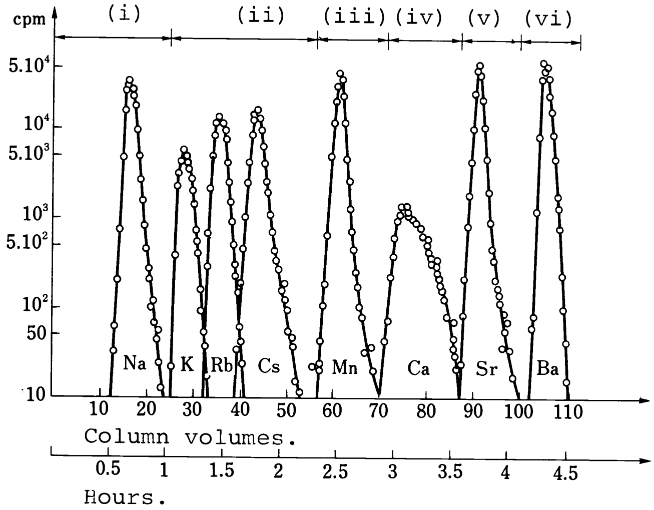

Fig.11. Separation of Na,K,Rb,Cs,Ca,Sr,Mn,and Ba.(Ref.10)

Elements:Na,K,Rb,Cs,Mn,Ca,Sr,Ba(HCl solution).Ion exchange resin:Dowex 50W-X12.H-form.(10-25μ wet).Column:10cm x0.6cm (D).Flow rate:1.4ml/min..Temperature:Room temperature. Eluent:HCl.(i)0.2M,(ii)0.55M,(iii)0.9M,(iv)1M,(v)1.8M(vi)4M.

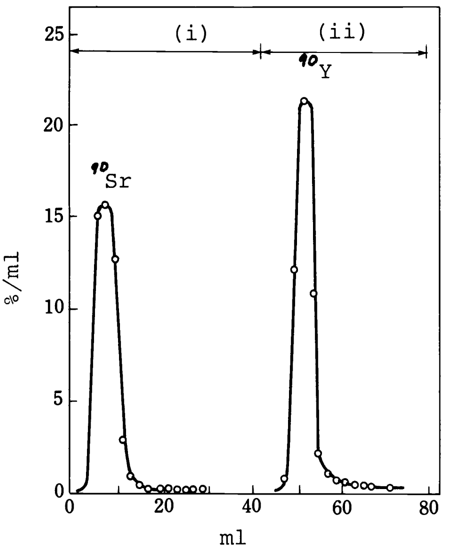

Fig. 12. Separation of Sr and Y. (Ref.9)

Elements:Sr-90,Y-90,Ion exchange resin: Superficially sulphonated resin.(0.20-0.34mm particle size).H-form.Capacity, 6x10^{-4}meq/g.Column:15cm x 1cm(ID).Flow rate:12.8ml/cm^{2}.min.Eluent:HCl.(i)0.1M, (ii)1M.

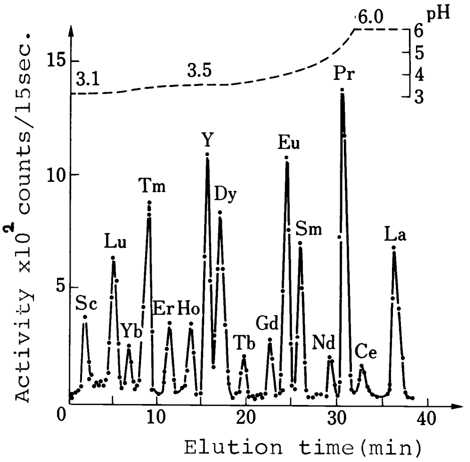

Fig.13. Separation of rare earth elements.(Ref.24)

Elements:Rare earth elements.Ion exchange resin:TSK LS-212 high performance ion exchange resin. Column:75mmX0.5mm(ID).Flow rate: 8 μl/min..Temperature:Room temperature.Eluent:0.4M Ammonium hydroxyisobutyrate(pH 3.1-6.0) (gradient elution).

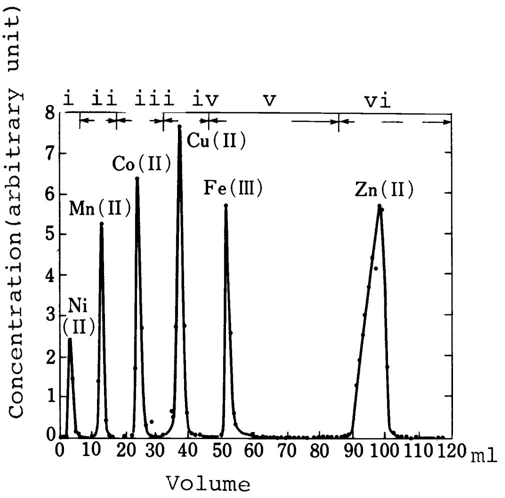

Fig.14. Separation of Ni,Mn,Co,Cu, Fe,and Zn.(Ref.26)

Elements:Ni(II),Mn(II),Co(II),Cu(II), Fe(III), Zn(II).(HCl solution).Ion exchange resin:Dowex 1.Column: 26cmX0.29cm^{2}.Flow rate:0.5cm/min. Eluents:(i)12M HCl,(ii)6M HCl,(iii) 4M HCl,(iv)2.5M HCl,(v)0.5M HCl,(vi) 0.005M HCl.

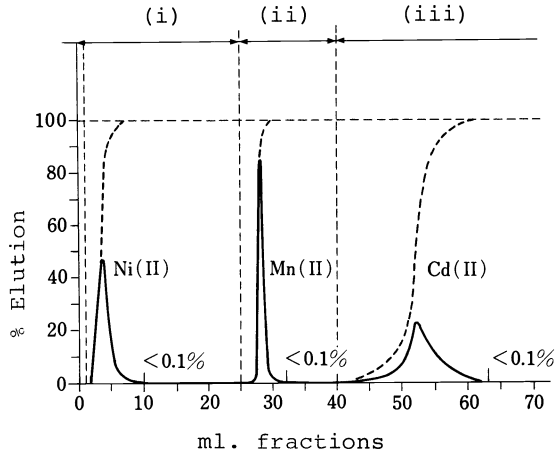

Fig. 15. Separation of Ni,Mn and Cd. (Ref.12)

Elements:Ni,Mn(II),Cd.(HCl-CH_3COOH solution).Ion exchange resin:Dowex 1-X8. Acetate-form.(100-200 mesh).Column: 7.5cm x 0.8cm(D).Flow rate:4ml/cm^{2}.min. Temperature:25°C.Eluents:15M CH_3COOH, (ii)10M CH_3COOH,(iii)0.5M CH_3COOH.

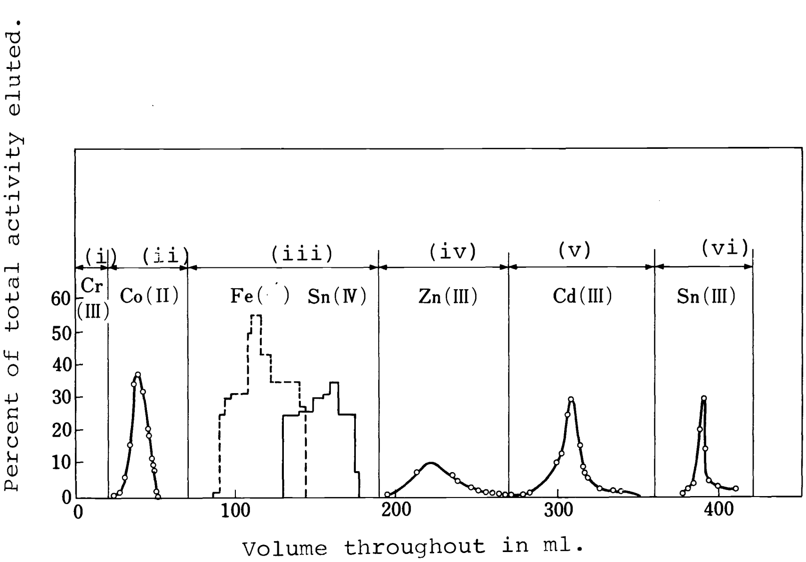

Fig.16. Separation of Cr,Co,Fe,Sn,Zn,Cd and Sb. (Ref.13)

Elements:Cr(III),Co(II),Fe(III),Sn(IV),Zn,Cd,Sb(III) (HCl solution).Ion exchange resin:Amberlite CG 400-X8. Cl-form.(100-200 mesh).Column:25cmX1.2cm(ID).Flow rate: 0.5-0.6ml/min..Temperature:25° C.Eluents:(i)8M HCl,(ii) 3M HCl,(iii)4M HCl-2M HF,(iv)and(v)0.3M $H_2C_2O_4$,(vi) 0.1M $HClO_4$.

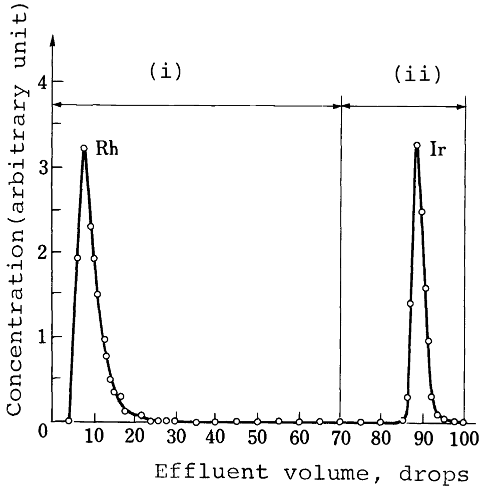

Fig.17. Separation of Rh and Ir. (Ref.14)

Elements:Rh,Ir.(HBr solution).Ion exchange resin:Dowex 1-X4.Br-form. (ϕ20-53μ).Column:3.0cm x 0.03cm^2. Flow rate:o.4cm/min.Temperature: 75°C.Eluents:(i)8M $HBr-Br_2$,(ii) 8.3M HBr-2%N_2H_4HCl.

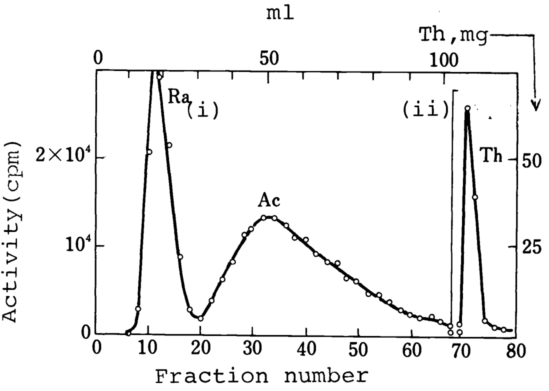

Fig.18. Separation of Ra,Ac and Th. (Ref.17)

Elements:Ra,Ac,Th.(HNO_3-CH_3OH solution),Ion exchange resin: Dowex 1-X8.Nitrate-form.(200-400 mesh).Column:23.5cm x 0.6cm. Flow rate:1ml/cm^2.min..Temperature: 22°C.Eluents:(i)65%CH_3OH-0.5M HNO_3, (ii)0.02M HNO_3.

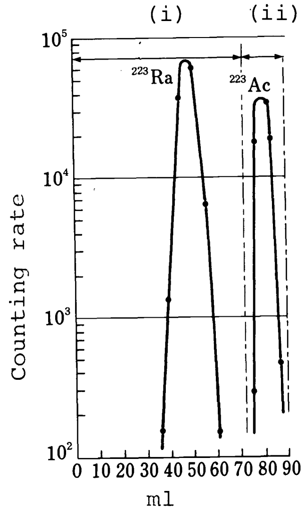

Fig.19. Separation of Ra and Ac. (Ref.15)

Elements:Ra and Ac(HNO_3 solution) Ion exchange resin:Dowex 50-X8. H-form.(200 mesh).Column: 50mm×5mm..Temperature:Room temperature.Eluents:(i)1M HNO_3 , (ii)3M HNO_3 .

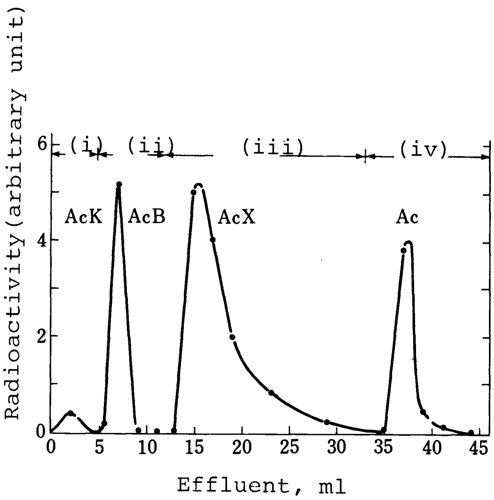

Fig.20. Separation of Ac,Fr,Pb, and Ra(Ref.27)

Elements:Ac,Fr(AcK),Pb(AcB),Ra (AcX).Ion exchange resin:Dowex 50-X8. H-form.(100-200 mesh). Column:8cm×6mm(ID).Eluents: (i)o.5M HClO4,(ii)1.5M HCl-15%CH3OH,(iii)9M HClO4,(iv) 6M HNO3.

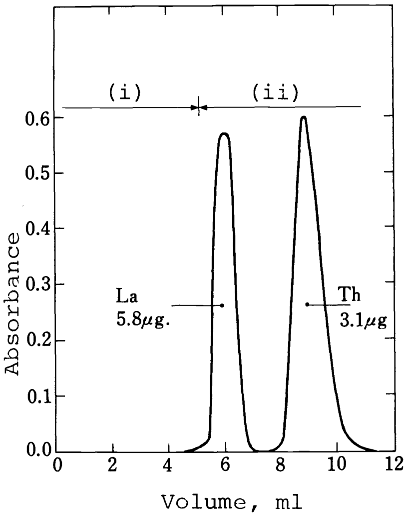

Fig.21. Separation of La and Th. (Ref.16)

Elements:La,Th.Ion exchange resin: Low capacity,macroreticular cation exchange resin(polystyrene sulphonated type).Capacity,0.84 meq/g. Column:13cm×0.4cm.Flow rate: 2ml/min..Eluents:(i)1M HCl,(ii) 4M HCl.

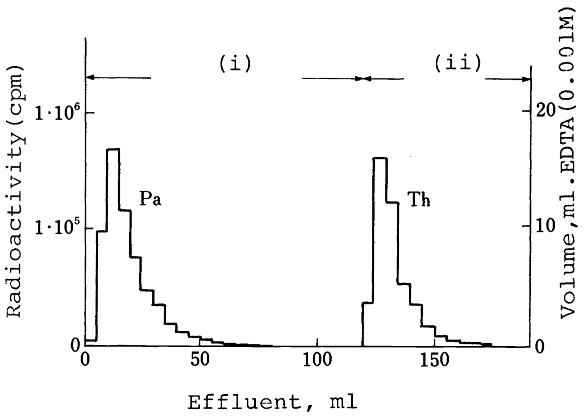

Fig.22. Separation of Pa and Th. (Ref.18)

Elements:Pa,Th.Ion exchange resin: Dowex 50W-X8.H-form.(100-200 mesh). Column:4cm×1cm(ID).Flow rate: ~0.8ml/min..Eluents:(i)1M NH_4SCN-0.5M HCl,(ii)2M NH_4SCN-0.5M HCl.

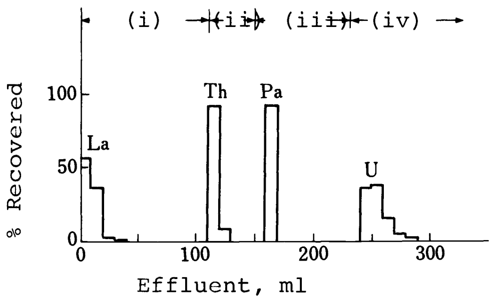

Fig.23. Separation of La,Th,Pa and U.(Ref.19)

Elements:La,Th,Pa(V),U(VI).Ion exchange resin:Dowex 1-X8. Thiocyanate-form.(100-200 mesh) Column:~10cm×1.0cm(ID).Flow rate: 0.3-0.5ml/min..Temperature:Room temperature.Eluents:(i)1.5M NH_4SCN-0.5M HCl,(ii)8M HCl,(iii) 3M HCl-0.005M HF,(iv)1M $HClO_4$.

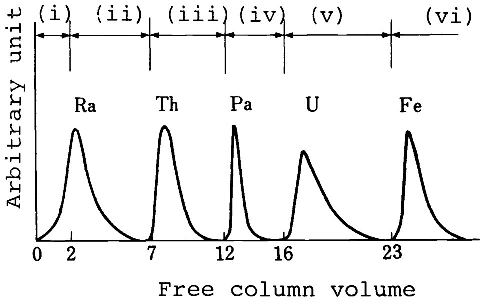

Fig.24. Separation of Ra,Th,Pa,U and Fe.(Ref.20)

Elements:Ra,Pa(V),Th,U(VI),Fe(III) (oxalate solution).Ion exchange resin:Dowex 1-X8.Oxalate-form. (200 mesh).Column:10cm x 0.6cm(ID). (1.5ml resin).Flow rate:0.1-0.2ml/min. Temperature:Room temperature.Eluents: (i)Feed solution,(ii)0.5M $H_2C_2O_4$, (iii)8M HCl,(iv)8M HCl-0.1M HF,(v) 6M HCl-1M $HClO_4$,(vi)1M HCl.

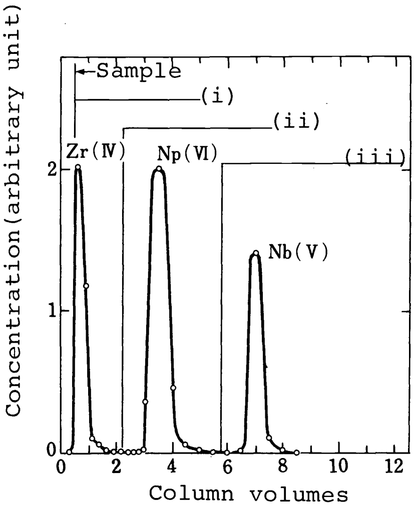

Fig.25. Separation of Zr,Np and Nb.(Ref.11)

Elements:Zr,Np(VI),Nb(V)(HCl-HF solution).Ion exchange resin:Dowex 1-X10. Cl-form.(-400 mesh).Column: 3cm×0.67cm^2 (2ml resin).Flow rate: 0.8cm/min..Temperature:25°C. Eluents:(i)6M HCl-1M HF-Cl_2,(ii) 0.5M HCl-1.0M HF-Cl_2,(iii)4M HNO_3-1M HCl-0.2M HF.

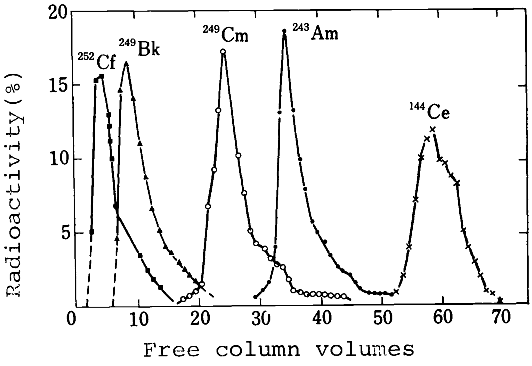

Fig.26. Separation of Cf,Bk,Cm,Am and Ce.(Ref.21)

Elements:Cf,Bk,Cm,Am,Ce(HNO_3 solution) Ion exchange resin:Dowex 50-X12. NH_4-form.(20-40μ particles).Column: 23inch x 0.07inch(D).(freecolumn volume,0.72ml).Flow rate:18ml/cm^2·min. Temperature:80±4°C.Eluents:0.25M α-hydroxyisobutyrate(pH=4.2). Pressure:1800-2500 psi.

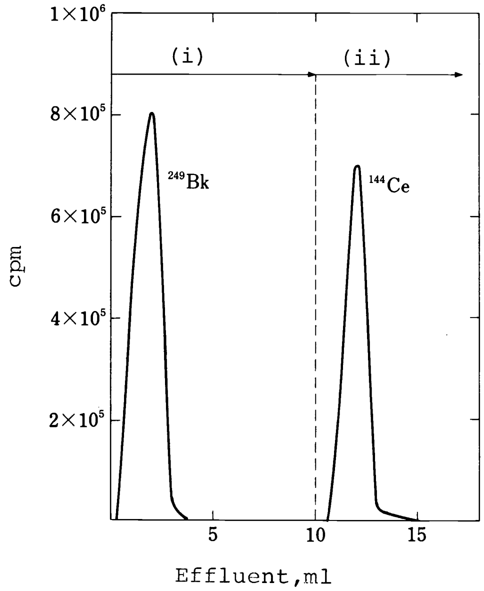

Fig.27. Separation of Bk and Ce. (Ref.22)

Elements:Bk(IV),Ce(IV).(HNO_3 solution). Ion exchange resin:Dowex 1-X4.Nitrate-form.(100-200 mesh).Column:50mm x5mm (50mg PbO_2 mixed with the resin as a solid oxidant).Flow rate:5-6 drops/min. Temperature:23°C.Eluents:(i)8M HNO_3, (ii)0.5M HNO_3.

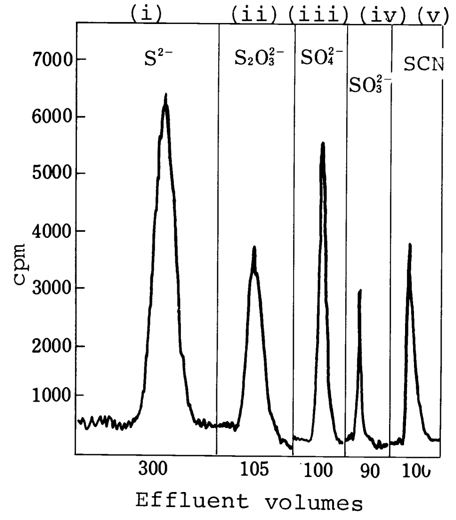

Fig.29. Separation of sulphide, sulphite,sulphate,thio-sulphate and thiocyanate. (Ref.25)

Species: S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, SCN^-
Ion exchange resin:Rexyn 201. Cl-form.(100-200 mesh).Column: 15cm×0.9cm(D).Flow rate:12ml/min. Temperature:Room temperature.

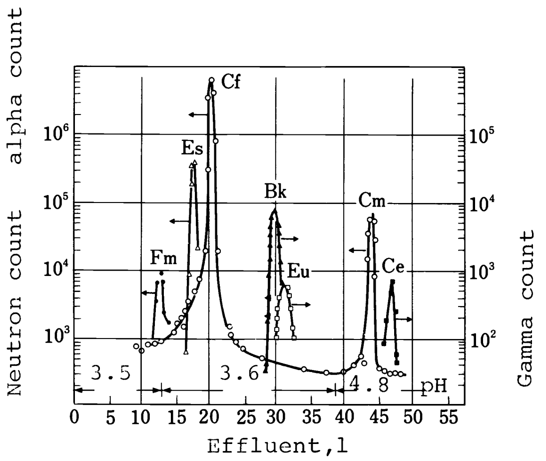

Fig.28. Separation of Fm,Es,Cf,Bk, Eu,Cm and Ce.(Ref.23)

Elements:Fm,Es,Cf,Bk,Eu,Cm,Ce. (HNO_3 solution).Ion exchange resin: Dowex 50W-X8. NH_4-form.(20-40 μ particle size).Column:4 feet×2 inch (containing 2.4 liters resin).Flow rate:8ml/cm²min..Temperature:75°C. Eluents:0.4M Ammonium α-hydroxy-isobutyrate(pH=3.5-4.8)(gradient elution).Pressure:500-700 psi.

(Fig.29)
Eluents:(i)0.04M NaCl-NH_3 (pH=10.6), (ii)0.04M NH_4NO_3-30%(v/v)acetone-NH_3 (pH=11),(iii)0.2M NaCl,(iv) 1.0M NaCl,(v)1.0M $NaClO_4$.

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