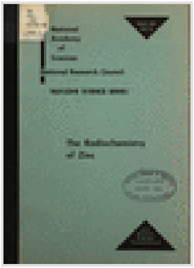

Radiochemistry of Zinc (1960)

Pages
66

Size
6 x 9

ISBN
030933957X

Hicks, Harry G.; Subcommittee on Radiochemistry; Committee on Nuclear Science; National Research Council

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NRC. Committee on Nuclear Science.
Nuclear Science series. No. 30-15.

CHEMISTRY—RADIATION AND RADIOCHEMISTRY

The Radiochemistry of Zinc

ross
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Lawrence Radiation Laboratory
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Livermore, California

June 1960

Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

Printed in USA. Price $0.75. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

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M. C. Sneed and R. C. Brasted, Comprehensive Inorganic Chemistry, Vol. IV (Van Nostrand, Princeton, 1955), pp. 9-63.

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G. H. Morrison and H. Freiser, Solvent Extraction in Analytical Chemistry (Wiley, New York, 1957).

C. Duval, Inorganic Thermogravimetric Analysis (Elsevier, New York, 1953).

II. GENERAL REVIEW OF THE RADIOCHEMISTRY OF ZINC

H. L. Finston and J. Miskel, Ann. Rev. Nuclear Sci. 5, 269 (1955).

III. TABLE OF ISOTOPES OF ZINC

Isotope	$T_{1/2}$	Type of decay	Method of preparation
Zn^{60}	2.1 min	β^+, EC	Ni^{58} $(\alpha, 2n)$
Zn^{61}	1.48 min	β^+	Ni^{58} (α, n)
Zn^{62}	9.33 hr	EC, β^+	Cu^{63} $(p, 2n)$ or Ni^{60} $(\alpha, 2n)$
Zn^{63}	38.3 min	β^+, 90%; EC, 10%	Cu^{63} (p, n) or Ni^{60} (α, n)
Zn^{64}	Stable 48.89%		
Zn^{65}	245 day	EC, 99%; β^+, 1%	Zn^{64} (n, γ), Zn^{66} $(n, 2n)$
Zn^{66}	Stable 27.81%		
Zn^{67}	Stable 4.11%		
Zn^{68}	Stable 18.56%		
Zn^{69m}	13.8 hr	I.T.	
Zn^{69}	57 min	β^-	Zn^{68} (n, γ)
Zn^{70}	Stable 0.62%		
Zn^{71m}	3 hr	β^-	Zn^{70} (n, γ)
Zn^{71}	2.2 min	β^-	Zn^{70} (n, γ)
Zn^{72}	49.0 hr	β^-	Fission

For more complete information on the radiations of the zinc isotopes, and for references to the original literature, see D. Strominger, J. M. Hollander, and G. T. Seaborg, Table of Isotopes, Revs. Modern Phys. 30, 585 (1958).

IV. REVIEW OF THOSE FEATURES OF ZINC CHEMISTRY OF CHIEF INTEREST TO RADIOCHEMISTS

1. Metallic Zinc

Zinc metal is easily obtained in very pure form, usually by distillation of the impure metal produced by electrolysis. It is moderately ductile and can easily be formed into shapes suitable for targets. The melting point, 420°C, is rather low and may pose a problem in high-intensity bombardments.

Metallic zinc is a good reducing agent, dissolving readily in mineral acids as well as in strong bases, thus showing its amphoteric character.

Oxidation potentials of zinc are given below:

$$\begin{array}{rcll} \mathrm{Zn} & = & \mathrm{Zn}^{++} + 2\,\epsilon^- & E^\circ = 0.762\ \mathrm{v} \\ \mathrm{Zn} + 2\,\mathrm{OH}^- & = & \mathrm{Zn(OH)}_2 + 2\,\epsilon^- & E^\circ = 1.245\ \mathrm{v} \\ \mathrm{Zn} + 4\,\mathrm{OH}^- & = & \mathrm{ZnO}_2^= + 2\,\mathrm{H}_2\mathrm{O} + 2\,\epsilon^- & E^\circ = 1.216\ \mathrm{v} \\ \mathrm{Zn} + 4\,\mathrm{NH}_3 & = & \mathrm{Zn(NH}_3)_4^{++} + 2\,\epsilon^- & E^\circ = 1.03\ \mathrm{v} \\ \mathrm{Zn} + 4\,\mathrm{CN}^- & = & \mathrm{Zn(CN)}_4^= + 2\,\epsilon^- & E^\circ = 1.26\ \mathrm{v} \end{array}$$

In general, no difficulty is encountered in the dissolution of metallic zinc, although very pure zinc is attacked only slowly by hydrochloric acid. Addition of a small amount of Ni^{++} or Co^{++} catalyzes the dissolution. Surfaces of metallic zinc will remain bright for long periods of time in the absence of water vapor.

Zinc is easily electroplated and can be used for a final counting sample. Two methods of electrolysis are described below.

1. Purified zinc is put into 10 ml of a solution that is 0.20 to 0.25M in NaOH, and 1 ml of 5% KCN is added.[1] The solution is then transferred to a glass cell fitted with platinum anode and cathode. Electrolysis is carried out at 0.1 to 0.2 amp, or more, for 1 to 2 hours.

2. Soluble salts of EDTA (ethylenediaminetetraacetic acid), or polysulfonic acids of anthracene or anthroquinone, are added to zinc cyanide solutions.[2] With these solutions, the current density can vary from 0.5 to 15 amp/dm^2 and the cathode yield is 95 to 98%. The zinc content is 20 to 70 g/l, and the total NaOH concentration is 15 to 80 g/l. A typical bath composition is: Zn, 25 g/l; total cyanide, 46 g/l; NaOH, 46 g/l; sodium anthracene trisulfonate, 15 to 25 g/l; and solubilized starch, 2 to 5 g/l.

Other methods of electrolysis are described in the literature.[3-9]

2. Soluble Salts of Zinc

Zinc exists in solution only with +2 oxidation state, which simplifies its chemistry in that oxidation-reduction reactions need not be considered.

The soluble salts of zinc include chloride, bromide, iodide, formate, acetate, sulfate, thiocyanate, perchlorate, fluosilicate, nitrate, cyanide, alkali metal zincates, and zinc-ammonia complex.

3. Insoluble Salts of Zinc

The common insoluble compounds of zinc are listed below in Table I. Following Table I is a discussion of the precipitation and coprecipitation characteristics of many of these compounds.

Table I. Insoluble compounds of zinc.

Compound	Solubility, g/100 ml H_2O
$ZnNH_4PO_4$	insol.
$ZnCO_3$	0.0206, at 25°C
$Zn_3K_2[Fe(CN)_6]_2$	v. sl. sol.
ZnF_2	sl. sol.
$Zn(OH)_2$	0.000042
$Zn(IO_3)_2$	0.87, at 25°C
$Zn(IO_4)_2$	insol.
$ZnHg(SCN)_4$	0.24, at 15°C
$Zn(C_2O_4)\cdot H_2O$	0.000715, at 26°C
ZnS	0.0007, at 18°C
Zn-1, 2-di(allylthiocarbamyl)hydrazine	quant., pH 7.5-8.6
Zn-anthranilate	insol., pH > 3.09
Zn-5-bromo-anthranilate	insol.
Zn-5-iodo-anthranilate	insol.
Zn-5-methyl-anthranilate	insol.
Zn-3, 5-dibromo-anthranilate	insol.
Zn-N-methyl-anthranilate	insol.
Zn-O-(2-amino-1-naphthylazo)benzoate	quant., pH 5.5-7
Zn-8-hydroxquinolate	quant., pH 4.6-13.4
Zn-8-hydroxyquinoline-5-sulfonic acid	quant., pH > 3.6
Zn-2-hydroxy-1-naphthaldehyde	insol.
Zn-mercaptobenzothiazole	quant., pH > 7
Zn-pyridine thiocyanate	insol.
Zn-quinaldate	insol.
Zn-5, 6-benzoquinaldate · H_2O	quant., pH 2.85
Zn-salicylaldoxime	insol., pH 8.5
Zn-tartrate, $C_4H_4O_6Zn\cdot H_2O$ (soluble in excess tartrate)	0.036, at 25°C
Zn-tetramethylaminodiphenylantipyrinylcarbinolthiocyanate	insol.
Zn-methyl xanthate[39]	0.36
Zn-ethyl xanthate[39]	0.15
Zn-n-butyl xanthate[39]	0.12
Zn borneol glycuronate	insol.

Zinc ammonium phosphate. The precipitation is carried out at the phenolphthalein endpoint and one would expect that many elements would coprecipitate, such as Cd, Fe, rare earths, etc.

Zinc carbonate. All elements with insoluble carbonates and hydroxides should coprecipitate.

Zinc potassium ferrocyanide. $Zn_3K_2[Fe(CN)_6]_2$ precipitated at pH 1 will carry down Sb(III), Bi(III), Cd(II), Ce(III), Co(II), Cu(II), Gd(III), Ga(III), Ge(IV), In(III), Ir(III), Fe(II), La(III), Pb(II), Mn(II), Hg(II), Nd(III), Ni(II), Sm(III), Sc(III), Ag(I), Th(IV), Ti(IV), Y(III), and Zr(IV), while Fe(III), Mo(VI), Pd(II), Ru(III), Te(IV), W(VI), U(VI), and V(V) do not carry.[10] In the presence of 1% EDTA, only Fe(II), Mn(II), Ag(I), and Zr(IV) coprecipitate. In the presence of nitriloacetic acid, Fe(II), Mn(II), Ag(I), and Zr(IV) carry. Ag(I) does not coprecipitate in the presence of thiosulfate and Zr(IV) does not coprecipitate from fluoride solutions. If the precipitation is carried out in 1<u>M</u> HCl, Cd(II) does not carry, and the precipitation is quantitative.[11]

Zinc hydroxide. Zinc hydroxide will precipitate in the pH range 7 to 13 in the absence of ammonium salts. The solubility product of $Zn(OH)_2$ in water at 20°C has been reported by Richard et al.,[12] to be 1.8×10^{-14}. Feitknect and Haberli[13] report the solubility product of $Zn(OH)_2$ with solutions of a variety of ionic strengths and anions to range from 5×10^{-17} to 6×10^{-16}. The reaction

$$Zn(H_2O)_3OH^+ + H^+ = Zn(H_2O)_4^{++}, \ pK = 9.36,$$

was studied by Achenza.[14]

In the pH range 6 to 12, zinc does not form radiocolloids and does not plate out on platinum except by precipitation of hydroxy forms.[15] Kvamme,[16] on the other hand, studied the adsorption of zinc on filter paper at pH's of 3.5 to 10.5. Maximum adsorption of zinc in trace concentrations (2.7×10^{-6} <u>M</u>) was 90% at pH 6.5. The adsorption decreases with increasing zinc concentration to 10% at 3×10^{-4} <u>M</u> and remains constant thereafter. The zinc also adsorbs well on glass and $Fe(OH)_3$ in this pH range.

Zinc will also coprecipitate $Fe(OH)_3$ and $Cr(OH)_3$ to some extent in nearly neutral solution even in the presence of ammonium ions.[17]

Kovalenko[18] studied the carrying of zinc on $Al(OH)_3$ precipitated from NH_4Cl - NH_4OH solutions. Adsorption increased with increasing initial Al^{+++} concentration, and decreased with increasing NH_4Cl and NH_4OH concentrations. Adsorption increased with increasing initial Zn^{++} concentration. There was very little adsorption at pH 4; the maximum adsorption was at pH 6. High concentrations of NH_4Cl and low concentrations of NH_4OH minimize coprecipitation.

Zinc periodate. Zinc will coprecipitate[19] with $Fe(IO_4)_3 \cdot 2Fe_2O_3 \cdot 7H_2O$ to the extent of 0.4% at pH 3.5 and zinc concentration of 7×10^{-3} M. The higher the zinc concentration, the lower the coprecipitation.

Zinc mercurithiocyanate. Cu(II), Fe(III) (in large amounts), Co(II), Ni(II), Mn(II), Bi(III), Cd(II), Ag(I), and Hg(II) are coprecipitated with zinc, while ClO_4^-, Cl^-, NO_3^-, $SO_4^=$, K^+, Na^+, NH_4^+, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Fe^{+++} (small amounts), Pb(II), As(III), As(V), Sb(III), Sb(V), and Sn(IV) do not interfere.[20] According to Rulfs and Kirby,[21] Fe(III), Ni(II), Cu(II), and Mn(II) color the precipitate but are of negligible weight.

Zinc oxalate. Ca, Sr, Ba, Fe(II), Mn(II), Co, Ni, Cd, Pb, and rare earths will coprecipitate with zinc oxalate from acetic acid solutions.[22]

Zinc sulfide. Precipitation of zinc sulfide by ammonium sulfide can carry half the elements in the periodic table (see ref. 23, p. 61). The sulfide can be precipitated under a wide variety of conditions (the following elements coprecipitated imply that the classical scheme of analysis has been used). With pH 2 to 3, and with formate, citrate, or chloroacetate buffer, Tl(I), Ga(III), In(III), Cd(II), and Ni(II) carry, but there is separation from Mn(II), Fe(II), and Al(III).[24] With sulfate-bisulfate buffer, pH 2, and 20% NH_4SCN, there is separation from Co(II).[25] There is separation from nickel under the following conditions: buffer with $NH_4OH - NH_4Cl$, precipitate with thioacetamide, heat, cool quickly and centrifuge as soon as precipitate starts to turn grey (NiS).[26] Zinc sulfide may also be precipitated from basic cyanide solutions.[27]

Cadmium can be separated from zinc by precipitation of the cadmium sulfide from 3 N H_2SO_4.[28]

Zinc sulfide can be carried on copper sulfide precipitated with thioacetamide at pH's lower than 0.5 and temperatures less than 80°C.[29]

Zinc diallyldithiocarbamido hydrazine. Zinc is precipitated quantitatively between pH 7.5 and 8.6 by an alcohol solution of the reagent, washed with acetone, dried at 105°C, and weighed as $Zn(C_8H_{12}N_4S_2)$.[30] Ni(II) interferes, Cu(II) and Pb(II) may be removed by first precipitating them at lower pH's--2.5 to 3.5 for Cu, and 5 to 6 for Pb.

Zinc anthranilate. Below pH 3.09, anthranilic acid in excess will precipitate zinc completely in one-half to one hour.[31] Hg(II) and Cd(II) coprecipitate,[31] Cu(II) does not carry.[32]

Zinc-8-hydroxyquinolate. This precipitate is far from specific, since nearly all metals except alkali and alkaline earths are coprecipitated (see ref. 23, p. 115).

Zinc-2-hydroxy-1-naphthaldehyde. Cu(II), Mg(II), Ca(II), Sr(II), Ba(II), Be(II), Pd(II), Mn(II), Ni(II), and Co(II) coprecipitate.[40]

Zinc mercaptothiazole. Precipitates zinc, aluminum, thorium, and bismuth quantitatively at pH 8 or above.[33]

Zinc pyridine thiocyanate. Cu(II), Cd(II), and Ni(II) pyridine thiocyanates will carry zinc; the zinc-carrying is lowered by lowering the zinc concentration, lowering the concentration of other metal, or increasing the temperature.[34] Cu(II), Co(II), Ni(II), and Fe(II) will coprecipitate with zinc pyridine thiocyanate.[35]

Zinc quinaldate. Fe(III) and Ni(II) coprecipitate.[36]

Zinc-5, 6-benzoquinaldate. Co(II), Mn(II), and Ni(II) coprecipitate.[37]

Zinc methyl xanthate. Ni(II), As(III), Cd(II), Co(II), and Cu(II) coprecipitate.[38]

Borneol glycuronic acid. Zinc is precipitated from an acid or neutral solution with borneol glycuronic acid.[38a] The reagent does not form insoluble compounds with other common metals except cadmium. The precipitate corresponds to $Zn(C_{16}H_{25}O_7)_2 \cdot 2H_2O$.

4. Analytical Determinations of Zinc

A general review of gravimetric and volumetric analyses is presented by Beamish and Westland.[41] The more common methods are listed below.

Gravimetric Determination

Zinc ammonium phosphate. According to Hillebrand et al.,[20] the precipitation of zinc ammonium phosphate followed by ignition to the pyrophosphate is the best gravimetric method for zinc. The conditions for precipitation are pH 6.5, temperature 80°-90°C, a tenfold excess of phosphate,[42] and a ratio of ammonium ion to zinc of about 200 to 1[43]; tartrate below 1N and citrate below 0.25N do not interfere.[44] The precipitate is $ZnNH_4PO_4 \cdot H_2O$ which may be dried at 100°-105°C (see ref. 20). Vance and Borup[42] recommend ignition at 500°C. Duval[45] recommends ignition at 610°C or above.

Zinc mercurithiocyanate. Zinc mercurithiocyanate can be precipitated from 5% H_2SO_4, HNO_3, or $HClO_4$ at room temperature by a solution of 31.5 g

NH_4SCN and 27.1 g $HgCl_2$ in 1000 ml of water. The reagent should be filtered after preparation and should be renewed every year or so. The precipitate can be dried from 71°-270°C,[45] and has the composition $ZnHg(SCN)_4$.[21, 46]

Zinc oxalate. The procedure for precipitating zinc oxalate is as follows: to 10 to 12 ml aqueous solution containing 0.5 to 50 mg zinc, add 85 ml glacial acetic acid containing 1 g ammonium oxalate.[47] Add 4 ml diethyloxalate, stir and heat quickly to about 100°C. Keep at this temperature for an hour and a half. After washing, ignite to ZnO at 900°C.

Zinc sulfide. Zinc sulfide is precipitated from H_2SO_4 solutions at pH 2 to 3 after fuming off chlorides and nitrates.[20] The precipitate is then ignited to ZnO at 1000°C.[45]

Zinc-1, 2-di(allylthiocarbamyl)hydrazine.[30] Add ammonia until solution is basic, add dilute H_2SO_4 until some precipitate remains, clarify solution with citric acid, and dilute to 200 ml. Add a slight excess of reagent, and heat in a water bath. Add sodium acetate and sodium hydroxide, digest, and filter. Wash with hot water and acetone, dry at 105°C, and weigh as $ZnC_8H_{12}N_4S_2$.

Zinc anthranilate. Precipitation is carried out in neutral solution(methyl orange end point) at about 100°C. Digest 15 to 20 minutes, wash with diluted reagent, then with alcohol. Dry at 105°-110°C, weigh as $ZnC_7H_6O_2N$.[42, 48, 49]

Zinc-O-(2-amino-1-naphthyl-azo)benzoate. Precipitation is quantitative[50] in the pH range 5.5 to 7. The conversion factor to zinc is 0.1012. High results are obtained in the presence of large amounts of ammonium salts.

Zinc-8-hydroxyquinolate. Miller and Hunter[51] give the following procedure for the precipitation: Adjust to methyl red end point and buffer with ammonium acetate acetic acid. Heat to 60°C, add slowly a 2% excess of reagent in 0.8N acetic acid, heat to nearly boiling for 2 to 3 minutes, cool 30 minutes, wash with water, dry at 160°C,[42, 45] and weigh as $Zn(C_9H_6NO)_2$. This compound will sublime in vacuum at 275°-325°C.[52]

Zinc-mercaptobenzothiazole. Zinc is precipitated by the reagent at pH 8, dried at 105°-120°C, and weighed as $Zn(C_7H_4NS_2)_2$.[33]

Zinc quinaldate. Zinc is precipitated by the reagent at pH 7 and 100°C, dried at 105°C, and weighed as $Zn(C_{10}H_6O_2N)_2 \cdot H_2O$.[36]

Zinc-5, 6, benzoquinaldate. Zinc is precipitated by the reagent at pH 2.85, and dried at 110°-115°C; the precipitate contains one molecule of water of crystallization.[37]

Zinc salicylaldoxime. Precipitation is complete at pH 8.5, and is digested for 10 minutes at 90°-100°C.[52a] The conditions must be controlled carefully or one obtains a mixture of mono- and di-salicylaldoximes. The mono ($ZnC_7H_5O_2N$) is the weighable form. According to Duval,[45] and Rynasiewicz and Flagg,[53] one must ignite to ZnO at about 950°C to obtain a reproducible weight.

Zinc tetramethyldiaminodiphenylantipyrinyl carbinol. Precipitation is complete in HCl or H_2SO_4 from 0.5 to 1.5N. The precipitate is dried from 105°-110°C; the conversion factor to zinc is 0.0556.

Figures 1, 2, and 3 and Table II are taken from Duval.[45]

Volumetric Determinations

Zinc mercurithiocyanate. The precipitate is dissolved in 4M to 7M HCl and is titrated with standard iodate. The end point is the disappearance of the iodine color in chloroform.[49, 55]

Zinc oxalate. The precipitate is dissolved in dilute sulfuric acid and the oxalate titrated with $KMnO_4$.[47]

Versene. Zinc can be titrated at pH 6.5 with disodium versenate to the Eriochrome black T end point.[56] Pribil[57] masks Ag(I), Cu(II), Mn(II), Ni(II), Co(II), and Hg(II) with CN^-, the $Zn(CN)_4^=$ being destroyed by reaction with chloral,[57] or formaldehyde.[61]

Colorimetric Determinations

Dithizone. Zinc may be determined in a solution of the zinc-dithizone complex in carbon tetrachloride or chloroform by the optical density at 530 mμ.[49]

Azo dyes. Das and Guha Sircar[58] used the red-brown complex formed at pH 3.4 to 7 by zinc 8-hydroxyquinolate and m-amino benzoic acid. No wave length was given.

Zincon. Rush and Yoe[59] determined zinc colorimetrically between pH 8.5 and 9.5 with zincon (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene) at 620 mμ.

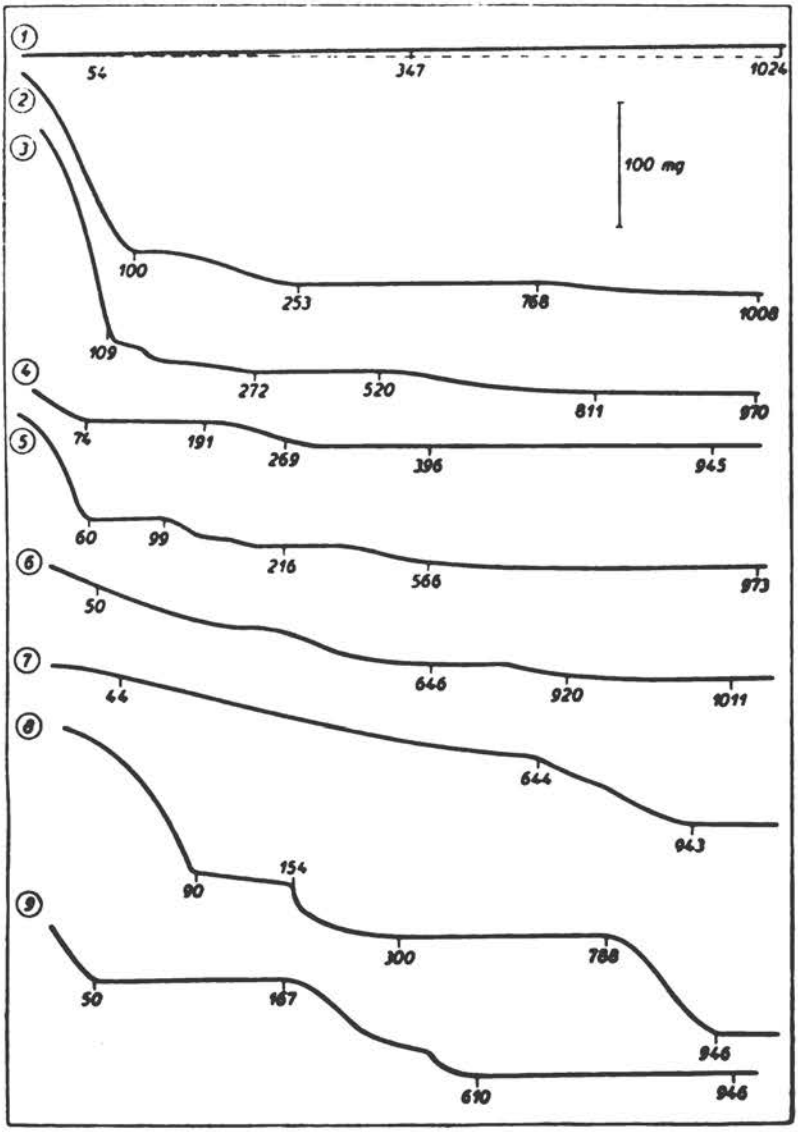

Fig. 1. Pyrolysis curves of zinc derivatives.

1. Electrolytic zinc. 2. Hydroxide via aqueous ammonia. 3. Hydroxide via mercury (II) oxide. 4. Hydroxide via dimethylamine. 5. Hydroxide via morpholine. 6. Hydroxide via piperidine. 7. Sulphide. 8. Sulphate. 9. Zinc ammonium phosphate.

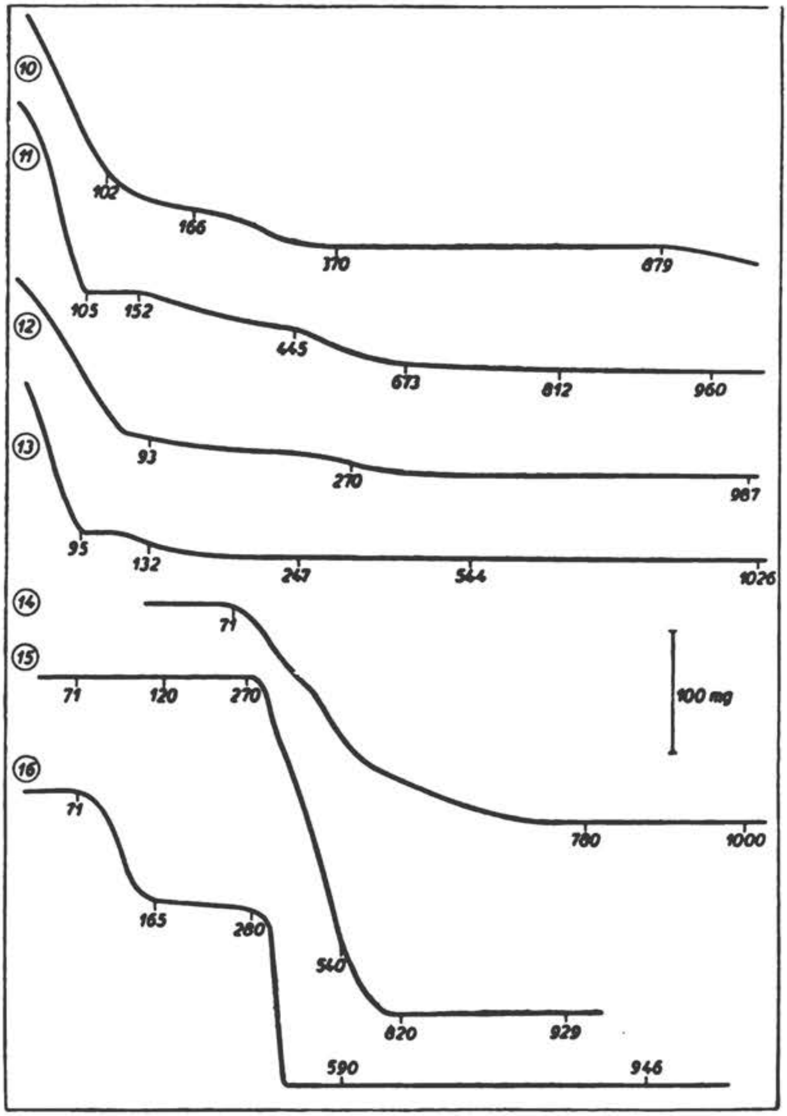

Fig. 2. Pyrolysis curves of zinc derivatives.

10. Basic carbonate via ammonium carbonate. 11. Zinc cyanamide. 12. Basic carbonate via guanidinium carbonate. 13. Basic carbonate via trimethylphenylammonium carbonate. 14. Dipyridinozinc (II) thiocyanate. 15. Tetrathiocyanatomercurate (II). 16. Oxalate.

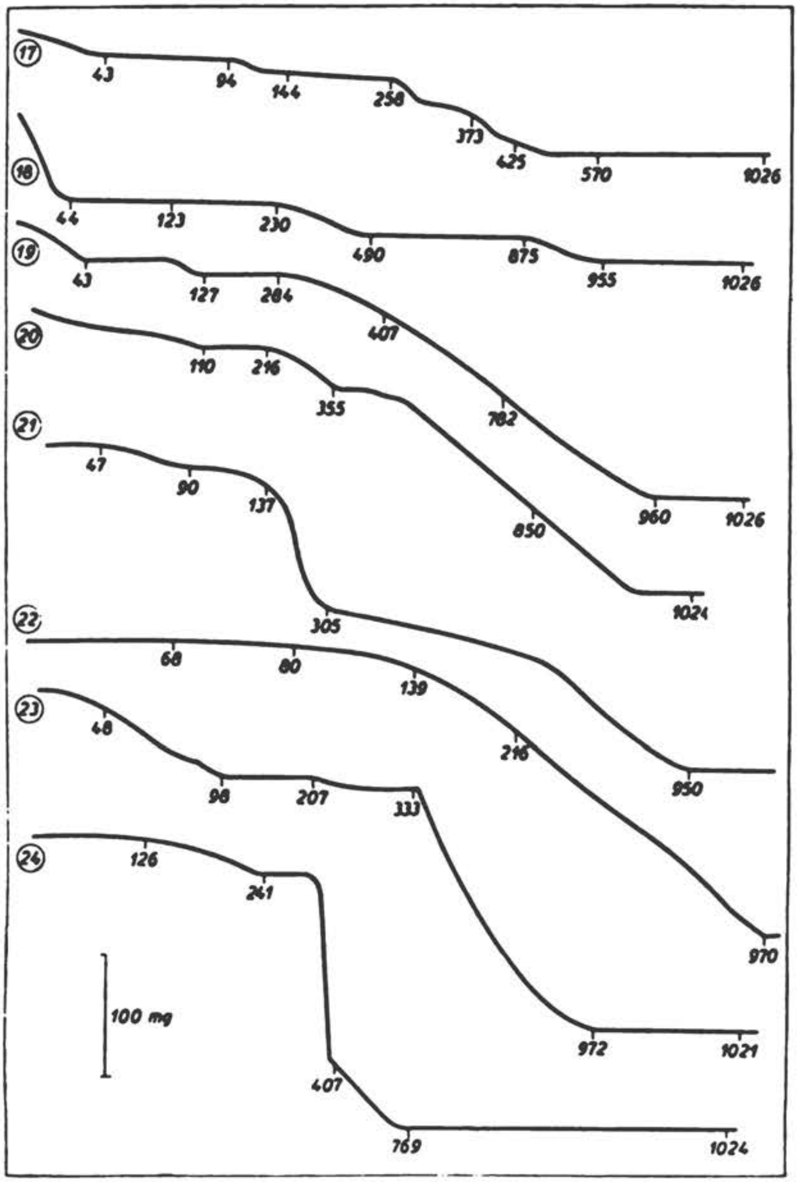

Fig. 3. Pyrolysis curves of zinc derivatives.

17. Anthranilate. 18. 5-Bromo-anthranilate. 19. Oxine complex.
20. 8-Hydroxyquinaldine complex. 21. Salcylaldoxime complex.
22. Dithizone complex. 23. 2.7-Diaminofluorene complex.
24. Quinaldine complex.

Table II. Thermogravimetric data of zinc compounds.[45]

Precipitating reagent	Form weighed	Temperature limits
Electrolysis	Zn	< 54°
Aqueous ammonia	ZnO	>1010°
Mercury (II) oxide	ZnO	> 970°
Dimethylamine	ZnO	>1000°
Morpholine	ZnO	> 910°
Piperidine	ZnO	> 920°
Hydrogen sulphide	ZnO	> 943°
*Sulphuric acid	$ZnSO_4$	300-788°
Sulphuric acid	ZnO	> 950°
*Ammonium phosphate	$ZnNH_4PO_4$	Between 50° and 167°
Ammonium phosphate	$Zn_2P_2O_7$	> 610°
Sodium pyrophosphate	$Zn_2P_2O_7$	> 610°
Ammonium carbonate	$5ZnO \cdot 2CO_2$	370-879°
Ammonium carbonate	ZnO	>1000°
*Cyanamide	$ZnCN_2$	105-152°
Cyanamide	ZnO	> 812°
Guanidinium carbonate	None	None
Trimethylphenylammonium carbonate	ZnO	> 247°
Thiocyanate + pyridine	$[Zn(C_5H_5N)_2](CNS)_2$	< 71°
Thiocyanate + pyridine	ZnO	> 780°
*Thiocyanatomercurate (II)	$Zn[Hg(CNS)_4]$	50-270°
Thiocyanatomercurate (II)	ZnO	> 820°
*Oxalic acid	$ZnC_2O_4 \cdot 2H_2O$	< 75°
Oxalic acid	ZnO	> 590°
Anthranilic acid	ZnO	> 500°
*5-Bromo-anthranilic acid	$Zn(NH_2 \cdot C_6H_3Br \cdot CO_2)_2$	< 123°
5-Bromo-anthranilic acid	ZnO	> 955°
Oxine	$Zn(C_9H_6ON)_2 \cdot 1\text{-}1/2\ H_2O$	< 65°
*Oxine	$Zn(C_9H_6ON)_2$	127-284°
8-hydroxyquinaldine	$Zn(C_{10}H_8ON)_2$	100-220°
Salicylaldoxime	None	None
Dithizone	$ZnC_{13}H_{10}N_4S$	< 68°
2. 7-Diaminofluorene	ZnO	> 972°
*Quinaldic acid	$Zn(C_{10}H_6O_2N)_2 \cdot H_2O$	< 126°

Taken directly from the table on page 284 of "Thermogravimetric Analysis" by C. Duval.[45]

*Suitable for gravimetric determination of zinc.

4-chlororesorcinol. Stewart and Barlett[60] extracted zinc into chloroform from solutions of diethyl-dithio-carbamate at pH 8.5. 4-chlororesorcinol was used as a colorimetric reagent after extraction.

5. Complex Ions of Zinc

Zinc, with the 4s and 4p orbitals available for bonding, forms a large number of complex ions and chelate compounds. These are of great importance in the understanding of the chemistry of zinc. Some of the complex ions are listed below in Table III. Log K is reported as the constant for formation of the given ion from the ion with one less ligand. The ligand is sometimes referred to in the table as A.

Table III. Complex ions of zinc.

Complexing agent	Reaction product	Log K	Ref.
NH_3	$ZnNH_3^{++}$	2.37	62
	$Zn(NH_3)_2^{++}$	2.44	62
	$Zn(NH_3)_3^{++}$	2.50	62
	$Zn(NH_3)_4^{++}$	2.15	62
	overall	9.4	62
ethylene diamine	ZnA^{++}	5.77	63
	ZnA_2^{++}	5.06	63
	ZnA_3^{++}	3.28	63
cis-1, 2-cyclo-hexane diamine	ZnA^{++}	5.73	63
trans-1, 2-cyclo-hexane diamine	ZnA^{++}	6.24	63
trans-1, 2-cyclo-heptane diamine	ZnA^{++}	6.11	63
Triethylene-tetramine	ZnA^{++}	11.9	80
tetraethylene-pentamine	ZnA^{++}	15.4	79
catechol disulfonic acid (tiron)	$ZnA^{=}$	10.92	64
	ZnA_2^{-6}	17.8	64
	$ZnA^{=}$ ($\mu = 0$)	11.68	65
	$ZnHA^{-}$ ($\mu = 0$)	4.58	65
citric acid	Zn Cit^{-}	4.71	66
	Zn Cit^{-}	4.25	67
	Zn Cit^{-}	3.55	69
	Zn $(Cit)_2^{-4}$	1.91	67
	Zn(OH) Cit, pH 7 to 12.5	9.4	68
CN^{-}	$Zn(CN)_4^{=}$	19.0	62
	$Zn(CN)_4^{=}$	17.0	70
glutaric acid	$ZnA_2^{=}$	2.3	71
acetic acid	$ZnA_4^{=}$	-0.2	62
$S_2O_3^{=}$	$Zn(S_2O_3)_2^{=}$	4.69	69
pyridine	ZnA_4^{++}	1.9	62
F^{-}	ZnF^{+}	0.73	72
	ZnF^{+}	0.77	73

Table III. (Cont'd)

Complexing agent	Reaction product	Log K	Ref.
Cl^-	$ZnCl^+$	0.19	74
	$ZnCl_2$	0.60	74
	$ZnCl_3^-$	0.71	74
	$ZnCl_4^=$	1.0	62, 75
Br^-	$ZnBr^+$	-0.60	74
	$ZnBr^+$	0.0	76
	$ZnBr_2$	>0.1	74
	$ZnBr_2$	-0.15	76
	$ZnBr_3^-$	>0.1	74
	$ZnBr_3^-$	-0.30	76
	$ZnBr_4^=$	-0.52	76
	$ZnBr_4^=$	-2.6	62
I	ZnI^+, ZnI_2, ZnI_3^-	>0.05	74
	$ZnI_4^=$	-5.4	62
OH^-	$ZnO_2^=$	15.4	62
SCN^-	$Zn(SCN)^+$ see ref 77	0.5	78
	$Zn(SCN)_2$	0.8	78
	$Zn(SCN)_3^-$	0.0	78
SCN^-	$Zn(SCN)_4^=$	1.3	78
	$Zn(SCN)_4^=$	4.2	62
bioxalate	$ZnHC_2O_4^+$	1.72	66
	$Zn(HC_2O_4)_2$	1.40	66
	overall	3.12	66
oxalate	$Zn(C_2O_4)$	3.88	66
	$Zn(C_2O_4)$	4.85	70
	$Zn(C_2O_4)_2^=$	2.35	66
	$Zn(C_2O_4)_2^=$	5.0	71
	overall	6.23	66
	overall	7.12	69
glycolic acid	ZnA	1.95	66
tartaric acid	$ZnA_2^=$	5.64	69
succinic acid	$ZnA_2^=$	3.7	71
malonic acid	$ZnA_2^=$	2.5	71
valine	ZnA^+	4.67	81
	ZnA_2	8.97	81

No quantitative date are available on the zinc-thioacetamide complex,[82] $Zn(SCNH_2CH_3)_2^{++}$, or the phosphate complexes. Shinigawa and Kobayashi[83] postulate that the ortho phosphate complexes involve formation of a chelate ring and strong dissociation of ordinarily-weak terminal hydrogen atoms. The relative strengths of the complexes are: Fe > Pb > Zn > Cu > Ni > Co, Cd > Mg > Ca > Sr > Ba > K > Na.

A qualitative discussion of the halide complexes is of value when considering separations using an anion resin column. For the higher complexes MX_3^- and $MX_4^=$ – where M is Zn^{++}, Cd^{++}, or Hg^{++}, and X is Cl^-, Br^-, or I^- – the equilibrium is more in favor of the complex ion, as the atomic number of the cation increases. The conclusions from various data[85, 86, 87] are that the relative strengths of zinc and cadmium complexes are

$$ZnCl_4^= > ZnBr_4^= > ZnI_4^= ,$$

$$CdI_4^= > CdBr_4^= > CdCl_4^= .$$

The $ZnCl_4^=$ and $CdCl_4^=$ complexes appear to be of nearly the same strength.[88]

Relative strengths of the bromide complexes are: Zn > Cu > Ga > Co > Ni.[89]

Figure 4 shows species in hydrochloric acid solution.[138]

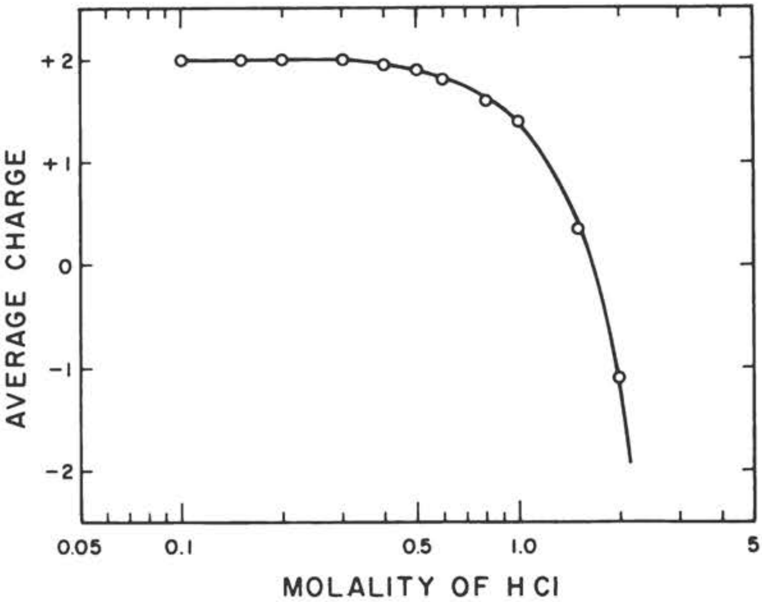

Fig. 4. Average charge of Zn(II) in HCl (anion exchange slope method).

6. Chelate Compounds of Zinc.

Zinc forms a bewildering array of chelate compounds, evident from a cursory inspection of Table IV. (Compilations of chelate compounds of many other elements are found in references 90 and 91.)

Table IV. Chelate compounds of zinc.

Ligand	Log K	Ref.
amino acetic acid	9.72	91
α-amino propionic acid	9.56	91
proline	10.2	91
glutamic acid	9.46	91
α-N-propylamino acetic acid	9.19	91
α-S-amino valeric acid	7.30	91
2-amino hexanoic acid	10.4	91
2, 6-diamino hexanoic acid	7.6	91
arginine	7.8	91
8-hydroxycinnoline	12.73	91
8-hydroxyquinoline	17.56	91
8-hydroxy-4-methylcinnoline	13.69	91
8-hydroxy-2-phenylquinoline	17.52	101
8-hydroxyquinoline-5-sulfonic acid	16.2	91
8-hydroxyquinoline-2-carboxylic acid	9.7	91
8-hydroxy-4-methylquinoline	20.24	91
8-hydroxy-2-methylquinoline	18.72	91
8-hydroxy-2, 4-methylquinazoline	14.78	91
tyrosine	9.1	91
2-(o-hydroxyphenyl)-benzimidazole	15.24	101
pteroylglutamic acid	7.5	91
α-isopropylaminoacetic acid	14.36	91
2-amino-4-methylpentanoic acid	8.93	91
1, 2-diamino propane	10.87	91
ethylene diamine	10.43	91
dimethylglyoxime	13.9	91
dimethylglyoxime-O-monomethyl ether	14.36	91
α, β-diamino propionic acid	11.5	91
tropolone	17.5	91
kojic acid	13.2	91
α-bromo tropolone	12.7	91

Table IV. (Cont'd)

Ligand	Log K	Ref.
α-methyl tropolone	15.7	91
β-methyltropolone	15.2	91
α-isopropyltropolone	16.2	91
β-isopropyltropolone	19.3	91
O, O-dimethyl purpurogallin	12.5	91
oxalic acid	7.36	91
malonic acid	3.3	90
ethyl malonic acid	3.04	90
diethyl malonic acid	3.24	90
dimethyl malonic acid	2.74	90
di-n-propyl malonic acid	3.15	90
methyl malonic acid	3.10	90
n-propyl malonic acid	3.12	90
2-mercaptoethylamine	18.90	91
α-amino-β-mercaptopropionic acid	18.2	91
quinoline-8-carboxylic acid	9.0	91
anthranilic acid	20.93	92
5-bromoanthranilic acid	5.68	92
dibenzoyl methane	19.65	91
dibenzoyl methane	15.07	99
p-chloro dibenzoyl methane	14.42	99
p-methyl dibenzoyl methane	15.28	99
p-methoxy dibenzoyl methane	15.64	99
m-methoxy dibenzoyl methane	15.07	99
acetylacetone	8.81	91
salicylaldehyde	8.10	91
salicylaldehyde-5-sulfonic acid	5.4	91
benzoylacetone	10.3	90
2-furoyl-benzoylmethane	9.56	90
2-thenoyl-2-furoylmethane	9.28	90
1, 3-diaminopropan-2-ol	9.02	91
histamine	10.50	91
1, 3-diamino-2, 2-dimethylpropane	10.41	91
2-o-hydroxyphenylbenzothiazole	13.66	91
imidoacetic acid	7.03	91
amino succinic acid	5.84	91

Table IV. (Cont'd)

Ligand	Log K	Ref.
β-carboxymethylaminopropionic acid	6.17	91
methyl iminodiacetic acid	7.66	91
cyanomethyliminodiacetic acid	5.8	91
N-(carbamoylmethyl)-imidodiacetic acid	7.03	91
glycylglycine	3.80	91
glycylglycylglycine	3.33	91
N-2-hydroxyethyliminodiacetic acid	8.33	91
di-(2-hydroxyethyl)amino acetic acid	5.36	91
3-hydroxy propyliminodiacetic acid	7.7	91
2-methoxyethyliminodiacetic acid	8.43	91
2-methylthioethyliminodiacetic acid	8.28	91
2-ethoxycarbamylaminoethyliminodiacetic acid	6.86	91
2-(dicarboxylmethyl)-aminoethyltrimethylammonium cation	5.34	91
3, 3'-dimethylbutyliminodiacetic acid	7.92	91
ethylenediaminediacetic acid	11.93	91
2-carboxyethyliminodiacetic acid	9.8	91
carboxymethyliminodiacetic acid	7.9	91
2-hydroxyethyliminodipropionic acid	4.6	91
ethylenediamine-N, N'-dipropionic acid	7.6	91
nitrilopropionic acid	5.3	91
phenyliminodiacetic acid	3.22	91
ethylene diamine-N, N, N', N'-tetraacetic acid(EDTA)	16.26	91
N'-2-(hydroxyethyl)-ethylenediamine-N, N', N-triacetic acid	14.5	91
ethylenediamine-N, N'-diacetic-N, N'-dipropionic acid	14.5	91
2, 2'-bis [di(carboxymethyl)-amino-] diethyl sulfide	13.17	91
ethylenediamine-N, N, N', N'-tetrapropionic acid	7.8	91
N, N, N', N'-tetrakis-(2-aminoethyl)-ethylene diamine	16.24	91
nitrilo acetic acid	10.45	91
2, 2'-diamino-diethylamine	8.9	91
2, 2'-diaminodiethylsulfide	5.31	91
2, 2', 2''-triaminotriethylamine	14.65	91
N, N'-di-(2-aminoethyl)-ethylenediamine	12.1	91
2-mercaptoethyliminodiacetic acid	15.92	91
diethylene triamine	12.0	90
triethylene tetramine	14.6	90

Table IV. (Cont'd)

Ligand	Log K	Ref.
propylenediamine	12.57	90
1, 2, 3-triaminopropane	6.7	90
O-phenanthroline	6.43	90
alanine	9.52	90
asparagine	8.7	90
aspartic acid	10.0	90
histidine	12.88	90
leucine	8.93	90
proline	10.2	90
tryptophan	9.3	90
valine	8.10	90
aminobarbituric acid-N, N-diacetic acid	3.2	90
ammonia triacetic acid	13.4	90
glycine-N-propionic acid	10.1	90
tiron		
N-hydroxyethyl ethylenediamine tetraacetic acid	14.5	94
N-hydroxyethylimino diacetic acid	8.6	96
N, N-dihydroxyethylglycine	5.4	97
pyrocatechol-3, 5-disodium sulfonate	11.07	93
1, 2-diaminocyclohexane tetraacetic acid	18.67	100
picolinic acid	9.42	102

7. Solvent Extraction of Zinc

A good general reference work on solvent extraction has been written by Morrison and Freiser.[102a]

Dithizone in Organic Solvents

The extraction of zinc by solutions of dithizone in chloroform or carbon tetrachloride has long been used for analysis. Figure 5 shows the pH dependence of zinc extraction in the presence of tartrate.[103]

It is apparent from Fig. 5 that zinc extracts quantitatively from pH 8 to pH 10, with two minutes mixing of the layers. When large amounts of Cu, Ag, and Hg are present, they may be removed first by extraction at pH 1.[104] The zinc may be recovered by extraction with 0.1 to 0.01N mineral acid. In this procedure, Pb, Cd, and some Bi accompany the zinc.

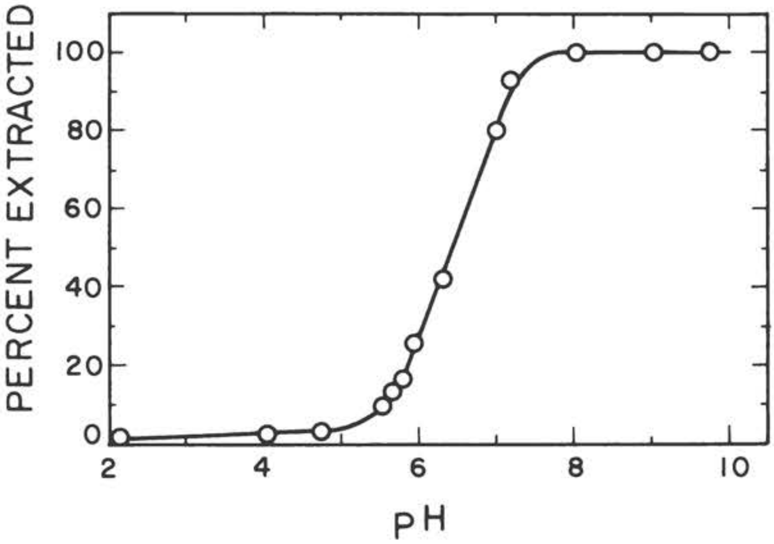

Fig. 5. Extraction of zinc by dithizone.

Various complexing agents may be added to the initial aqueous phase to prevent extraction of other metals. Cyanide, for instance, prevents extraction of Ni and Co. Apparently the best procedure is that of Crowther, Warburton, and Bracewell[105] who first extract Ni with a chloroform solution of dimethylglyoxime. Then they extract 10 μg of zinc from one gram of uranium in 5 ml of 40% ammonium citrate solution, pH 8.0 to 9.0, and wash the chloroform solution of dithizone with water. The dithizone layer is then washed with a 0.05% solution of Na_2S, and the zinc remains in the organic phase. This procedure separates from Tl, Hg, Bi, Au, Pt, Pd, Cd, Ni, Co, Pb, Cu, and Mn.

Schweitzer and Honaker[106] have investigated anions which interfere with the extraction. Their data appear in Table V. The initial zinc concentration was 10^{-5} $\underline{M}$, the dithizone concentration in the organic solvent 1.8×10^{-3} $\underline{M}$, and the ionic strength 0.10. They define the extraction coefficient as follows:

$$E = K \frac{(HD)^2}{(H^+)^2}$$

The range of conditions shown in Table VI makes the solvent extraction of zinc with dithizone an attractive procedure indeed. However, for normal radiochemical procedures there is a serious drawback because of the solubility of both dithizone and zinc dithizonate in the above solvents. For carrier-free applications, such solubility considerations vanish.

Table V. Effects of various anions upon the extraction of zinc into dithizone solutions.[106]

Organic solvent	Anion in aqueous phase	Anion molarity	pH for 50% extraction	K
chloroform	perchlorate	0.10	3.5	0.03
	iodide	0.10	--	--
	bromide	0.10	3.5	0.03
	thiocyanate	0.10	3.5	0.03
	acetate	0.01	3.6	0.02
		0.10	3.6	0.02
	chloride	0.10	3.6	0.02
	citrate	0.01	3.9	0.005
		0.10	5.9	5×10^{-7}
		1.00	6.7	1×10^{-8}
	oxalate	0.01	4.3	8×10^{-4}
		0.20	5.3	8×10^{-6}
	nitrilo acetate	0.001	4.2	0.001
		0.01	7.0	3×10^{-9}
	EDTA	0.001	no extn.	--
		0.01	no extn.	--
	phthalate	0.01	2.7	1
carbon tetrachloride	perchlorate	0.10	1.9	50
	bromide	0.10	1.9	50
	citrate	0.01	2.0	30
		0.10	2.0	30
	EDTA	0.001	no extn.	--
benzene	perchlorate	0.10	2.3	8
	citrate	0.01	2.4	5
chloro-benzene	perchlorate	0.10	2.1	20
dichloro-methane	perchlorate	0.10	2.7	1

Methyl-dioctylamine in Organic Solvents

Mahlman, Ledicotte, and Moore[107] showed that in hydrochloric acid solutions, zinc extracts well into solutions of methyl-dioctylamine in organic solvents. Figure 6 shows the extraction behavior of a number of elements into dichloroethylene solutions of methyl-dioctylamine. The solvent seems

Table VI. Solubility of zinc dithizonate and dithizone in various organic solvents.[106]

Solvent	K	Solubility, g/l	
		Dithizone	Zinc dithizonate
$CHCl_3$	0.03	20.3 ± 0.03	21.0 ± 0.8
CH_2Cl_2	1	12.6 ± 0.5	16.4 ± 0.3
C_6H_6	8	3.6 ± 0.1	2.3 ± 0.3
C_6H_5Cl	20	2.5 ± 0.1	4.6 ± 0.3
CCl_4	50	0.74 ± 0.02	0.72 ± 0.06

to play a significant role here, in that extraction of zinc into dichloroethylene and xylene solutions above $2\underline{M}$ HCl is quantitative, while only 75% is extracted into chloroform solutions.[107] Moore[108] showed that zinc is easily separated from Hf, Zr, Pa, and Th by this extraction. Scroggie and Deal[109] extract completely 100 µg of zinc from 5 ml $2\underline{M}$ HCl into 10 ml 8% methyl-dioctyl-amine in methyl-isobutyl ketone, with 3-minute mixing time with a non-equilibrated organic phase.

Moore[108] points out that the extraction conditions are very similar to conditions for adsorption on anion resin of the quaternary ammonium type. For instance, uranium extracts from dilute sulfate solutions and zinc does not.[110]

According to Scroggie and Dean,[109] zinc extracts as $ZnCl_3^-$ or $ZnCl_4^{=}$, proceeding probably through hydrogen bonding and ion association with the amine ion. Schindewolf[111] found that the logarithm of the extraction coefficient was linear with the logarithm of the amine concentration with a slope of +2. The extraction of one zinc atom takes two amine molecules and probably has the form $(RH)_2ZnCl_4$. (RH^+ stands for the substituted ammonium ion.)

The zinc species is consistent with that found by Kraus and Nelson,[138] i.e., $ZnCl_4^{=}$ in $2\underline{M}$ HCl. Schindewolf used HCl, LiCl, and CsCl solutions and showed that the change in extraction coefficient is independent of the concentration in the organic phase and must therefore have its cause in the aqueous phase. The reaction is then:

$$(1)\quad 2RH^+Cl^- + ZnCl_4^{=} = (RH)_2ZnCl_4 + 2\,Cl^- .$$

The slope of +2 at lower chloride concentrations suggests that the extraction of zinc can be described by

$$(2)\ \ Zn^{++} + 2\ Cl^{-} = ZnCl_2\ ,$$

$$(3)\ \ ZnCl_2 + 2RH^{+}Cl^{-} = (RH)_2ZnCl_4.$$

The lowering of the extraction coefficient at high chloride concentrations can be described by the reverse of reaction (1). Therefore the slope of the curve at high chloride concentrations should approach -2. This effect is seen clearly with CsCl. Maxima occur at 2M HCl, 1M CsCl, but none occurs with LiCl.

Tributyl Phosphate

Irving and Edgington[112] extracted zinc into kerosene, benzene, and carbon tetrachloride solutions of tributyl phosphate from hydrochloric acid solutions. Maximum extraction (extraction coefficient = 34) occurred from 2M to 3M HCl. Ni(II), Mn(II), Co(II), and Cu(II) did not extract, while U(VI), In(III), and Fe(III) did. At higher hydrochloric acid concentrations, the extraction coefficient decreased. The chloro-complexes apparently extract in roughly the same order as the adsorption on anion resin. If kerosene is used as a diluent, there are three phases formed above 5M hydrochloric acid: the upper is kerosene, the middle is tributyl phosphate saturated with hydrochloric acid, and the lower is aqueous. Benzene and carbon tetrachloride did not exhibit this rather inconvenient phenomenon.

Peppard, Gray, and Marcus[113] extracted zinc with undiluted tributyl phosphate purified from monobutyl and dibutyl phosphates. Their data are presented in Fig. 7. They conclude that H_2ZnCl_4 is the extracting species which is salted out at higher chloride concentrations.

Thenoyltrifluoroacetone

A good separation from cadmium is effected by extraction of zinc into dibutyl ether solutions of thenoyltrifluoroacetone (TTA).[114] First, 10 mg of zinc is extracted into 40 ml 0.4M TTA from 20 ml aqueous solution of pH 4.5 (buffered with 0.1M formic acid and 1M sodium formate) with two minutes mixing. Then the organic layer is washed four times with the buffered solution, and the zinc back-extracted with two portions of a pH 3.0 buffered solution (0.6M chloroacetic acid and 0.4M sodium chloroacetate). Zinc recovery is 92% and the separation from cadmium is 10^5.

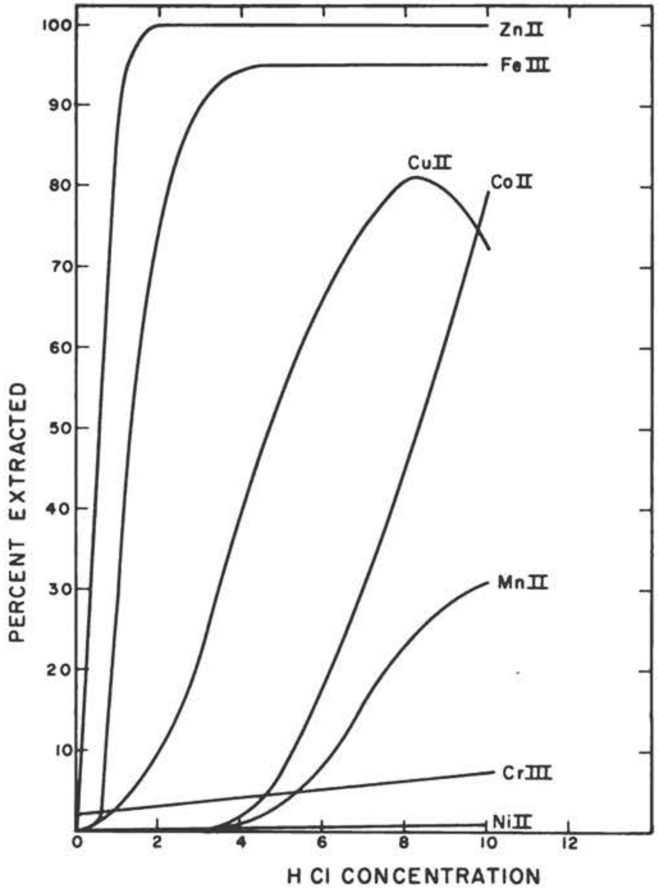

Fig. 6. Extraction of zinc from HCl solutions into 5% methyl dioctylamine in dichloromethane.

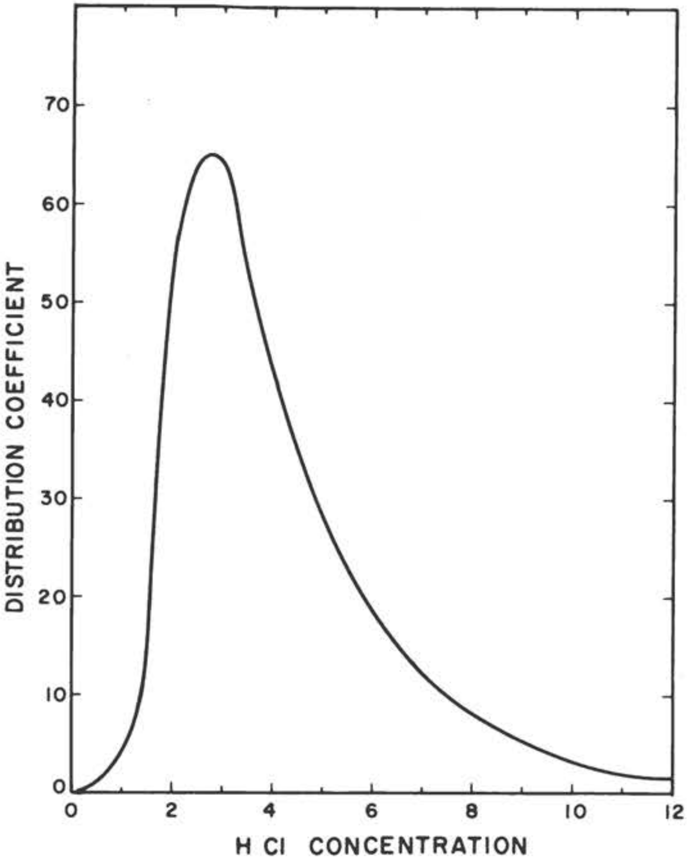

Fig. 7. Extraction of zinc into pure tributyl phosphate from HCl solutions.

Methyl-Isobutyl Ketone

Zinc extracts into methyl-isobutyl ketone (hexone) from a solution 1M in hydroiodic acid and 6M in sulfuric acid.[114] Zinc returns to the aqueous phase with three equilibrations with 6M hydrochloric acid. Cd(II), Ag(I), Pd(II), Cu(II), and Hg(II) stay in the hexone but Pb(II) is not separated from zinc.

Zinc Thiocyanate Extraction

Zinc extracts into diethyl ether from solutions 0.5M in hydrochloric acid containing ammonium thiocyanate.[115] Varying the proportion of ammonium thiocyanate changes the extraction coefficient, as shown in Table VII.

Table VII. Extraction of zinc thiocyanate into diethyl ether.[115]

Zn conc.	NH_4SCN conc.	HCl conc.	Extn. coeff.
0.1M	1M	0.5M	23.7
0.1M	3M	0.5M	37.8
0.1M	5M	0.5M	18.3
0.1M	7M	0.5M	12.9

Cadmium does not extract under these conditions.[116]

Rosenheim and Huldschinsky[117] extracted zinc thiocyanate into amyl alcohol-diethyl ether mixtures. Kinnunen and Wennerstrand[118] investigated a number of solvents and have extracted zinc thiocyanate complex quantitatively into hexone, methyl isopropyl ketone, methyl n-propyl ketone, n-butyl phosphate, and amyl alcohol-diethyl ether solutions. Amyl alcohol, ethyl acetate, diethyl ether, and diisopropyl ketone are poorer solvents.

The best solvent for the zinc thiocyanate complex is hexone.[118] Extraction conditions are as follows: The hydrochloric acid concentration should be less than 0.5M, and an excess of ammonium thiocyanate corresponding to at least a 4% solution is necessary for the complete extraction of 125 mg zinc from an aqueous solution volume of 50 ml. In neutral or alkaline medium, extraction is incomplete, and the zinc may be back-extracted quantitatively with dilute ammonium hydroxide. Fe(III), Ag(I), and Cu(II) also extract, although Fe(III) can be masked with fluoride, and Ag(I) and Cu(II) with thiourea. If fluoride is present, Pb(II) and Ca(II) interfere. In the presence of Ca and Pb, Fe can be masked with sodium pyrophosphate or tartrate. Large salt concentrations aid extraction of zinc.

Zinc Pyridine Thiocyanate into Chloroform[119]

The solution is adjusted to the methyl red endpoint. For 80 ml of solution, add 5 ml 2M NH_4SCN and 1 ml pyridine. Then 10 ml of chloroform extracts 95% of the zinc. Fe(II), Mn(II), and Cu(II) also extract, but Ga(III), In(III), Pb(II), Ti(IV), Bi(III), Sb(III), and U(VI) do not extract.

Cyclohexanone

Hartkamp and Specker[120] extract cadmium with cyclohexanone solutions 0.1M in KI or NH_4I and 0.25M in NH_4OH. Zinc does not extract, while 99.4% of the cadmium extracts in one equilibration.

Oxine Derivative

A solution of 7[α(o-carbomethoxyanilino) benzyl]-8-hydroxyquinoline in chloroform extracts Cu(II), Zn(II), Cd(II), and Hg(II) at pH 6.[121]

Naphthyl Thiocarbazone

Zinc (50μg) extracts quantitatively into 10 ml of a solution of naphthyl thiocarbazone in chloroform from 30 ml of a solution buffered with citrate of pH 8.25 to 10.5.[122]

Zinc Dithiocarbamate

Zinc and lead dithiocarbamates are extracted from fluoride solutions by ethyl acetate or chloroform at pH 3 for zinc and pH 0.3 for lead.[123] Zinc and lead are brought back into the aqueous phase with 8M HNO_3.

Zinc Diethyldithiocarbamate

Zinc and cadmium are extracted into chloroform from dithiocarbamate solutions buffered to pH 8.5 with a citrate buffer.[60] The chloroform layer is washed once with water and the zinc and cadmium returned to the aqueous phase with 0.16M hydrochloric acid. This procedure separates from Pb(II), Bi(III), Co(II), Tl(III), Sb(III), Ag(I), Cr(III), Fe(III), Mg(II), Al(III), Ca(II), Ni(II), Cu(II), Na(I), and K(I).

Butanol

Zinc perchlorate extracts into butanol from water.[124] The extraction coefficients for some other perchlorates are listed in Table VIII.

Table VIII. Extraction of metal perchlorates into butanol.[124]

Element	Extraction coeff.	Element	Extraction coeff.
Co	7.2	Mg	9.4
Ni	7.7	Ca	9.5
Mn	7.6	Sr	12.9
Zn	8.3	Cu	6.9

8. Ion Exchange Behavior of Zinc

The intent of this section is to present the behavior of zinc on various ion exchange resins in as many different media as possible. Coryell and Marcus[125] present a comprehensive review of ion exchange mechanisms, resins, and techniques.

Cation Exchange

Meyer, Argersinger, and Davidson[126] have studied activity coefficients in the $ZnCl_2$-HCl-Dowex 50 × 8 system. They consider the reaction

$$Zn^{++} + 2\ HR = ZnR_2 + 2\ H^+ ,$$

where R^- represents the active resin group. They define K as

$$K = \frac{a^2_{H^+}}{a_{Zn^{++}}} \cdot \frac{a_{ZnR_2}}{a^2_{HR}} = \frac{m^2_{H^+}}{m_{Zn^{++}}} \cdot \frac{\gamma^4_{HCl}}{\gamma^3_{ZnCl_2}} \cdot \frac{N_{ZnR_2}}{N^2_{HR}} \cdot \frac{f_{ZnR_2}}{f^2_{HR}} ,$$

where f = resin activity coefficient on a mole fraction basis. For convenience, they further define

$$K_m = \frac{m^2_{H^+}}{m_{Zn^{++}}} \cdot \frac{N_{ZnR_2}}{N^2_{HR}} , \text{ and } K_a = K_m \frac{\gamma^4_{HCl}}{\gamma^3_{ZnCl_2}} ,$$

so that

$$K = K_a \frac{f_{ZnR_2}}{f^2_{HR}} .$$

Data from their study appear in Table IX.

Table IX. Activity coefficients in the $ZnCl_2$-HCl-Dowex 50 × 8 system.[126]

Mole fraction ZnR_2	$\mu = 0.5$	$K = 10.2$	$\mu = 1.0$	$K = 11.7$
	f_{ZnR_2}	f_{HR}	f_{ZnR_2}	f_{HR}
0	0.818	1.000	0.855	1.000
0.1	0.855	0.998	0.897	0.998
0.2	0.891	0.991	0.933	0.991
0.3	0.921	0.980	0.962	0.981
0.4	0.947	0.965	0.985	0.969
0.5	0.968	0.947	1.003	0.954
0.6	0.989	0.924	1.017	0.939
0.7	1.008	0.891	1.025	0.924
0.8	1.013	0.881	1.025	0.927
0.9	1.009	0.901	1.015	0.987
1.0	1.000		1.000	

Soldano and Boyd[127] have studied the self-diffusion of cations in heteroionic cation exchangers. They report a self-diffusion coefficient for Zn^{++} on Dowex 50 × 8 of 1.16×10^{-8} cm^2/sec at 25°C, the activation energy being 8520 cal/mol.Spiegler and Coryell[128] report a value of 4.1×10^{-7} cm^2/sec for the self-diffusion coefficient.

Bonner and Smith[129] present data on the adsorption of a large number of cations on Dowex 50 (Table X).

The data in Table X show that the separation of Zn^{++} from other cations on Dowex 50 is, at best, a group separation. The group containing zinc is not vastly different from the classical one. However, in the presence of complexing agents, a cation resin becomes a much more versatile reagent. In the section on complex ions, it is evident that the $CdI_4^=$ complex is much stronger than the $ZnI_4^=$ complex. The author has separated cadmium and zinc on Dowex 50 × 8 under the following conditions: sulfuric acid concentration, 0.05M; hydroiodic acid concentration, 0.001M; total volume, 10 ml. The cadmium does not adsorb, while the zinc remains completely on a column 4 cm long and 0.6 cm in diameter. Zinc may be recovered, after washing with the iodide solution by elution with 20 ml of 3$\underline{M}$ perchloric acid or 10 ml of 2$\underline{M}$ hydrochloric acid.

Brown and Hayes[130] separate zinc and magnesium by complexing zinc with cyanide at the bromthymol blue endpoint. Passing the solution through

Table X. Relative adsorption of metal ions on Dowex 50.[129]

Metal ion	Percent cross-linkage		
	4%	8%	12%
Li^+	1.00	1.00	1.00
H^+	1.32	1.27	1.47
Na^+	1.58	1.98	2.37
NH_4^+	1.90	2.55	3.34
K^+	2.27	2.90	4.50
Rb^+	2.46	3.16	4.62
Cs^+	2.67	3.25	4.66
Ag^+	4.73	8.15	22.9
Tl^+	6.71	12.4	28.5
UO_2^{++}	2.36	2.45	3.34
Mg^{++}	2.95	3.29	3.51
Zn^{++}	3.13	3.47	3.78
Co^{++}	3.23	3.74	3.81
Cu^{++}	3.29	3.85	4.46
Cd^{++}	3.37	3.88	4.95
Ni^{++}	3.45	3.93	4.06
Ca^{++}	4.15	5.16	7.27
Sr^{++}	4.70	6.51	10.1
Pb^{++}	6.56	9.91	18.0
Ba^{++}	7.47	11.5	20.8

the sodium form of amberlite IR-120 removes the magnesium from the solution while the anionic zinc cyanide complex is not adsorbed.

Fritz and Umbreit[131] use EDTA in a similar manner. Their column is 4 cm long containing 5 g Dowex 50 × 4. They pass 55 ml of solution through the resin, and 30 ml of wash with the buffered EDTA solution. They use a glycine buffer acidified with hydrochloric acid. Adsorption of the zinc at pH 1.2, wash, elution with pH 2.1 and wash, should separate zinc from Fe(III), Bi(III), Cu(II), Zr(IV), Sc(III), Y(III), Sm(III), La(III) and U(VI); but not Th(IV), Yb(III), or Hg(II).

Oliver and Fritz[132] have worked in a number of systems employing two complexing agents. They add two reagents to a binary system, one to form a positive complex with one component, another to form a negative complex with the other. The solution is then passed through an ion exchange resin column

Table XI. Adsorption of zinc on Dowex 50 × 4 from 0.02M EDTA solutions.[131]

pH	% Zinc adsorbed
1.2	100
1.5	83.5
1.8	39.4
2.1	0.0

where one component adsorbs while the other elutes. They report a separation of zinc and uranium at pH 9 by forming a negatively charged complex of uranium with sulfosalicylic acid, and a positively charged complex of zinc with ethylene diamine. The resulting solution is passed through a column of Dowex 1 × 8 anion exchange resin; the uranium adsorbs and the zinc elutes. Separation of zinc and iron may be effected in the same system at pH 10. Elements forming negative complexes with sulfosalicylic acid are Fe, U, Al, Th, Zr, and Y; those forming positive complexes with ethylene diamine under the same conditions are Cu, Ni, Zn, and Cd. Quantitative separation of binary mixtures containing one element of each group was performed at pH's 8, 9, and 10 using Dowex 50 × 12 and Amberlite IRA-401.

Kraus, Michelson, and Nelson[133] report a strong adsorption of some anionic species by cation exchange resins. This strange behavior appears to be confined to those complexes which are very strongly adsorbed by anion exchange resins from concentrated chloride solutions. In a solution 10M in LiCl and 0.1M in HCl, $AuCl_4^-$, $FeCl_4^-$, and $GaCl_4^-$ have K_D's of greater than 10^5. In 12M hydrochloric acid, $AuCl_4^-$, $FeCl_4^-$, and $GaCl_4^-$ have K_D's of the order of 100. In either case, Zn(II), Mn(II), Co(II), Bi(III), and Sn(IV) show no tendency to adsorb, while Sb(V) and Tl(III) adsorb only slightly. This phenomenon could prove to be a rather useful one.

Davies and Thomas[134] pointed out that the concentration of water in the resin phase is higher than in the liquid phase. This suggests that addition of miscible organic solvents should have a large effect upon resin behavior. Kember, McDonald, and Wells,[135] eluting metal ions from cation resins with mixtures of methyl ethyl ketone, water, and hydrochloric acid, found that this system did improve separations. If they used anhydrous ketone and HCl gas, everything eluted quickly. They concluded that the resin phase and the liquid phase must be in water equilibrium but need not be in acid equilibrium.

Carleson[136] investigated the methyl n-propyl ketone-hydrochloric acid system. He separated Zn(II), Cd(II), Cu(II), Co(II), Mn(II), Ba(II), Bi(III), and Ni(II) as follows: the metal ions were adsorbed on Dowex 50; with ketone plus 2% 10M HCl, the order of elution and separation was, Bi(III), Zn(II), and Cd(II) together, Cu(II), and Co(II); with ketone plus 15% 8M HCl, Mn(II) eluted; with ketone plus 30% 8M HCl, Ni(II) eluted; with 8M HCl, Ba(II) eluted.

Ionescu, Constantinescu, and Topor[137] eluted zinc from cation resins KU-2 or R-21 with 79.5% acetone, 0.5% conc. HCl, 20% water, or 59% acetone, 1% conc. HCl, 40% water (volume percentages) and obtained a good separation from copper.

Anion Exchange

Kraus and Nelson[138] have studied the behavior of zinc on Dowex 1 × 8 in hydrochloric acid solutions. The distribution coefficient is shown in Fig. 8 as a function of hydrochloric acid concentration.[138]

Behavior of other elements is shown in Fig. 9, taken from earlier work by Kraus and Nelson.[88]

Horne,[139] and Pierson and Schindewolf[140] have shown that the species adsorbing on Dowex 1 is $ZnCl_4^=$ which agrees very well with the species present in solution as determined by Kraus and Nelson[138] and shown in Fig. 4.

The temperature coefficient of the adsorption process is small.[146]

As the cross-linking of the resin increases, the K_D for zinc increases in chloride solutions.[141]

Kraus, Nelson, Clough, and Carlston[142] reported K_D's of many metal ions in Dowex 1 to be increased more than a hundredfold in 12M LiCl over those in 12M HCl. Some of the metals they mention are Sc(III), Mn(II), Co(II), Zn(II), Au(III), Fe(III), and Ga(III). The difference is probably due to large differences in activity coefficients in the resin phase when the resin is immersed in these two media. Horne[139] noted that at the chloride concentration of two molar, the K_D of zinc was highest for $Li^+ > H^+ > Na^+ > NH_4^+ > K^+ > Cs^+$. Kraus and Nelson[143] show the effect of the cation of the supporting electrolyte in Fig. 10.

The half-time of either adsorption or desorption of $ZnCl_4^=$ on 50-100 mesh Dowex 1 at 25°C is 5 minutes.[144] The half-time for exchange of zinc in solution with zinc on the resin is 13 ± 2 minutes.[145]

Yoshino and Kurimura[146] studied the effect of organic solvents on the K_D of zinc on Dowex 1 × 8 in HCl solutions. Their data are presented in Figs. 11 and 12. They showed that the addition of some organic solvents markedly increases the adsorption of zinc in low hydrochloric acid concentrations. They suggest that these solvent effects may be explained by the increase in the formation of negatively charged chloride complexes of zinc as a consequence of the decrease in the tendency for hydration of the zinc ions in mixed solvents.

Huber and Irvine[89] adsorbed Cu(II), Co(II), Zn(II), and Ga(III) on Dowex 1 in strong hydrobromic acid solutions. Ni(II) did not adsorb, Co(II)

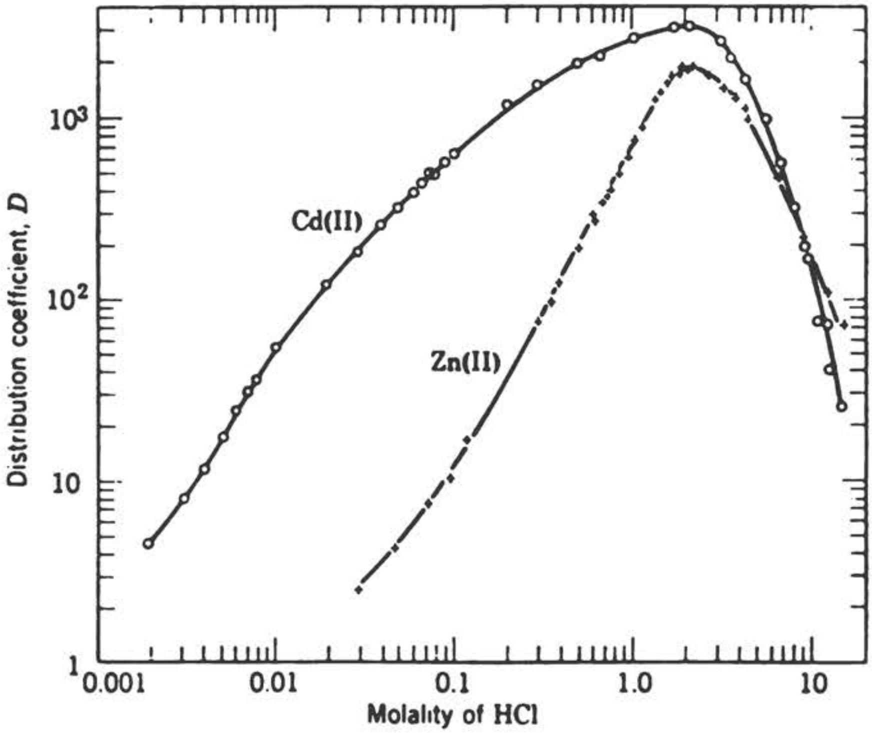

Fig. 8. Adsorption functions of Cd(II) and Zn(II) in HCl.

eluted with 5M HBr, Ga(III), with 3M HBr, Cu(II) with 1M HBr, and Zn(II) with water.

Faris[147] studied the adsorption of many elements from hydrofluoric acid on Dowex 1 × 10, 200 mesh, in the concentration range from 1M to 24M (Fig. 13). Zinc does not adsorb at any concentration, and may be separated easily from Mo(VI), Te(IV), Sb(V), Sn(IV), Zr(IV), Nb(V), Pd(II), and As(V) with 5M HF.

Horne, Holm, and Meyers[148] studied the adsorption of zinc on Dowex 1 × 8 in a variety of media. They found no adsorption in concentrations up to 8M in acetic acid, 2.5M in sulfuric acid, 5M in hydrofluoric acid or perchloric acid, and 13M in HNO_3. Adsorption coefficients for other media are as follows: phosphoric acid, increases rapidly in the 1M to 3M region to 18 and remains constant at higher concentrations; cyanide, $K_D = 1.8 \times 10^5$ at 0.5M NaCN, drops to 4000 at 2M NaCN and remains constant at higher concentrations; oxalic acid, $K_D = 1000$ at 0.01M $H_2C_2O_4$, drops to 10 at 0.2M, and stays constant at higher concentrations; $ZnO_2^=$ does not adsorb well. Meyers and Horne[140] report good adsorption of zinc from hydroxylamine hydrochloric solutions of zinc from 1M to 7M.

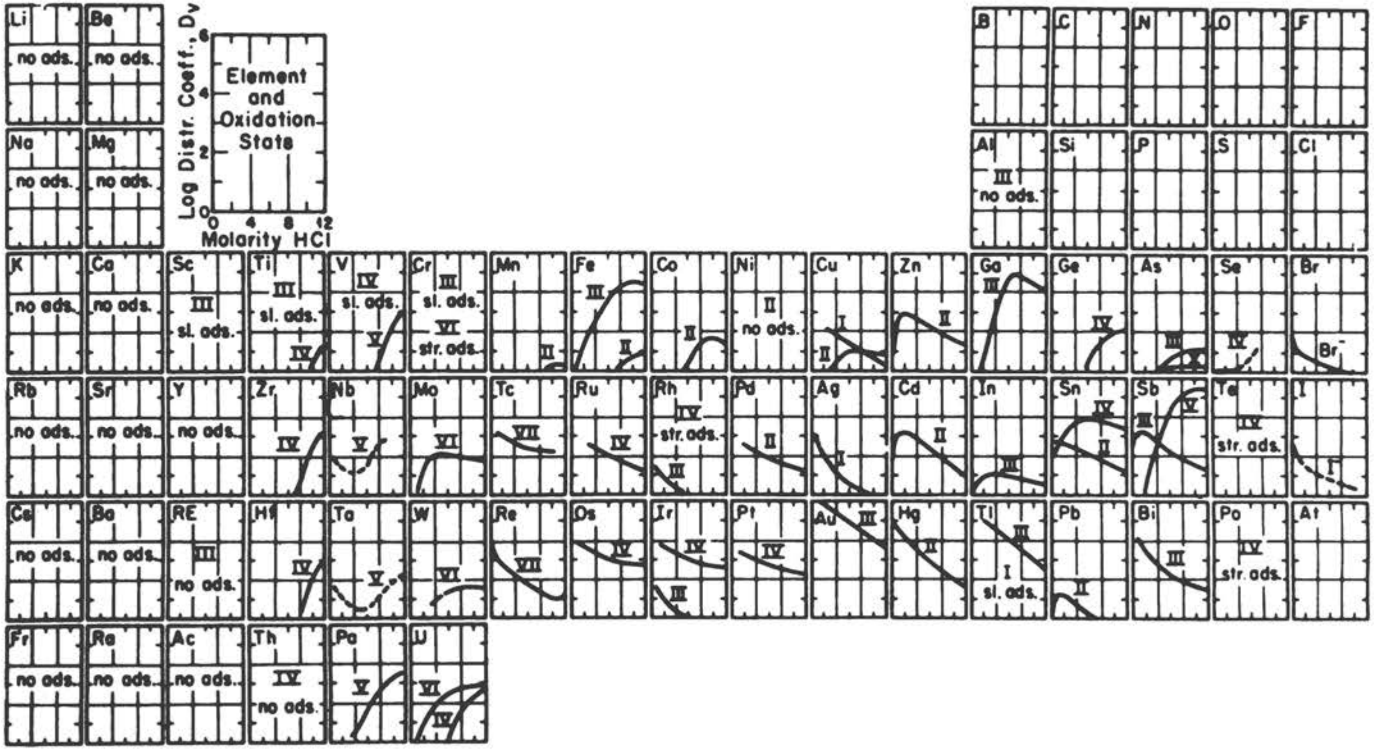

Fig. 9. Adsorption of the elements from hydrochloric acid.

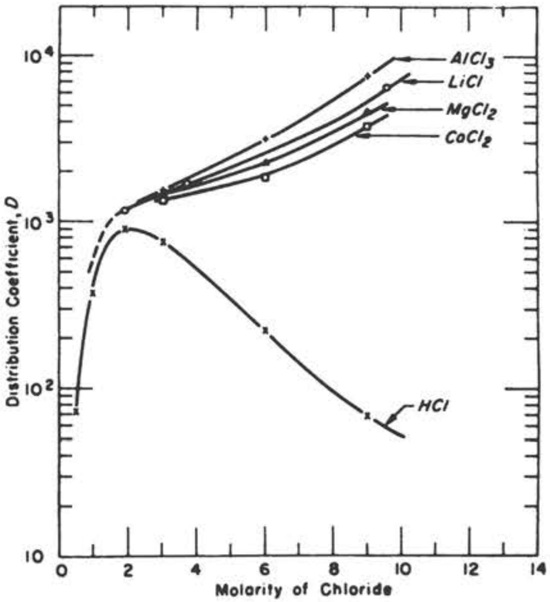

Fig. 10. Adsorption of zinc (II) from chloride solutions (~10 per cent loading of resin).

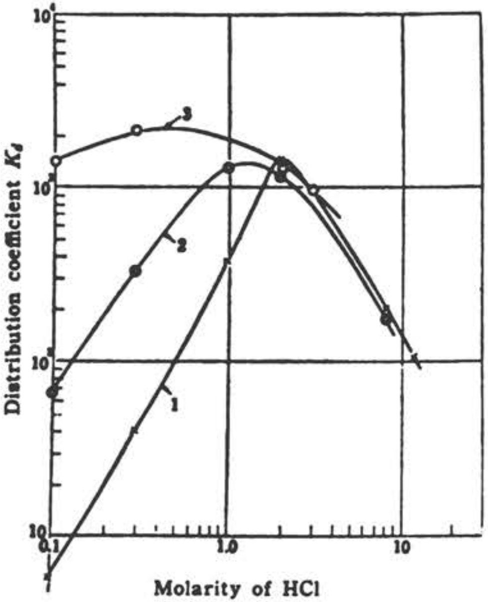

Fig. 11. Anion exchange adsorption of Zn(II).

1. in HCl solution
2. in HCl - 30% (v/v) methanol mixutre
3. in HCl - 60% (v/v) methanol mixture

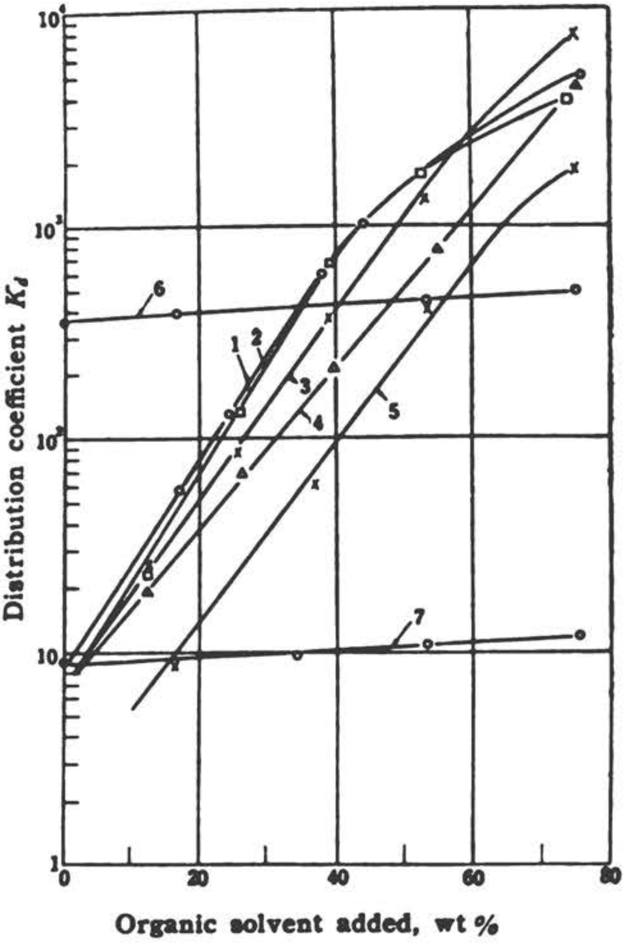

Fig. 12. Effects of various organic solvents on the anion exchange adsorption of Zn(II) in 0.1 M HCl.

1. Acetone
2. Ethanol
3. Methanol
4. n-Propanol
5. Methanol (Dowex 1-X4)
6. $RNO_3 + Cl^-$, $\mu = 0.003$, (NaCl) Methanol
7. $RNO_3 + Cl^-$, $\mu = 0.1$, (KNO_3) Methanol

Lindenbaum, Boyd, and Myers[149] have studied a new type of resin, Stamex S-44, a sulfonium anion exchanger.[150] They report that zinc has higher K_D's on Stamex S-44 than on Dowex 1 for both hydrochloric acid and lithium chloride solutions.

Table XII summarizes the data of Jentzck and Frotscher[151] obtained with Wolfatit L-150 and hydrochloric acid solutions.

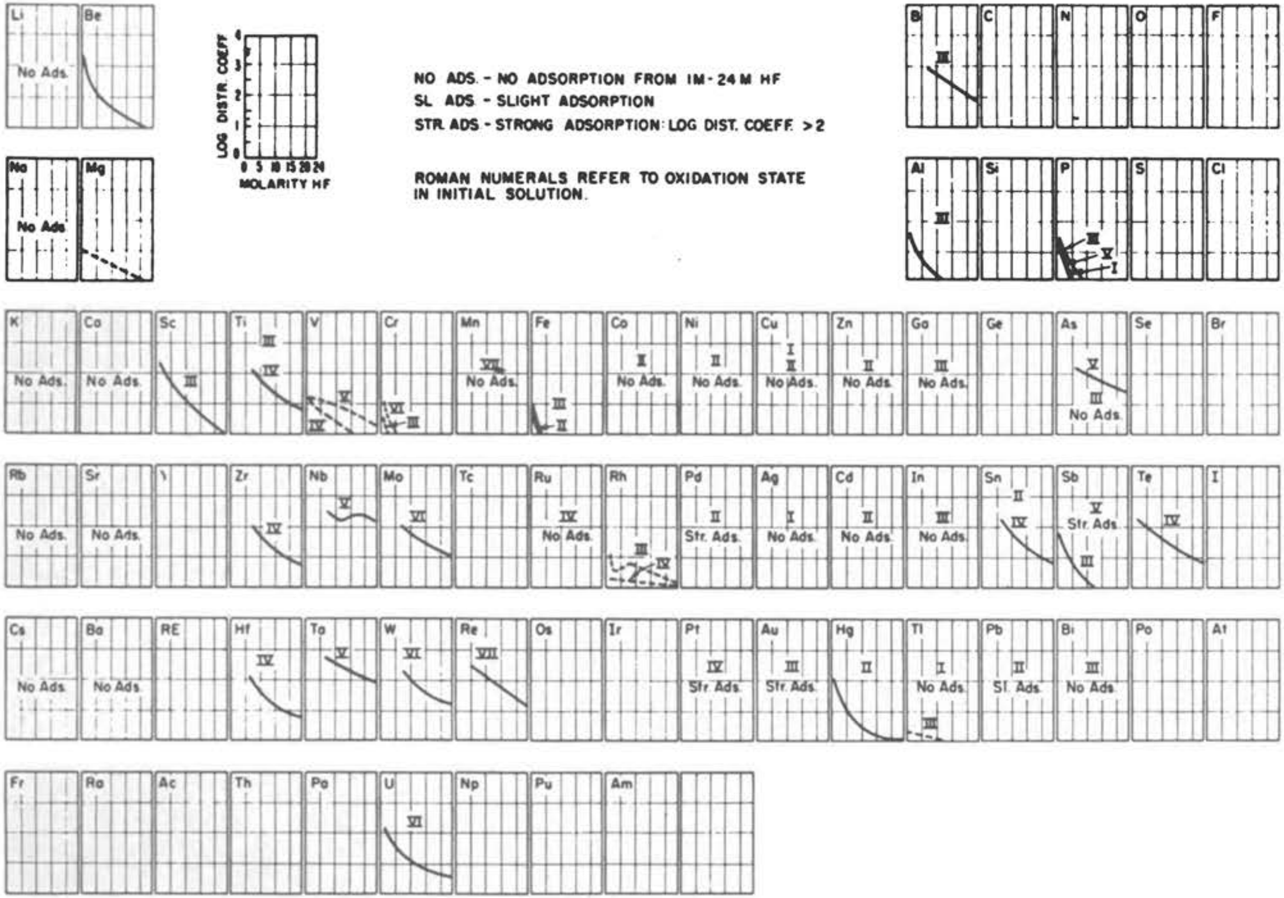

Fig. 13. Removal of elements from solution in 1 M to 24 M hydrofluoric acid with 200-mesh anion exchange resin.

Table XII. Elution of various metal ions from Wolfatit L-150 with hydrochloric acid.

Element	Hydrochloric acid concentration (molarity)										
	12.5	11-10	7.5	6.5	5	4	1.5	1	0.5	0.05	0.005
Al	x										
Mg	x										
Li	x										
Na	x										
K	x										
As(III)		x									
Ca		x									
Ni		x									
Fe(II)			x								
Co				x							
Mn(II)				x							
Fe(III)					x						
Cu						x					
Sn(IV)							x				
In								x			
Zn									x		
Cd										x	
Pb											x

Kraus and Moore[152] separated zinc from Ni(II), Co(II), Cu(II), and Fe(III) by passing a solution 12$\underline{M}$ in hydrochloric acid through a Dowex-1 column previously conditioned with concentrated hydrochloric acid. Ni(II) appeared in the eluate. Eluting with successively more dilute acid, Mn(II) eluted with 6$\underline{M}$ HCl, Co(II) with 4$\underline{M}$ HCl, Cu(II) with 2.5$\underline{M}$ HCl, Fe(III) with 0.5$\underline{M}$ HCl, and Zn(II) with 0.005$\underline{M}$ HCl.

Miller and Hunter[153] adsorbed zinc on IRA-400, chloride form in 2$\underline{M}$ HCl, washed with 2$\underline{M}$ HCl, and eluted with either water or 0.25$\underline{N}$ HNO_3 as a separation from Al(III), Mg(II), Ca(II), Co(II), Ni(II), Mn(II), Cr(III), Th(IV), Zr(IV), Ti(IV), U(VI), Be(II), and Cu(II). Zn(II), Cd(II), and In(III) are eluted together along with 20% of the Sn(IV) and small amounts of Sb(III), Bi(III), and Pb(II). The majority of Sn(IV), Sb(III), Bi(III), and Pb(II) remains adsorbed.

Freegarde[154] separated zinc and copper as follows: zinc was adsorbed on Dowex 1 in 0.12$\underline{M}$ HCl with 100 g NaCl per liter (the copper eluted), and was eluted with either 2$\underline{M}$ NaOH with 20 g/l NaCl or 0.005$\underline{N}$ HCl, or 1$\underline{N}$ HNO_3.

Kallmann, Steele, and Chu[155] adsorbed zinc and cadmium on Dowex 1 with 0.12$\underline{N}$ HCl containing 10% NaCl. Zinc was eluted with 2$\underline{M}$ NaOH, cadmium with 1$\underline{M}$ HNO_3.

Berg and Truemper[156] separated zinc, cadmium, and mercury on a Dowex 1, 60 to 100 mesh column 1.16 cm i.d. and 6 cm long in quantities up to 100 mg of each. The flow rate was 1.5 to 2 ml per minute. The metals were adsorbed from 0.5$\underline{M}$ HCl and washed with 2$\underline{M}$ HCl. Zinc was eluted with 180 ml of a solution 75% 0.01$\underline{N}$ HCl – 25% methanol, cadmium eluted in the fraction 200-500 ml; mercury was then eluted with 0.01$\underline{M}$ HCl – 0.1$\underline{M}$ thiourea solution.

Baggott and Willcocks[157] separated zinc and cadmium on Dowex 1 by adsorbing cadmium from a dilute solution of KI, while zinc passed through the column.

Hunter and Miller[158] adsorbed zinc and cadmium on IRA-400 from 2$\underline{M}$ HCl, and washed with 5$\underline{M}$ HI, then water. The zinc was eluted with 0.25$\underline{N}$ HNO_3.

Kallmann, Oberthin, and Liu[159] separated zinc and cadmium by adsorbing the $CdI_4^=$ on Dowex 1 from 0.75$\underline{N}$ H_2SO_4 with 5% KI solutions while the zinc did not adsorb. Cadmium was recovered by elution with 3$\underline{N}$ HNO_3.

The use of iodide as a preferential complexing agent for cadmium is, in the opinion of the author, the most convenient, easiest, and most effective method of separating zinc and cadmium.

9. Isotopic Exchange of Zinc

In general, the rates of zinc tracer exchange with zinc compounds are too rapid to measure; even chelates show this rapid exchange. Leventhal and Garner[160] found complete exchange in less than 30 seconds (at 25°C) of traced dipyridine zinc acetate and the following zinc complexes: acetylacetone, acetylacetone ethylenediamine, benzoylacetone ammoniate, nicotinyl acetone, and dipyridine thiocyanate. Atkins and Garner[161] found that Zn^{65} tracer did not exchange with zinc in the phthalocyanine complex, but did exchange with zinc complexed with diphenylthiocarbazone, 8-hydroxyquinoline, anthranilic acid, and salicylaldehyde.

Ionescue, Negoescu, and Gainar[162] studied the slow exchange between $Zn^{65}SO_4$ solution and ZnO at 0°, 15°, 25°, and 35°C but no further data were given.

Miyagaki[163] has evidence that the zinc in sphalerite will exchange with zinc in solution in contact with the ore.

Barriera[164] reports that Zn^{65} in sulfate solutions exchanges slowly with zinc metal sheet with a half-time of the order of 10 days. Matsuura[165] studied this system carefully and found that heterogeneous exchange occurs uniformly within the interior of zinc dust that has been left in contact with $Zn^{65}SO_4$ solution. He also found that a few thousand layers at the surface of zinc foil are available for exchange. Apparently the diffusion of zinc atoms through the solid, or recrystallization of the zinc metal in the presence of solution, limited the rate of exchange. The rate-determining step below $10^{-3}\underline{M}$ in zinc is the adsorption of Zn^{++} on the surface. The fraction, F, of exchange is given approximately by the expression

$$F \cong 1 - A_r e^{-k_r t} + A_s e^{-k_s t} ,$$

where $$k_s = (0.20\, q/v)\,(1 - 0.5\,\mu^{1/2}), \text{ in hr}^{-1}.$$

For Zn-Zn^{++} exchange, q/v is the ratio of surface area to volume of solution, μ is the ionic strength, t is time, A_r and A_s are constants, and k_r is another constant similar to k_s.

10. Paper Chromatography

Chapter 43 of Chromatography by Lederer and Lederer[166] is an excellent review of the field of inorganic paper chromatography. Little, if any, more recent data on zinc behavior in paper chromatography has been found. Separations of this type are excellent for microgram quantities, but—because of the capacity of paper—milligram or larger quantities of metals cannot as yet be separated conveniently.

Ions can be made to migrate through the liquid entrained in the paper by impressing a potential gradient parallel to the direction of migration. Lederer and Ward[168] have separated metal ions into rather interesting groups by this means. Their data are shown in Table XIII.

Chapter 18 of Lederer's book Paper Electrophoresis[167] gives an up-to-date review of the field with respect to inorganic separations, earlier chapters review theory and techniques. Maki[169] separated Ni(II), Co(II), and Zn(II) using $Na_4P_2O_7$ at pH's less than 2, metaphosphate below pH 1.7, and trimetaphosphate below pH 5.6 using paper electrophoresis. Maki[170] also separated Zn(II) from Ni(II), Co(II), and Mn(II) with a mixture of acetone and methanol acidified with hydrochloric acid.

Schumacher[171] used a similar technique called focussing ion exchange. He adds a complexing agent to one electrode of his system, impresses a potential gradient, and allows the ions to migrate. At the point along the

Table XIII. Movement of metal ions in $0.5\underline{N}$ hydrochloric acid in 50 minutes under a potential gradient of 3.6 v/cm.[168]

Anionic		Iso-electric	Cationic	
2.5-1.5 cm	1.5-0.5 cm		0.5-1.5 cm	1.5-2.5 cm
Hg(II), Pd(II)	Au(III), Ir(IV), Bi(III), Tl(III)	Cd(II)	Mo(VI), Zr(IV), Rh(III), As(III), Sn(II), Sb(III), Pb(II)	Cr(III), U(VI), Ti(IV), Be(II), Fe(III), Co(II), Ni(II), Al(III), Cu(II), Zn(II), Sr(II), Ba(II)

paper where the metal complex is uncharged, the migration ceases. Using this technique, he and Streiff[172] have separated 10 μg each of Fe(III), Ni(II), Zn(II), Al(III), U(VI), Co(II), Cr(III), and Mn(II) added at the center of the paper in a solution of pH about 5. The anode solution contained $0.5\underline{M}$ hydrochloric acid, the cathode solution $0.5\underline{M}$ sodium hydroxide and $0.5\underline{M}$ sodium nitriloacetate, the current flow was 100 ma at 500 v. Separation was complete in five minutes.

V. DISSOLUTION OF SAMPLES CONTAINING COMPOUNDS OF ZINC

Minerals

According to Hillebrand et al.,[20] the solution of zinc minerals offers no difficulties and can usually be accomplished by attack with hydrochloric acid, hydrochloric acid followed by nitric acid, or nitric acid alone. The insoluble residue, which ordinarily contains no zinc, can then be decomposed by fusion with sodium carbonate, followed by solution of the melt in acid.

Soils

In general, zinc analysis of soils does not require complete dissolution of the soil. Martin[173] digests the soil with a mixture of hydrochloric, nitric, and perchloric acids, then evaporates to dryness and ignites at 300°-350°C. After leaching with dilute acid, the filtrate is then extracted with dithizone in chloroform. Martin[173] also digested soil with sulfuric acid, diluted, filtered, and extracted the filtrate with dithizone. Shaw and Dean[174] leached soils by heating with a solution of pH 7.0 to 8.5, cooling, then extracting the mixture with dithizone for 1 to 2 hours. Baron[175] determined the easily soluble zinc in soils by extracting zinc with a solution of ammonium acetate, ammonium sulfate, and acetic acid at pH 4, followed by extraction of zinc from the aqueous phase by dithizone in chloroform.

Plants

Heinen and Benne[176] ashed plant materials as follows: weigh 2 g of finely ground, air-dried plant material into a porcelain crucible. Add 10 ml of $1\underline{N}$ H_2SO_4 solution, mix thoroughly with the sample. Include crucibles for blank determinations. Heat on a steam bath until most of the water is removed, then dry in a hot-air oven at 105°C to remove remaining water. Heat in a muffle furnace at 500°-550°C until ashing is complete. Remove from the furnace, cool, moisten the ash with a little water. Then add 10 ml of $1\underline{N}$ HCl (more if necessary for some plant materials to insure an acid ash extract), and heat on a steam bath until all soluble material is brought into solution. (Adding 3 to 5 ml conc. HCl and boiling for two minutes is a good alternative.) Add a few ml of hot water, filter off the insoluble matter and collect the filtrate. Wash the filter until washings are no longer acid to methyl red indicator. Analyze for zinc using the dithizone procedure.

Organic Materials

Marcali[177] ashes the sample in a platinum crucible at 500°-550°C, leaches the ash with $1\underline{N}$ hydrochloric acid, filters, washes, and analyzes the filtrate and wash by the dithizone method.

Hamm[178] ashes tissue as does Marcali, but leaches with $0.1\underline{N}$ hydrochloric acid. He then passes the leach through a column of cation resin (Lewatit S-100), and washes the column with water to remove iron and phosphate. Zinc is eluted with $5\underline{M}$ hydrochloric acid and the eluate analyzed by the dithizone method.

Saredo and Lerni[179] digest tissue with 30% nitric acid for 3 to 4 hours, filter, concentrate to a syrup, add concentrated sulfuric acid, and distill off the mercury. The residue is then examined for Pb, Ba, Cu, As, or Zn.

Helwig, Ashikawa, and Smith[180] separated P, Fe, Co, and Zn from neutron-irradiated biological ash as follows: evaporate the ash to dryness with nitric acid, convert to the chlorides with hydrochloric acid, make the solution $12\underline{M}$ in hydrochloric acid and pass through a Dowex 1 column and wash with concentrated hydrochloric acid. Phosphorous elutes. Co is eluted with $4\underline{M}$ hydrochloric acid, Fe with $0.5\underline{M}$, and Zn with $0.005\underline{M}$.

Banks, Tupper, and Wormal[181] digested tissue with acid, filtered, and analyzed the filtrate for zinc by the dithizone method.

Rechenberger[182] split the zinc from blood proteins with $6\underline{M}$ hydrochloric acid and 20% trichloroacetic acid, then analyzed the solution by the dithizone method.

VI. COUNTING TECHNIQUES

All zinc isotopes have an abundance of electromagnetic radiation and can well be counted by a sodium iodide crystal and photomultiplier tube. At this laboratory, we find that counting the electromagnetic radiation, or even bremsstrahlung, is far more precise than counting electrons. The main source of error with electron counting is the nonuniformity of the sample itself, and the concomitant error in the self-scattering and self-absorption of the counting sample.[183]

Gamma-ray spectra from IDO-16408 are shown in Figs. 14, 15, and 16.[184]

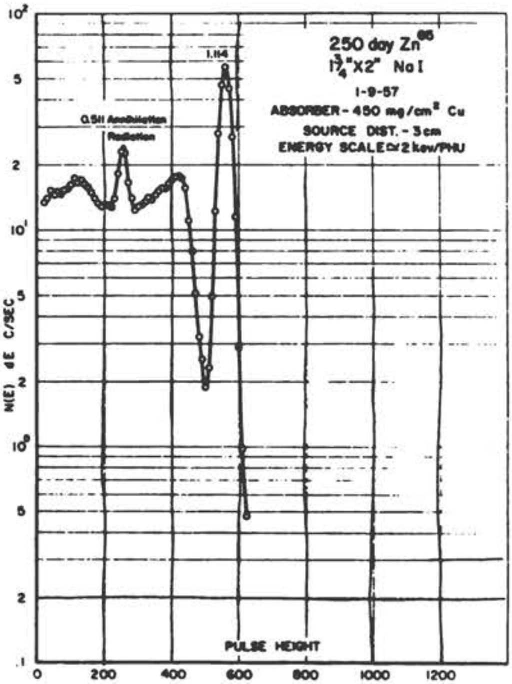

Fig. 14. Gamma-ray spectrum of $Zn.^{65}$

VII. COLLECTED RADIOCHEMICAL SEPARATIONS PROCEDURES FOR ZINC

Leddicotte et al.[185] have given a review of neutron activation analyses for most of the elements. They list sample type, method of analysis, the nuclide involved, observed concentration, and sensitivity of the method. Many of the procedures that follow are applicable to this type of work.

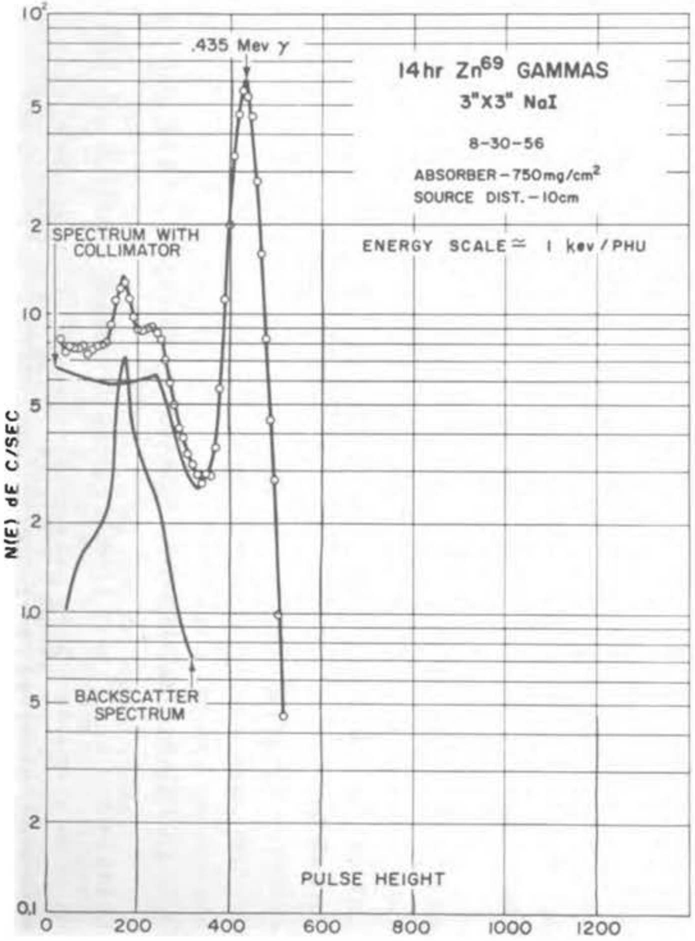

Fig. 15. Gamma-ray spectrum of Zn.^{69}

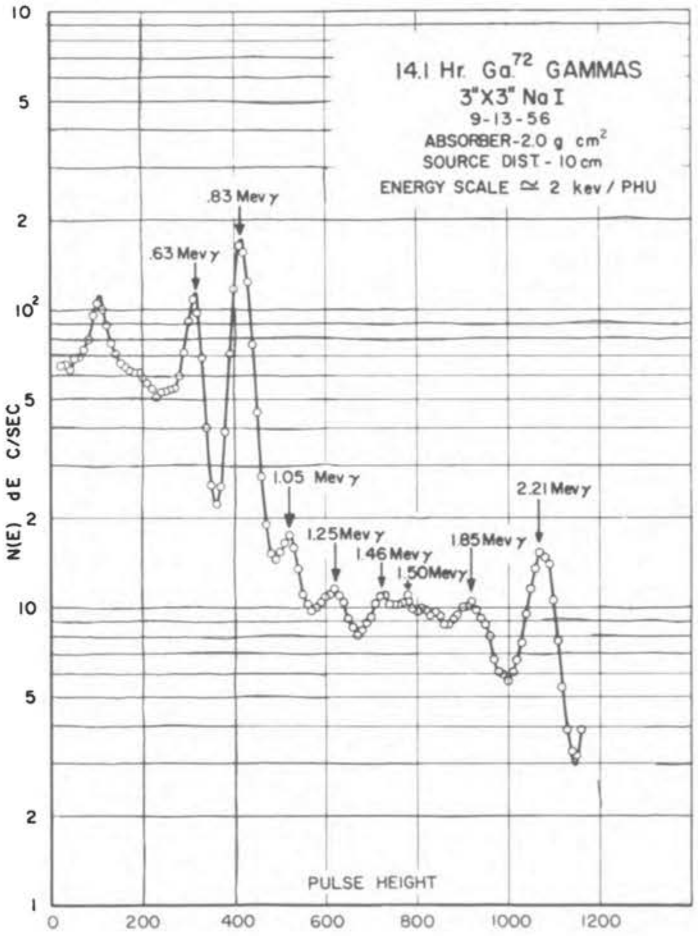

Fig. 16. Gamma-ray spectrum of Ga.^{72}

PROCEDURE 1 – Separation of Zinc from Fission Products

Source: H. G. Hicks, W. E. Nervik, P. C. Stevenson, and D. R. Nethaway.

1. Add zinc carrier and cadmium holdback to the active solution and adjust to 1<u>N</u> in acid or less. HCl, HNO_3, $HClO_4$, and H_2SO_4 solutions are suitable.
2. Cool in an ice bath, add 5 ml zinc reagent (see note 1), stir. Add 2 drops concentrated $HClO_4$ to start precipitation, stir, digest ten minutes, centrifuge, wash $ZnHg(SCN)_4$ with 1<u>M</u> $HClO_4$.
3. Dissolve in 1/2 ml hot concentrated HNO_3, dilute to 20 ml, add 3 drops Y, Zr, and Cd holdbacks. Make 1<u>M</u> in OH^- with carbonate-free NaOH, centrifuge, discard precipitate. Add 2 drops each of Fe and Cd to the supernatant solution, stir, and centrifuge. Discard precipitate.
4. Adjust the supernatant liquid to 2<u>M</u> in acid with HCl, pass through a resin column of Dowex 21 K (10 cm long, 6 mm diam, 50-100 mesh) that has been pre-equilibrated with 2<u>M</u> HCl, Zn is adsorbed. Wash with 10 ml 0.5<u>M</u> HCl containing 3 drops of 4% KI solution. Elute Zn with 20 ml boiling water containing 3 drops of 4% KI solution.
5. Direct the eluate onto a resin column of Dowex 50 (5 to 6 cm long, 6 mm in diam, 50-100 mesh). Discard anion columns, wash cation column with 10 ml 1<u>M</u> $HClO_4$. Elute Zn with 20 ml 3<u>M</u> $HClO_4$.
6. Add 5 ml 6<u>M</u> NaOH and 3 drops Cd to the eluate and repeat steps 2 through 5.
7. Neutralize to green endpoint of bromthymol blue with NaOH and HAc. Add 3 ml $(NH_4)_2$ HPO_4 buffer (note 2), digest in hot bath 10 minutes. Wash twice with dilute buffer (note 3), once with acetone, dry at 110°C, weigh as $ZnNH_4PO_4$.

Note 1. Dissolve 64 g NH_4SCN and 54 g $HgCl_2$ in one liter of water, filter. This solution should be relatively fresh.

Note 2. Dissolve 15 g $(NH_4)_2HPO_4$ in some water. Neutralize carefully with NH_4OH to phenolphthalein indicator, dilute to 140 ml.

Note 3. Two or three drops of buffer in 30 ml water.

PROCEDURE 2 – Separation of Zinc from Fission Products

Source: J. M. Siegel and L. E. Glendenin, Procedure for Isolation of Zinc Activities in Fission, in <u>Radiochemical Studies: The Fission Products</u>, Book 3, C. D. Coryell, Ed. (McGraw-Hill, New York, 1951), p. 1432.

1. To a suitable volume of irradiated uranyl nitrate solution (notes 1 and 2) add 10 mg zinc carrier, 1 to 2 ml sat. oxalic acid, and sufficient HNO_3

to make the solution 1M in HNO_3. Cool in running tap water or ice bath, and add 3 ml of $HgCL_2$-KSCN reagent. Stir the cold solution occasionally for 3 to 5 min (note 3), centrifuge the $ZnHg(SCN)_4$, discard the supernatant solution.

Alternative extraction step (note 2). Add to a suitable volume of sample 10 mg of zinc carrier and sufficient 2M Na_2CO_3 with about 2 ml per gram uranyl nitrate (note 4) to complex the uranium and precipitate $ZnCO_3$. Centrifuge and wash the precipitate with 5 ml 0.2M Na_2CO_3. Dissolve $ZnCO_3$ in 10 ml of 1M HNO_3, cool, and add 1 ml sat. oxalic acid and 3 ml $HgCl_2$-KSCN reagent. Stir the cold solution occasionally for 3 to 5 min, centrifuge the $ZnHg(SCN)_4$, and discard the supernatant solution.

2. Add 1.5 ml of 6M HNO_3 to the $ZnHg(SCN)_4$ and 3 ml H_2O. Boil until the precipitate dissolves, and continue boiling for 1 to 2 min to remove decomposition products. Dilute to 10 ml and cool in running tap water or ice bath. To the cold solution, add 1 ml sat. oxalic acid and 3 ml $HgCl_2$-KSCN reagent. Stir the cold solution occasionally for 3 to 5 min, centrifuge the $ZnHg(SCN)_4$ and discard the supernatant solution.
3. Repeat step 2.
4. To the $ZnHg(SCN)_4$ add 1.5 ml 6M HNO_3 and 3 ml water. Boil until the precipitate dissolves and continue the boiling for 1 to 2 minutes. Dilute to 10 ml, cool, and saturate with H_2S (note 5). Centrifuge and discard HgS. To the clear supernatant liquid add 1 ml of 6M NaOH (note 6) and 5 mg bismuth carrier, and saturate with H_2S. Centrifuge and discard the Bi_2S_3. Repeat the Bi_2S_3 scavenging twice with 5 mg bismuth carrier and H_2S. Add 2 ml of 6M $NH_4C_2H_3O_2$ (pH ~ 5), saturate with H_2S, centrifuge out the white ZnS, and discard the supernatant solution.
5. Dissolve the ZnS with 5 ml conc. HBr and evaporate to dryness over an open flame. Repeat evaporation twice with 5 ml portions of conc. HBr. Take up residue in 10 ml of 0.5M NaOH, add 1 ml 2M Na_2CO_3, and heat to boiling. Keeping the solution under constant agitation, add about 2 mg of Fe^{+++} carrier and about 5 mg barium carrier drop by drop. Digest the hot solution for 1 min, centrifuge, and discard the $Fe(OH)_3$-$BaCO_3$ precipitate. Repeat the hydroxide-carbonate scavenging twice with about 2 mg Fe^{+++} and 5 mg barium carriers.
6. To the clear supernatant solution carefully add 4 ml of 6M HCl and 1 ml sat. oxalic acid. Cool the solution in running tap water or in an ice bath, add 3 ml $HgCl_2$-KSCN reagent, and stir occasionally for 3 to 5 min. Centrifuge the $ZnHg(SCN)_4$ and discard the supernatant liquid.
7. Suspend the $ZnHg(SCN)_4$ in about 5 ml of H_2O; transfer, with the aid of a

wash bottle, to a weighed filter-paper disc (note 7) in a small Hirsch funnel; and filter with suction. Wash the precipitate with 3 portions of absolute alcohol and three portions of anhydrous ethyl ether. Transfer the paper with the precipitate to a small watch glass, and place in a vacuum desiccator. Evacuate for 2 min, release the suction, and then evacuate for 5 min more. Weigh the precipitate as $ZnHg(SCN)_4$ (note 8) and mount for counting.

Note 1. The volume, after the addition of the reagents, should be at least 10 ml and may be as much as 25 ml.

Note 2. Zinc mercuric thiocyanate cannot be precipitated in the presence of HNO_2 or other strong oxidizing agents. If HNO_2 is present, or if the HNO_3 concentration is unknown, the solution may be evaporated to near dryness (after the zinc carrier has been added) and taken up in 10 ml of $1\underline{M}$ HNO_3. These difficulties may be circumvented by the alternative extraction step in step 1.

Note 3. It may be necessary to scratch the wall of the centrifuge cone with a glass stirring rod to start the crystallization.

Note 4. If much free acid is present or if the initial volume is greater than 10 ml, the addition of solid Na_2CO_3 and the gentle heating may be required to effect the complete solution of the uranium.

Note 5. Some sulfur may be formed, but is removed in subsequent scavengings.

Note 6. The acid concentration should be about $0.3\underline{M}$ after the addition of the NaOH.

Note 7. The filter paper must be washed with H_2O, ethanol, and ether, and dried under the same conditions as in the procedure before the weighing.

Note 8. The zinc carrier solution should be standardized as $ZnHg(SCN)_4$.

PROCEDURE 3 – Cu Spallation, Designed to Separate from Elements of Z < 30

Source: R. E. Batzel, Univ. of Calif. Rad. Lab. Report UCRL-432.

1. The copper metal target is dissolved in concentrated HNO_3 or HCl and H_2O_2. Zinc carrier and holdback agents are added.
2. The copper is removed as CuS from a $1\underline{M}$ acid solution. NH_4OH is then added to make the solution alkaline, and H_2S is added to complete ZnS precipitation.
3. Wash precipitate with dilute NH_4OH containing H_2S.
4. After the centrifugation, 2 to 3 ml of $5\underline{M}$ HCl is added, the precipitate stirred well, and the solution centrifuged almost immediately (after about

one minute). ZnS and MnS are dissolved, while CoS and NiS are attacked slowly.

5. The supernatant liquid is boiled to remove H_2S, and about 1 ml concentrated NH_4OH is added to neutralize the HCl; then an equal volume (3 to 4 ml) of glacial acetic acid is added. The solution is heated almost to boiling and saturated with H_2S to precipitated ZnS.
6. The precipitate is dissolved in 1$\underline{M}$ HCl, the H_2S boiled off, and 2 mg Fe^{+++} added. Two or three pellets of NaOH are added and the $Fe(OH)_3$ removed, leaving the zinc in solution as zincate.
7. The solution is made 1$\underline{M}$ in acid with HCl, and zinc reagent (note 1) is added to precipitate $ZnHg(SCN)_4$. Wash with 1$\underline{M}$ HCl twice, dry, weigh.

Note 1. The zinc reagent was made by dissolving 64 g NH_4SCN and 54 g $HgCl_2$ in one liter of water and filtering.

PROCEDURE 4 – Copper Spallation Target

Source: G. Carleson, Acta Chem Scand. 8, 1673-1700 (1954).

1. Dissolve the copper metal target in hot HCl and H_2O_2, precipitate the Cu with H_2S, centrifuge, save supernatant liquid.
2. Evaporate supernatant liquid to a small volume on a steam bath with a warm air stream. Add equal amounts to two strips of filter paper with a calibrated micropipet. After 15 minutes equilibration in chromatography chambers, the complete separation of different cation species is attained by eluting one strip with methyl-n-propyl ketone plus 15% 8$\underline{M}$ HCl, and the other with the same ketone plus 15% 10$\underline{M}$ HCl. The exact positions on the strips determined by scanning. Each ion species, Mn and Ni from

Table XIV. R_f values.

Element	Ketone + 15% 8$\underline{M}$ HCl	Ketone + 15% 10$\underline{M}$ HCl
acid front	0.68	--
Zn	0.67-0.80	0.75
Cu	0.40-0.87	0.65
Ni	0.03 - 0.06	0.04
Co	0.30-0.40	0.69
Fe	0.83-0.90	0.95
Mn	0.08-0.12	0.26
Cd	--	0.86

the second solvent mixture, and Co, Zn, Fe, and Cu contaminations from the first, is completely cut out of the strips and gently ashed into a small platinum dish.

3. The CuS is washed, dissolved in conc. HNO_3, diluted to known volume, and an aliquot counted.

Table XIV lists some of Carleson's R_f determinations.

PROCEDURE 5 – Scheme of Analysis

Source: T. H. Handley, Identification of Radioelements, in Analytical Chemistry Division Quarterly Progress Report, ORNL-955, Jan. 1951, p. 47.

An aliquot containing an adequate number of counts per minute is placed in a glass centrifuge cone. Add about 5 mg of the following carriers: Ag, Cu, Fe, Co, Sr, and Na. In most instances, it is recommended that the carrier be added for that element which constitutes the product, eliminating one of the above carriers, depending upon which group the product element falls in. Groupings are given in Table XV.

Group I. If chlorides are present, make the solution alkaline with NH_4OH to ensure mixing of Ag carrier and activity. Make acid with conc. HCl and boil for several minutes. Centrifuge and decant the supernatant, retaining it, and wash the precipitate twice with 5 to 10 ml distilled H_2O. Finally add 1 ml distilled H_2O and make a slurry. Evaporate to dryness and mount for counting.

Group II. To the supernatant from Group I of about 15 ml volume, add 3N NH_4OH slowly until a precipitate begins to form, then add 1 ml of conc. HCl and heat to boiling. Pass H_2S through the soln. for several minutes. Centrifuge and decant supernatant, retaining it, wash the precipitate twice with 5 to 10 ml H_2O, mount and count.

Group III. Transfer supernatant to 50-ml beaker, boil to remove H_2S, add 2 or 3 drops 30% H_2O_2, and boil again. Add conc. NH_4OH until precipitation begins, then 1 ml more. Centrifuge and decant supernatant, saving it; wash precipitate twice with 5 to 10 ml H_2O, mount and count.

Group IV. Pass H_2S through supernatant from Group III for several minutes, centrifuge, save supernatant, wash and count precipitate.

Group V. Acidify supernatant from Group IV with HCl, boil to remove H_2S, make just alkaline to phenolphthalein and add 2 to 3 ml $(NH_4)_2C_2O_4$. Let stand for several minutes, and centrifuge. Decant supernatant and save. Wash and count precipitate.

Group VI. Evaporate supernatant to dryness, flame to remove NH_4^+ salts, take up in dilute HCl, mount and count.

Each group now must be separated into its components by various means.

Table XV. Distribution of radioelements in the scheme.
(Adapted by Handley from Lundell and Hoffman.[23])

Possibly lost:

Au, Hg, Ce, Si, P, Cl, Ge, As, Se, Br, Ru, Sn, Sb, Te, I, Re, Os, Ir.

Group I:

(a)[*] Si, Nb, Ag, Ta, W.
(b)[*] P, S, Cl, Br, Zr, I, Re, Hf, Tl, Pb, Ru, Th, Pa.

Group II:

(a)[*] Hg, Pb, Bi, Po, Cu, Ge, As, Se, Mo, Ru, Rh, Pd, Cd, Sn, Sb, Te, Re, Os, Ir, Pt, Au.
(b)[*] V, Fe, Co, Ni, Zn, In, W, Tl.

Group III:

(a)[*] Be, Sc, Cr, Fe, Ga, Y, Re, Zr, In, Re, Hf, Au, Th, Ac, Pa, U.
(b)[*] Si, P, V, Co, Zn, Nb, Hf, W, Ir.

Group IV:

(a)[*] Mn, Co, Zn, Ni, Tl.
(b)[*] V, W.

Group V:

(a)[*] Ca, Sr, Ba, Ra.

Group VI:

(a)[*] Na, (Si)[**], (Cl)[**], K, (V)[**], Rb, Cs, (W)[**].

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[*] After (a), precipitated more or less completely; after (b), sometimes precipitated entirely or partially.

[**] Elements in parentheses unlikely.

PROCEDURE 6 – Carrier-Free Separation of Zn^{65} from Copper Bombarded with Deuterons

Source: C. E. Mellish, AERE-I/M-39.

1. Dissolve only the bombarded face of the spectroscopically pure copper target in HNO_3, evaporate to dryness, and dissolve the residue in 2$\underline{M}$ HCl.
2. Pass the solution through a 10-cm × 1.5-cm (diam) column of De Acidite FF resin, and wash with a few ml 2$\underline{M}$ HCl to remove all the copper.
3. Elute the zinc with water.

In a typical run, 20 mC of Zn^{65} was separated with a specific activity of 10 C/g.

PROCEDURE 7 – Carrier-Free Separation of Zn^{65} from Copper Targets Irradiated with Deuterons

Source: M. Lederer, Anal. Chim. Acta 8, 134 (1953).

1. 20 g copper is dissolved in aqua regia, evaporated to dryness, and dissolved in 0.1$\underline{N}$ HCl.
2. CuS may be precipitated, or the solution placed directly on sheets of filter paper. The chromatogram is developed with butanol shaken with 1$\underline{M}$ HCl.
3. After 20 hours the sheets are air dried. A green band is visible in the R_f 0.1 region.
4. The band of zinc can be detected with an x-ray counter 2 to 3 cm ahead of the Cu band (the liquid front is at 27 cm).

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