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NUCLEAR SCIENCE SERIES

The Radiochemistry of the Rare Earths, Scandium, Yttrium, and Actinium

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The Radiochemistry of the Rare Earths, Scandium, Yttrium, and Actinium

By P. C. STEVENSON
and W. E. NERVIK

Lawrence Radiation Laboratory
University of California
Livermore, Calif.

Issuance Date: February 1961

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Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

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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

INTRODUCTION

This report has been prepared as one of a series of monographs on the radiochemistry of the elements for the Subcommittee on Radiochemistry of the Committee on Nuclear Science within the National Academy of Sciences. Information presented here has been obtained in a search which included the Chemical Abstracts from 1947 to April 25, 1960; Nuclear Science Abstracts from 1947 to April 15, 1960; Abstracts of Declassified Documents for 1947 and 1948; Analytical Abstracts from 1954 to April 1960; and the authors' personal experiences from 1950 to the present. Data have been included primarily for radiochemists working with the rare earths, but it is hoped that others will also find the information useful.

Although the list of references is long, no pretense can possibly be made that it is complete. We have attempted to cover all phases of rare-earth chemistry that could conceivably be of interest to a radiochemist and to include all of the more significant references in each phase. During the course of the writing, however, we were continually finding important articles which had been missed in the literature search and doubtless there are many which we still have not found. We would be most appreciative if these omissions could be brought to our attention so that they may be included in future revisions of the manuscript.

The authors wish to acknowledge most heartily the assistance of Carl Wensrich and Carol Patrick of the LRL library staff. Without their aid in obtaining reprints of the references this volume could hardly have been prepared.

We also wish to express our sincerest appreciation to Mrs. Margaret Dixon for typing the final manuscript with alacrity, precision, and perseverance.

W. E. Nervik
P. C. Stevenson

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The Radiochemistry of the Rare Earths, Scandium, Yttrium, and Actinium

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Livermore, Calif.

I. GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF THE RARE EARTHS, SCANDIUM, YTTRIUM, AND ACTINIUM

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III. TABLE OF ISOTOPES

Data are reproduced in Figs. 1-5 from the G.E. Chart of the Nuclides (KAPL), 5th Ed., Revised to April 1956. For more detailed information consult: D. Strominger, J.M. Hollander, and G.T. Seaborg, "Table of Isotopes," Revs. Modern Phys. 30, No. 2, Pt. 2, 585-904 (1958).

IV. CHEMISTRY OF THE RARE EARTHS, SCANDIUM, YTTRIUM, AND ACTINIUM

IV.1. METALS, AMALGAMS, AND VARIOUS OXIDATION STATES

IV.1A. METALS

Although the rare earths have been known for more than one hundred years, it is only during the last fifteen years or so that techniques have been developed for separating pure compounds of individual members of this group of elements. The best methods for preparing pure rare-earth metals are less than ten years old, and intensive effort has gone into study of the properties of these newly available materials.

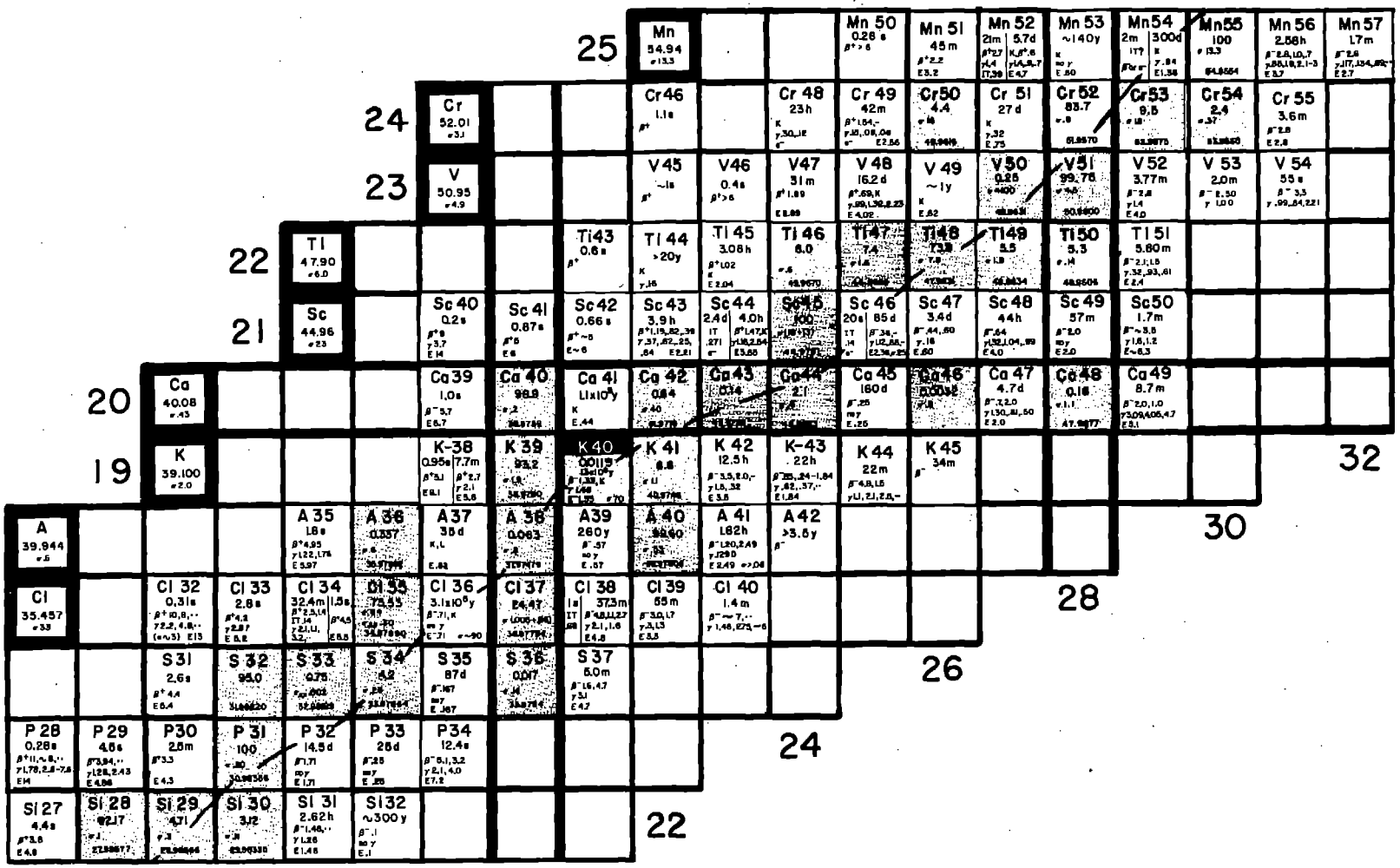

25
24
23
22
21
20
19
Mn 54.94
Cr 52.01
V 50.95
Ti 47.90
Sc 44.96
Ca 40.08
K 39.100
A 39.944
Cl 35.457
Mn 50 0.28 s
Mn 51 45 m
Mn 52 21m | 5.7d
Mn 53 ~140y
Mn54 2m | 300d
Mn55 100
Mn 56 2.58h
Mn 57 1.7m
Cr46 1.1s
Cr 48 23h
Cr 49 42m
Cr50 4.4
Cr 51 27 d
Cr 52 83.7
Cr53 9.5
Cr54 2.4
Cr 55 3.6m
V45
V46 0.4s
V47 31m
V 48 16.2 d
V 49 ~1y
V50 0.25
V51 99.75
V 52 3.77m
V 53 2.0m
V 54 55 s
Ti43 0.6 s
Ti 44 >20y
Ti 45 3.08h
Ti 46 8.0
Ti47 7.4
Ti48 73.9
Ti49 5.5
Ti50 5.3
Ti 51 5.80m
Sc 40 0.2 s
Sc 41 0.87 s
Sc42 0.66 s
Sc 43 3.9 h
Sc 44 2.4d | 4.0h
Sc 46 20 s | 85 d
Sc 47 3.4d
Sc 48 44h
Sc 49 57m
Sc50 1.7m
Ca 39 1.0 s
Ca 40 98.9
Ca 41 1.1x10⁵y
Ca 42 0.64
Ca 43 0.14
Ca 44 2.1
Ca 45 160 d
Ca 46 0.0032
Ca 47 4.7d
Ca 48 0.18
Ca 49 8.7 m
K-38 0.95s | 7.7m
K 39 93.2
K 40 0.0119 1.3x10⁹y
K 41 6.8
K 42 12.5 h
K-43 22h
K 44 22 m
K 45 34m
A 35 1.8 s
A 36 0.337
A37 35 d
A 38 0.063
A39 260y
A 40 99.60
A 41 1.82h
A42 >3.6y
Cl 32 0.31 s
Cl 33 2.8 s
Cl 34 32.4m | 1.5s
Cl 35 75.53
Cl 36 3.1x10⁵y
Cl37 24.47
Cl 38 1s | 37.3m
Cl 39 55 m
Cl 40 1.4 m
S 31 2.6 s
S 32 95.0
S 33 0.75
S 34 4.2
S 35 87d
S 36 0.017
S 37 5.0 m
P 28 0.28 s
P29 4.6 s
P30 2.5m
P 31 100
P 32 14.5 d
P 33 25d
P34 12.4 s
Si 27 4.4 s
Si 28 92.17
Si 29 4.71
Si 30 3.12
Si 31 2.62 h
Si32 ~300 y
22
24
26
28
30
32

Fig. 1.

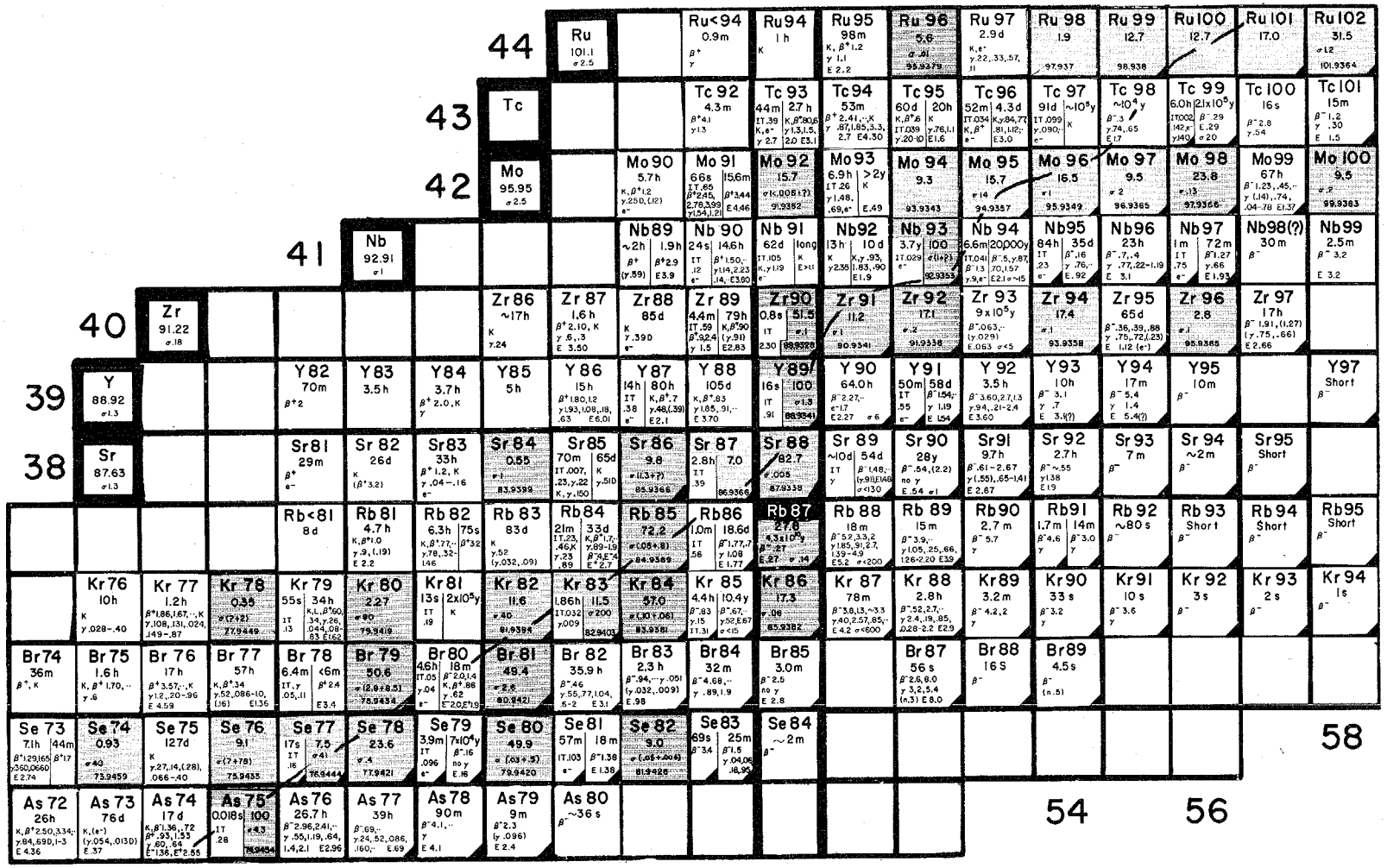
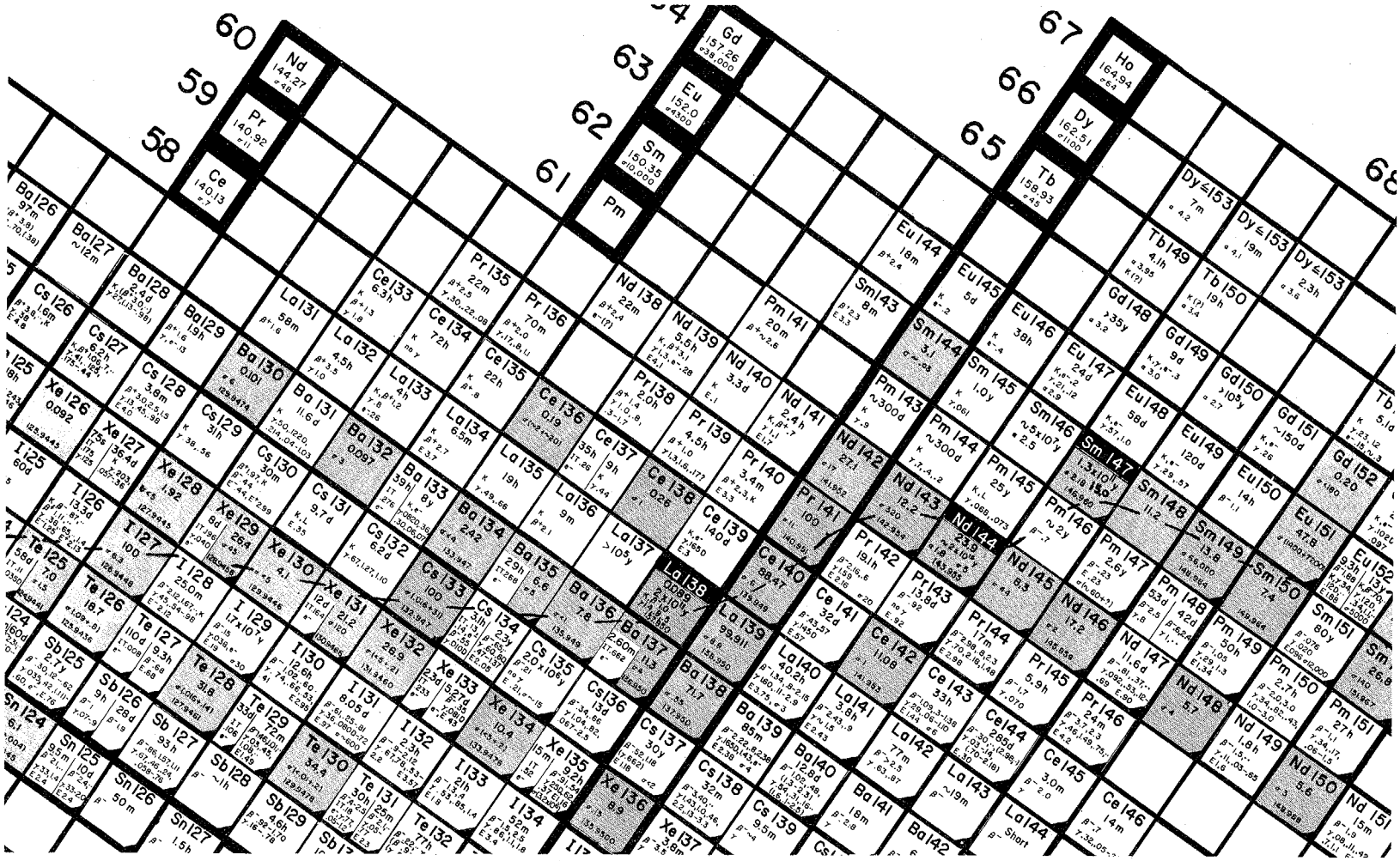
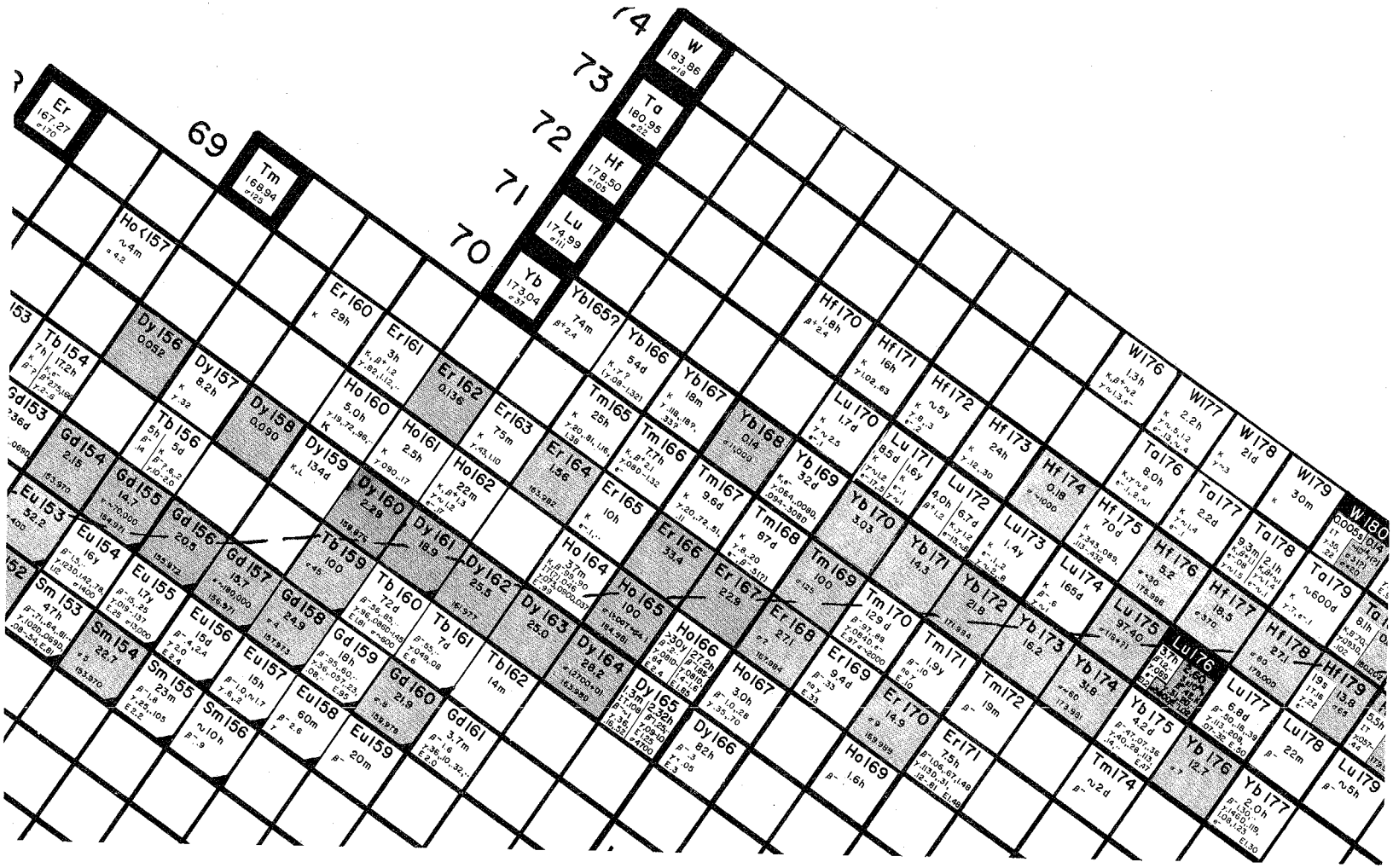


Fig. 2.


58
59
60
61
62
63
65
66
67
Ce 140.13 ≈3
Pr 140.92 ≈11
Nd 144.27 ≈48
Pm
Sm 150.35 ≈10,000
Eu 152.0 ≈4300
Gd 157.26 ≈35,000
Tb 158.93 ≈45
Dy 162.51 ≈1100
Ho 164.94 ≈64
Ba126 97m
Ba127 ~12m
Ba128 2.43d
Ba129 19h
Ba130 0.101
Ba131 11.6d
Ba132 0.097
Ba133 39h 8y
Ba134 2.42
Ba135 2.9h 6.6
Ba136 7.8
Ba137 11.3
Cs126 1.6m
Cs127 6.2h
Cs128 3.6m
Cs129 31h
Cs130 30m
Cs131 9.7d
Cs132 6.2d
Cs133 100
Cs134 2.3y
Cs135 2.0x10⁶y
Cs136 13d
Cs137 30y
Cs138 32m
Cs139 9.5m
Xe126 0.092
Xe127 36.4d
Xe128 1.92
Xe129 26.4
Xe130 4.1
Xe131 21.2
Xe132 26.9
Xe133 5.24d
Xe134 10.4
Xe135 15m
Xe136 8.9
Xe137 3.8m
I125 60d
I126 13.3d
I127 100
I128 25.0m
I129 1.7x10⁷y
I130 12.6h
I131 8.05d
I132 2.3h
I133 21h
I134 52m
I135 6.7h
Te125 58d 7.0
Te126 18.7
Te127 110d 9.3h
Te128 31.8
Te129 33d 72m
Te130 34.4
Te131 30h 25m
Te132 77h
Sb125 2.7y
Sb126 9h 28d
Sb127 93h
Sb128 ~1h
Sb129 4.6h
Sn124 6.1
Sn125 9.5m 10d
Sn126
Sn127 1.5h
La131 58m
La132 4.5h
La133 4h
La134 6.5m
La135 19h
La136 9m
La137 >10⁵y
La138 0.089 1.1x10¹¹y
La139 99.911
La140 40.2h
La141 3.8h
La142 77m
La143 ~19m
Ce133 6.3h
Ce134 72h
Ce135 22h
Ce136 0.19
Ce137 35h 9h
Ce138 0.26
Ce139 140d
Ce140 88.47
Ce141 32d
Ce142 11.08
Ce143 33h
Ce144 285d
Ce145 3.0m
Ce146 14m
Pr135 22m
Pr136 70m
Pr137 ~1h
Pr138 2.0h
Pr139 4.5h
Pr140 3.4m
Pr141 100
Pr142 19.1h
Pr143 13.8d
Pr144 17m
Pr145 5.9h
Pr146 24m
Nd138 22m
Nd139 5.5h
Nd140 3.3d
Nd141 2.4h
Nd142 27.1
Nd143 12.2
Nd144 23.9
Nd145 8.3
Nd146 17.2
Nd147 11.6d
Nd148 5.7
Nd149 1.8h
Nd150 5.6
Pm141 20m
Pm143 ~300d
Pm144 ~300d
Pm145 25y
Pm146 ~2y
Pm147 2.6y
Pm148 42d 53d
Pm149 50h
Pm150 2.7h
Pm151 27h
Sm143 8m
Sm144 3.1
Sm145 1.0y
Sm146 ~5x10⁷y
Sm147 1.3x10¹¹y 15.0
Sm148 11.2
Sm149 13.8
Sm150 7.4
Sm151 80y
Eu144 16m
Eu145 5d
Eu146 38h
Eu147 24d
Eu148 58d
Eu149 120d
Eu150 14h
Eu151 47.8
Eu152 9.3h 13y
Gd148 >35y
Gd149 9d
Gd150 >10⁵y
Gd151 ~150d
Gd152 0.20
Tb149 4.1h
Tb150 19h
Dy≤153 7m
Dy≤153 19m
Dy≤153 2.3h
Tb
Fig. 3.


74
73
72
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70
69
W 183.86
Ta 180.95
Hf 178.50
Lu 174.99
Yb 173.04
Tm 168.94
Er 167.27
Ho 164.94
Dy 162.50
Tb 158.93
Gd 157.25
Eu 151.96
Sm 150.35
Yb165?
Yb166
Yb167
Yb168
Yb169
Yb170
Yb171
Yb172
Yb173
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W179
W180

Fig. 4

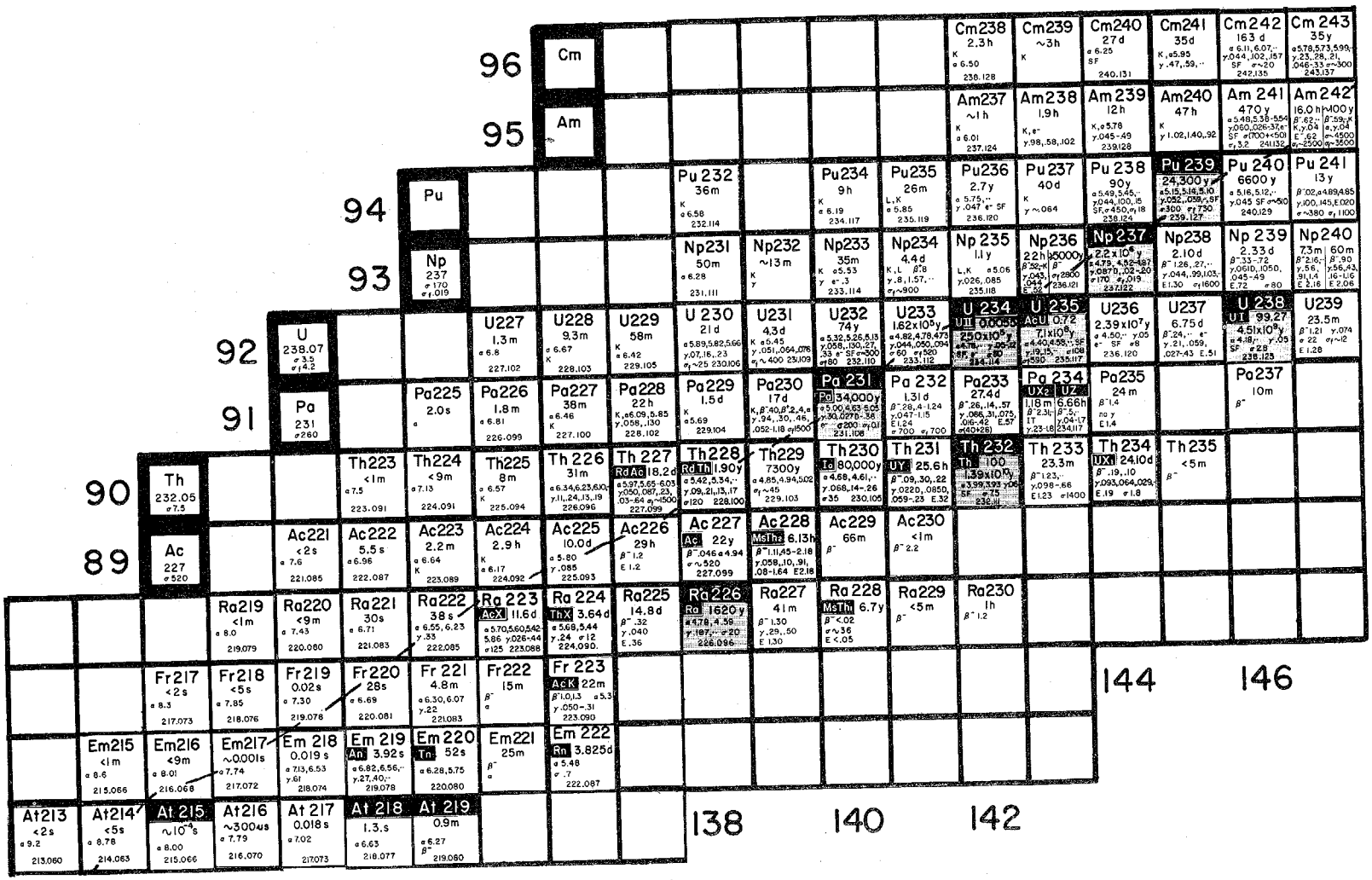


Fig. 5

[Scandium and yttrium are, strictly speaking, not rare earths, but their chemical behavior is very similar to that of the lanthanide group (lanthanum to lutetium) and they will be included in all subsequent discussions of the chemistry of these elements. Actinium is a homologue of lanthanum and is included as representative of the actinide group of elements (actinium to nobelium), which also behave very much like the lanthanides in most chemical operations. Thus, in all discussions of the "rare earths" or "lanthanides" which follow, scandium, yttrium, and the tripositive members of the actinide group are meant to be included.]

The rare-earth elements are quite electropositive and, completely aside from the separation of pure compounds, preparation of the pure metals is not an easy task. Trombe[489] has written an excellent comprehensive review on all aspects of the preparation and properties of the rare-earth metals, while Spedding and Daane[449, 454] and Banks et al.[16] have published fine reviews of the work that has been done in this field at Iowa State College. Although it might have very little application to radiochemical procedures, Huffine and Williams[548] have written an excellent review of the techniques used to refine and purify rare-earth metals, and Morrice and co-workers[549] have described details of the electrolytic reduction of ceric oxide and cerous fluoride to cerium metal in a molten fluoride solvent.

Electrodeposition of metallic rare earths from aqueous media does not usually give satisfactory results because the newly deposited metal reacts with water to give the oxide. Lange, Herrmann, and Strassmann,[256] however, report a procedure for separating Sr^{90}-Y^{90} mixtures by electrolysis in dilute aqueous nitric acid solution. The exact nature of the carrier-free Y^{90} deposit on the cathode was not determined but the Y^{90} yields were good (90-98%) and the separation from Sr^{90} was fair. Sr^{90}-Y^{90} separation factors of approximately 100-200 per deposition were obtained and the authors report that with four deposition cycles the Y^{90} contained on the order of only 1×10^{-5}% Sr^{90} impurity. Hamaguchi, Ikeda, and Kawashima[187] have also described a procedure for the electrolytic separation of Sr^{90}-Y^{90} mixtures.

Techniques have been developed for producing rare-earth metals by electrolysis of fused salts using cathodes of carbon, molybdenum, tungsten, mercury, or, at higher temperatures, molten cadmium or zinc.[489] These procedures are capable of giving good results but the best method currently in use for production of pure metals seems to be that developed by Daane and the Spedding group at Iowa State.[449, 454] This method involves reduction of the anhydrous rare-earth fluorides by metallic calcium in tantalum crucibles under an inert atmosphere. Operating temperatures are kept high enough to melt both the rare-earth metal and the CaF_2 slag so that when the

crucible has cooled the tantalum and slag may be peeled away and the rare-earth metal obtained as a solid ingot.

Metallic scandium, yttrium, and all of the rare earths except samarium, europium, and ytterbium have been prepared by this technique. Promethium and the actinides, of course, are not included since they are not normally available in macroscopic amounts; although Stone[465] has described a method for preparing Ac metal by reducing AcF_3 in vacuo with lithium metal at 1000°C. When attempts were made to reduce the Sm, Eu, and Yb halides with calcium no metal was produced but the divalent salts were found in the slag. These elements behaved the same whether alone or mixed with other rare earths and, indeed, reduction by calcium has been used by the Spedding group to separate Gd-Sm and Lu-Yb mixtures, the Sm and Yb in each case being found in the slag. In the Lu-Yb case, for instance, a sample which contained 30% Yb initially was reduced to lutetium metal containing less than 0.25% ytterbium impurity in one step.[449]

The Iowa State group has succeeded in obtaining pure metallic Sm, Eu, and Yb by a process which involves reduction of the pure oxide by lanthanum metal in a tantalum crucible.[449, 454] Lanthanum is the least volatile of the rare-earth metals and lanthanum oxide has the highest heat of formation of the rare-earth oxides. At the proper temperature, therefore, the reaction

$$La + Sm_2O_3 \rightleftarrows La_2O_3 + Sm$$

can be made to go to completion by distilling off the samarium metal as it is formed. The distilled metal is condensed on a cool part of the tantalum reaction vessel and may often be obtained better than 99.9% pure.

This technique of reducing the rare-earth oxide with lanthanum and distilling off the newly formed metal has also been used by Spedding and Daane[449] on a mixture of rare earths. The vapor pressures of the rare-earth metals are sufficiently different so that by fractional distillation a significant separation of the metals may be obtained. The authors report a possible order of volatility of some of the rare earths as: Eu > Yb > Sm > Lu > Tm > Ho, Dy > Er > Gd. Trombe[488] has also described the distillation separation of a mixture of rare-earth metals, with the order of volatility: Sm > Nd > Pr, Ce > La.

Since the pure rare-earth metals have been available for such a short time, an accurate determination of all of their physical properties has not as yet been completed to everyone's satisfaction. A tabulation by Spedding and Daane,[454] however, is shown in Table I and indicates the surprisingly wide variation of some of the physical properties of this group of very similar elements. A more recent compilation of the physical properties of

Table 1. Properties of rare earth metals (454)

Element	Melting point (°C)	$\Delta H_{melting}$† (kcal/mole)	Boiling point (°C)	$\Delta H_{vaporization}$ (kcal/mole)	Transformation temperatures (°C)	C_p at 0°C (cal/mole deg.)	Structure	Lattice constants (Å)	Density (g/cm³)
La	920 ± 5	2·4	4515	81	260 868	6·65	hcp	$a = 3·770$ $c = 12·159$	6·162
Ce	804 ± 5	2·2	3600	79	(100–200°K) 754	6·89	fcc	$a = 5·1612$	6·768
Pr	935 ± 5	2·4	3450	79	798	6·45	hcp	$a = 3·6725$ $c = 11·8354$	6·769
Nd	1024 ± 5	2·6	3300	69	868	7·20	hcp	$a = 3·6579$ $c = 11·7992$	7·007
Sm	1052 ± 5	2·6	1900*	46*	917	6·49†	Rhombo-hedral	$a = 8·996$ $\alpha = 23°13'$	7·540
Eu	900*	2·3	1700*	40*		6·00†	bcc	$a = 4·606$	5·166
Gd	1350 ± 20*	3·7	3000*	72*		11·20	hcp	$a = 3·6360$ $c = 5·7826$	7·868
Tb	1400–1500*	3·9	2800*	70*		6·54†	hcp	$a = 3·6010$ $c = 5·6936$	8·253
Dy	1475–1500*	4·1	2600	67		6·72	hcp	$a = 3·5903$ $c = 5·6475$	8·565
Ho	1475–1525	4·1	2700*	68*		6·45	hcp	$a = 3·5773$ $c = 5·6158$	8·799
Er	1475–1525*	4·1	2600*	67*		6·65	hcp	$a = 3·5588$ $c = 5·5874$	9·058
Tm	1500–1550*	4·4	2400*	51*		6·45†	hcp	$a = 3·5375$ $c = 5·5546$	9·318
Yb	824 ± 5	2·2	1800†	32*	798	6·00†	fcc	$a = 5·4862$	6·959
Lu	1650–1750*	4·6	3500*	75*		6·45†	hcp	$a = 3·5031$ $c = 5·5509$	9·849
Sc	1550–1600*	3·8	2750*	73*		6·01†	hcp	$a = 3·3090$ $c = 5·2733$	2·995
Y	1475–1525*	4·1	3500*	94*		6·01†	hcp	$a = 3·6474$ $c = 5·7306$	4·472

* Estimates from work in Ames Laboratory.

† Estimates made by D.R. Stull and G.C. Sienke, "The Thermodynamic Properties of the Elements in Their Standard States," The Dow Chemical Company, Midland, Michigan.

rare-earth metals, alloys, and compounds has been completed by Gibson, Miller, Kennedy, and Rengstorff,[172] and Savitskii[409] has also completed a recent review of the properties, application, and production of rare-earth metals.

The rare-earth metals, being quite electropositive, have high heats of oxidation and react readily with most oxidizing agents. Reaction rates, however, may vary considerably amongst the individual rare earths under certain conditions. Spedding and Daane,[449] for instance, state that a bar of lanthanum metal left exposed to moist air will crumble to powder in a few weeks time, but samarium and neodymium will remain bright for months under the same conditions. Trombe[489] reports that europium metal reacts rapidly with water but samarium does not, and cerium and lanthanum react only slowly even in hot water. No specific data are available in the literature but it seems reasonable to assume that in acid solution with "normal" dissolution techniques these differences in reaction rates would be completely negligible.

IV. 1B. AMALGAMS AND VARIOUS OXIDATION STATES

The rare earths exist in aqueous solution, under normal conditions, only as the trivalent ions. Their like charge and similar ionic radius, of course, account for their very similar chemical behavior. Certain of the rare earths, however, can exist in other than the +3 oxidation state, and this fact is often of value in effecting their separation from other members of the group.

Cerium is the only rare earth which has a useful +4 oxidation state. (Pr^{+4} and Tb^{+4} have been prepared as their oxides but there is no evidence to indicate that they are stable in aqueous solution.) The Ce^{+3}-Ce^{+4} couple has a potential of -1.61 volts in acid solution,[257] and cerous cerium is easily oxidized by strong oxidizing agents such as $S_2O_8^{=}$, Co^{+3}, or, in strong acid, BrO_3^{-}. Brezhneva and co-workers[45] used ozone as an oxidant for cerium on nitric acid solution. The oxidation is acid dependent. Their data are presented in Figs. 7 and 8. Ozone is particularly convenient for remote-control operations and for operations in which it is not desired to add nonvolatile matter to the solution. Ce^{+4} behaves very much like Zr^{+4} and Th^{+4} and may, for instance, be separated from all the other rare earths by precipitation as the iodate. Ce^{+4} is not completely stable, however, but oxidizes water very slowly.[238] Duke and Anderegg[108] have shown that the reaction is surface catalyzed and Evans and Uri[129] have shown that it is photosensitive, so reasonable precautions must be taken if Ce^{+4} solutions are to be kept for any length of time.

Europium, ytterbium, and samarium form +2 ions which have proven to be very useful in separating these elements from the rest of the rare-earth group. Europium has the lowest oxidation potential ($Eu^{+2} = Eu^{+3}$, $E° = 0.43$; $Yb^{+2} = Yb^{+3}$, $E° = 0.578$; $Sm^{+2} = Sm^{+3}$, $E° > 0.9$)[257] of these three elements and is the easiest to reduce. Europous europium may be obtained by passing a solution containing Eu^{+3} over zinc in a Jones reductor,[148, 298] by slurrying an Eu^{+3} solution with zinc dust,[233] or by reduction with chromous chloride at low pH's. Eu^{+2} behaves very much like Ba^{+2} (i.e., it precipitates as $EuSO_4$ but the hydroxide does not precipitate in NH_4OH) and may be separated from the rest of the rare-earth group by simple chemical procedures. Eu^{+2} is not very stable towards oxidation, however, and care must be taken to keep its solution free from O_2 and other oxidizing agents.

Yb^{+2} and Sm^{+2} are much less stable than Eu^{+2} in aqueous solution. They evolve hydrogen in water and are oxidized at the slightest provocation so their preparation by simple reduction methods is no easy task. Clifford and Beachell,[81] however, have succeeded in separating samarium from a

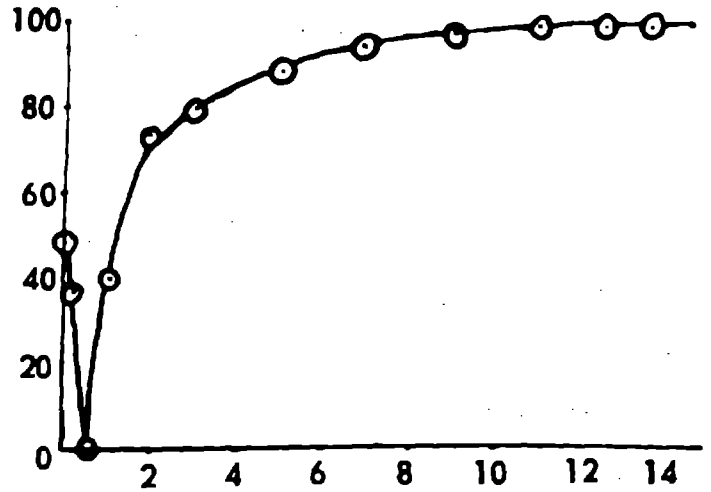


Fig. 7. Percent oxidation of cerium by ozone as a function of nitric acid concentration (one molar per liter) (45)

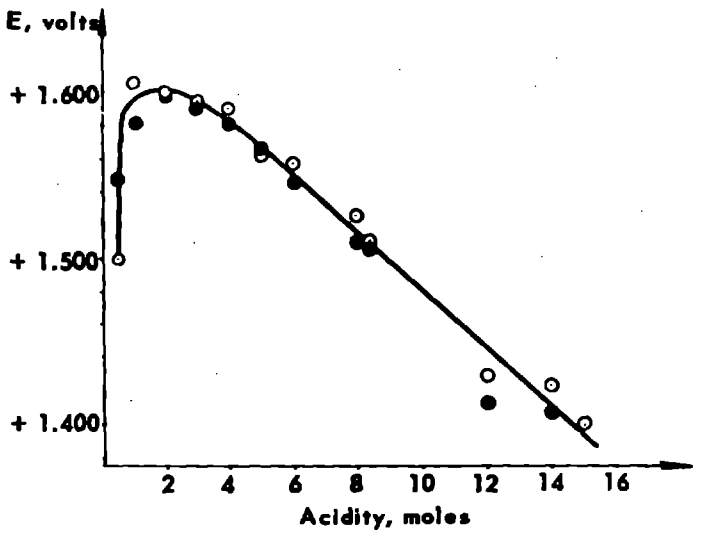


Fig. 8. Oxidation-reduction potential of Ce^{+4}/Ce^{+3} couple as a function of nitric acid concentration (one molar per liter). The sign of the potential is according to the European (Russian) convention (45)

lanthanide mixture by reducing with Mg in solvents of ethanol-HCl or 50-50 dioxane-ethanol saturated with strontium and barium chlorides. Ambrozhii and Luchnikova[8] have also reported reduction of Sm^{+3} by Mg in an ethanol-HCl solvent. The $SmCl_2$ is deposited on the magnesium surfaces and is not very stable, but it persists long enough so that the supernatant solution may be decanted and the magnesium washed, which, after all, is all that is needed to effect a separation from the original rare-earth contaminants.

A more effective method for reducing Eu, Sm, and Yb involves the use of electrolysis in aqueous solution. McCoy,[299, 300] using a basic citrate-acetate solution, a mercury cathode, and a platinum anode, has succeeded in obtaining amalgams of each of these metals. The yield per pass was approximately 90% for Eu, 20% for Yb, and 10% for Sm but by multiple passes essentially all of each of these elements could be recovered from the original solution. Riabtchikov, Skliarenko, and Stroganova,[398] however, have made an excellent systematic study of all the factors affecting ytterbium reduction in the same type of system used by McCoy, and have succeeded in getting Yb yields of approximately 98% per pass.

When the electrolyte contains the proper anion it is possible to obtain the insoluble divalent rare-earth salt directly by electrolysis. Thus Yntema[542] and Ball and Yntema[13] got europous and ytterbous sulfate instead of the amalgam when the electrolyte contained some sulfuric acid, and Chang[72] has precipitated europous oxine-sulfonate by electrolysis of an ammoniacal solution of 8-hydroxyquinoline-5 sulfonic acid.

A variation of the electrolytic reduction method has been published by Onstott,[344, 345, 347] who purified europium, samarium, and the other rare earths by electrolysis with a lithium amalgam cathode. This technique seems to be more efficient than that used by McCoy, and good yields of high-purity Eu and Sm can be obtained without undue effort.

Marsh, in an excellent series of papers,[280-283, 288] has developed procedures for isolating Eu, Sm, and Yb by using sodium amalgam without electrolysis. Reduction is carried out in acetic acid solution and proceeds quite vigorously. Lanthanum and the lighter rare earths are also reduced by sodium amalgam but their yields are low and they do not usually present a problem. Moeller and Kremers[312] have studied the effect of various anions on the reduction of ytterbium by sodium amalgam and conclude that in dilute solution the efficiency of the reduction is inversely proportional to the coordinating tendency of the anion, with perchlorate and chloride giving the best results. In concentrated solutions, however, acetate is to be preferred because of the formation of troublesome sludges with perchlorate or chloride.

Holleck and Noddack[201] have used strontium amalgam to reduce rare earths to the +2 state in sulfate solution. Eu, Yb, and Sm seem to be reduced with the greatest efficiency, although some reduction of Sc, Gd, Ce, Pr, and Nd is reported; but it is not clear that this technique has any advantages over the sodium amalgam reduction method.

A far out procedure for separating divalent species of the rare-earth elements has been published by Achard.[2, 3] The method involves high-temperature vacuum distillation of the Yb^{+2}, Eu^{+2}, and Sm^{+2} oxides from

a mixture of +3 rare earth oxides and carbon. He succeeded in separating all of the Yb as pure YbO from a mixture of Y, Tb, Dy, Ho, Er, and Yb oxides by mixing the oxides with 25% of their weight of carbon and heating for three hours at 1400°C in a vacuum of 10^{-3} mm Hg. In another experiment, complete separation of a binary mixture of Lu and Yb oxides was achieved by three distillations. Sm and Eu are also removed from mixed rare earths by this method and may be separated from each other by accurate control of the temperature.

IV. 2. SOLUBLE SALTS

There is a surfeit of information available in the literature on the solubilities of certain rare-earth salts. For many years fractional crystallization was the best method known for separating these elements and many authors published articles in this field. Fractional crystallization is of no significant value in modern radiochemical techniques, however, so no attempt will be made to review the subject here.

Rare-earth salts are quite soluble in most acids, including hydrochloric, nitric, perchloric, sulfuric, acetic, etc., but accurate values for the solubilities are not readily available. Such values as are available in the "Handbook of Chemistry and Physics,"[199] Lange's "Handbook of Chemistry,"[255] and Seidell's "Solubilities of Inorganic and Metal Organic Compounds"[430] are reproduced in Table 2 and indicate the range of solubilities of several common salts of these elements.

Very little is known about the solubility of simple rare-earth salts in organic solvents. Stewart and Wendlandt,[463] however, have recently published an article on the solubility of lanthanum nitrate-6 hydrate in a large number of organic solvents, which, for lack of better information, may be taken as indicative of the general behavior of all the rare earths.

IV. 3. INSOLUBLE SALTS

IV. 3A. INSOLUBLE SALTS AND GRAVIMETRIC COMPOUNDS

IV. 3A-1. Introduction

There is always a problem, when discussing the soluble, insoluble, and complex salts of the rare-earth elements, in deciding just where to draw the lines of demarcation. "Soluble salts," obviously, will precipitate if the concentrations are high enough; "insoluble salts" are not insoluble in all solutions; and complex salts may dissolve, precipitate, and then dissolve again as the pH is raised. Thus, the lines of demarcation must be chosen rather arbitrarily. In the last section, "soluble salts" were meant to in-

clude those rare-earth compounds which do not precipitate in most radiochemical operations. In this section, those insoluble rare-earth salts which are used as gravimetric compounds or as quantitative precipitants in radiochemical separations procedures will be discussed. And Section IV-4 will cover the large family of rare-earth complex and chelate compounds.

IV.3A-2. Hydroxide

While it is undoubtedly convenient to discuss the chemical behavior of the "rare earths" as a group (including scandium, yttrium, the lanthanides, and the actinides in one great melange), it is often not very realistic. Individual elements of the group will behave differently from all the other members of the group in all chemical reactions. The differences of behavior are usually very small, but they can be quite large, and every chemist working with these elements should develop a fine sense of when these large and small differences can be used to his advantage.

A simple illustration of this point may be served by the rare-earth hydroxides. Precipitation of the rare-earth hydroxides is a standard operation which is used in almost all rare-earth radiochemical separation procedures. The precipitation is quantitative, easy to perform, and all the rare-earth elements behave as a group most of the time. Under certain conditions, however, quite different results may be obtained. Moeller and Kremers,[313] in an excellent review of the basicity of the rare earths, conclude that the order of decreasing basicity is: Ac, La, Ce^{+3}, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu, Sc, Ce^{+4}.

The data of Table 3, taken mostly from the Moeller and Kremers article, substantiate this conclusion and indicate several very interesting features. Lanthanum is the most basic element for which data are presented in Table 3; $La(OH)_3$ has the highest solubility in water, the highest pH of precipitation incidence, and the highest solubility product of any of the rare earths. $Ce(OH)_4$ and $Sc(OH)_3$, on the other hand, are at the opposite extremes in each of these categories. The differences between adjacent elements are not large, but the differences over the entire group are significant. These differences, of course, form the basis for all of the rare-earth fractional precipitation procedures. Separations are certainly not quantitative, but they are large enough to have warranted a considerable amount of work up to the time when more efficient techniques were developed.

Thus, the behavior of the rare-earth hydroxides may be considered as typical of the insoluble rare-earth salts; they are all quite insoluble and they can all be precipitated together if that is desired, or, by varying the conditions of precipitation, significant separations within the group may be carried out.

Table 2. Solubility of rare-earth salts

	Solubility (g/100 ml H_2O, at °C temp shown in superscript)			
	Chloride	Nitrate	Sulfate	Acetate
Scandium	vs	s	$39.9^{25°}$	
Yttrium	$217^{20°}$, $233^{50°}$	$134^{22°}$, $211^{66°}$	$9.76^{20°}$, $4.6^{100°}$	$9.03^{25°}$
Lanthanum	vs	$151^{25°}$	$3.9^{0°}$, $0.9^{100°}$	$20.4^{18°}$, $16.9^{25°}$
Cerium +3	100	$63.7^{25°}$, $73.9^{50°}$	$25^{0°}$, $7.6^{40°}$	$26.5^{15°}$, $16.2^{76°}$
+4				
Praseodymium	$334^{14°}$, $\infty^{100°}$	$60^{22°}$, $75^{56°}$	$20^{0°}$, $3.5^{80°}$	$27.4^{25°}$
Neodymium	$246^{13°}$, $512^{100°}$	$153^{25°}$	$8^{20°}$, $1.5^{100°}$	26.2
Samarium	s		$2.7^{20°}$, $2.0^{40°}$	$15^{25°}$
Europium			$2.6^{20°}$, $2.2^{40°}$	
Gadolinium	s	vs	$3.3^{20°}$, $2.5^{40°}$	$11.6^{25°}$
Terbium	s	s	$3.56^{20°}$, $2.51^{40°}$	
Dysprosium	s	s	$5.1^{20°}$, $3.3^{40°}$	s
Holmium			$8.18^{20°}$, $4.54^{40°}$	
Erbium	s	s	$16^{20°}$, $6.53^{40°}$	
Thulium	vs			
Ytterbium	vs		$34.8^{20°}$, $22.9^{40°}$	vs
Lutetium			$66^{20°}$, $22^{40°}$	

Table 3. The rare-earth hydroxides

Element	Hydroxide solubility product (at 25°C)	Water solubility (gram molecules per 10^6 liters)	pH at precipitation incidence				Reference
			NO_3^-	Cl^-	Acetate$^-$	SO_4^-	
Sc	1×10^{-28}				6.1		313
Y	5.2×10^{-22}	1.2-1.9	7.39	6.78	6.83	6.83	313
La	1×10^{-19}	7.8-9.2	8.35	8.03	7.93	7.61	313
Ce^{+3}	$0.8\text{-}1.5 \times 10^{-20}$	4.1-4.8	8.1	7.41	7.77	7.07	313
Ce^{+4}	2×10^{-48}		(2.65)				241, 495
Pr	2.7×10^{-20}	5.4	7.35	7.05	7.66	6.98	313
Nd	1.9×10^{-21}	2.7	7.00	7.02	7.59	6.73	313
Sm	6.8×10^{-22}	2.0	6.92	6.83	7.40	6.70	313
Eu	3.4×10^{-22}	1.4	6.82		7.18	6.68	313
Gd	2.1×10^{-22}	1.4	6.83		7.10	6.75	313
Tb							
Dy				(4.91)			495
Ho							
Er	1.3×10^{-23}	0.8	6.76		6.59	6.50	313
Tm	3.3×10^{-24}	0.6	6.40		6.53	6.21	313
Yb	2.9×10^{-24}	0.5	6.30		6.50	6.16	313
Lu	2.5×10^{-24}	0.5	6.30		6.46	6.18	313
Ac							

The most frequent use of the rare-earth hydroxides in radiochemical procedures involves the separation of the rare earths as a group from contaminating elements; but the hydroxide may be used also as the final precipitate and ignited to the oxide for gravimetric determinations. The data of Table 1 indicate that it should be possible to separate Ce^{+4} or Sc^{+3} from other members of the rare-earth group by precipitation as the hydroxide, but this method has not been reported in any radiochemical separation procedures. Scandium hydroxide is likely to present difficulties, since Vickery[506] has shown quite conclusively that scandium is somewhat amphoteric, forming a scandate ion in strong alkali, and also that scandium is capable of forming a soluble hexammino scandium cation in excess ammonia.

An interesting radiochemical separation involving rare-earth hydroxides has been reported by Duval and Kurbatov[113] who recovered carrier-free scandium activity from a calcium target by adsorbing the scandium hydroxide on filter paper at a pH of approximately 8.5. Schweitzer and Jackson,[426] and Schweitzer, Stein, and Jackson[427] used essentially the same technique to separate Ba^{140}-La^{140} and Sr^{90}-Y^{90} mixtures by adsorption of the basic radiocolloids on glass frit filters. The authors report that the method is fairly rapid, that the separation is good, and that the yields can be made to approach 100% by proper control of the experimental conditions.

Meloche and Vratney[308] have recently published a study of the solubility products of several rare-earth hydroxides as a function of temperature in the 10°-40°C temperature range.

IV. 3A-3. Fluoride

The rare-earth fluorides are also used extensively for group separations of the rare earths from other elements in radiochemical purification procedures. They are quite insoluble and precipitate easily even in strong acid solution. It is unfortunate that so very little quantitative data are available on the solubility of these salts. Kury[250] has studied the reaction

$$RE\,F_3 \rightleftarrows RE^{+3} + 3F^-$$

and reports the solubility product values:

	K_s
La^{+3}	1.4×10^{-18}
Ce^{+3}	1.4×10^{-18}
Gd^{+3}	6.7×10^{-17}

Weaver and Purdy[512] have also studied the cerous fluoride system and obtained a K_s value of $(8.1 \pm 1.1) \times 10^{-16}$ radiometrically and $(1.1 \pm 0.5) \times$

10^{-15} by conductometric methods. The Weaver and Purdy curve for CeF_3 solubility as a function of pH is reproduced in Fig. 9 and may be indicative of the behavior of the other rare earths.

The behavior of scandium differs very considerably from that of the other rare earths in fluoride solution. In 1M acid solution, ScF_3 may be precipitated essentially quantitatively. At lower acid concentrations, with ammonium ion present, the ScF_6^{-3} complex forms,[140] and in a buffered NH_4^+ solution at pH5 the rare-earth fluorides may be precipitated quantitatively while essentially all of the scandium remains in solution.[41]

Some evidence exists to indicate that the actinide fluorides are somewhat more soluble than the rare-earth fluorides. Pressly[353, 379] has developed a procedure for separating Am-Pm mixtures by precipitating PmF_3 in solutions of fluosilicic acid. Am remains in solution. The separation is not clean-cut, however, and multiple precipitations are required to get large separation factors.

Perros and Naeser[363] have reported the existence of a soluble K-Pr-F salt, produced when PrF_3 or Pr_6O_{11} is added to a melt of potassium hydrogen fluoride, but no information is available on the stability of this praseodymium fluoride complex in aqueous solution.

IV. 3A-4. Oxalate

The oxalate anion is probably used more than any other for precipitation of the rare-earth elements. In dilute acid solution it is reasonably specific for this group of elements; the precipitate settles rapidly, has a granular crystalline structure that permits thorough washing, and the oxalate may easily be ignited to the oxide for accurate gravimetric determinations.

A considerable amount of information has appeared in the literature about the behavior of the rare-earth elements in various aqueous oxalate media. It is not practical to give all the data here, but an attempt will be made to cover the more significant details. The solubility of all of the rare-earth oxalates in water is quite low. As can be seen from the curve of Fig. 10, which has been reproduced from Vickery's book on the lanthanons,[495] the hydrated oxalate solubilities range from about 0.4 mg/liter for Ce^{+3} to about 4 mg/liter for Lu. In these same units, data of Feibush, Rowley, and Gordon[131] indicate that the solubility of yttrium oxalate is approximately 0.9 mg/liter, while Fischer and Bock[140] state that the solubility of scandium oxalate is about 156 mg/liter at 25°C. No specific data are available on the solubility of actinium oxalate in water, but Salutsky and Kirby[404] report that in 0.1N HNO_3-0.5N oxalic acid the actinium oxalate solubility is 24 mg/liter. Fried, Hagemann, and Zachariasen[154] have also prepared actinium oxalate by precipitation from dilute acid solution but give no precise solubility data.

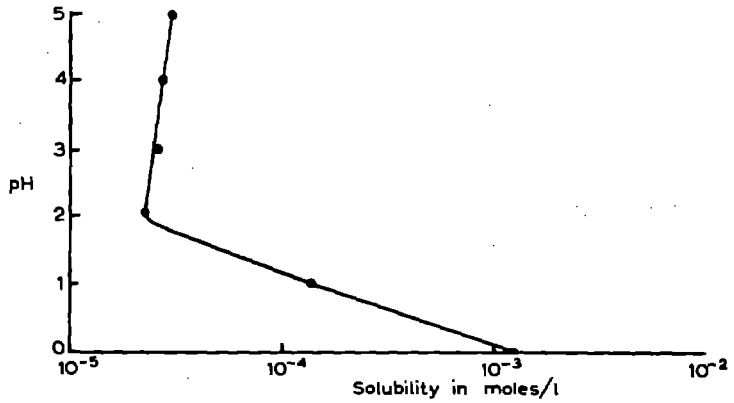


Fig. 9. pH—solubility relationship for cerous fluoride (512)

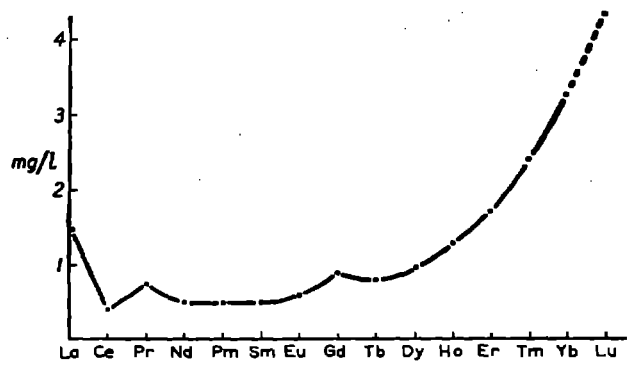


Fig. 10. Solubilities of the hydrated oxalates in water at 25°C (495)

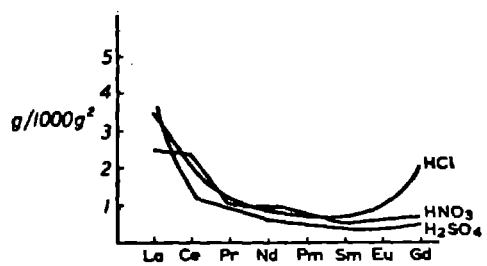


Fig. 11. Solubilities of rare-earth oxalates in 1N acid at 25°C (495)

The rare-earth oxalates are usually precipitated in dilute oxalate solution at a pH of 2 to 3. In more acid solutions (Fig. 11) the solubilities increase considerably and the very finely divided precipitates are slow to form.

In Fig. 10, it is evident that oxalates of the heavy rare earths are more soluble in water than are those of the light rare earths. In alkali oxalate solutions this difference in solubility is increased, with the lighter earths being practically insoluble and the heavy earths somewhat soluble. Vickery,[495] for example, states that the relative solubilities of the oxalates in ammonium oxalate are: Th 2663, Yb 104, Y 10.99, Ce 1.8, Nd 1.44, Pr 1.13, and La 1.0. Scandium is a special case – Vickery[507] presents very convincing evidence that scandium forms not only an anionic oxalate complex in excess oxalate, but also a cationic hexammino scandium ion in the presence of excess ammonium ion, which seriously increases the solubility of the compound. Although these relatively high solubilities have been utilized for the fractional precipitation separation of the heavy rare earths, their main interest for radiochemists lies in the losses and low yields that might occur if the chemist does not realize that they exist. The rare earths are often separated from one another on ion-exchange resin columns and recovered by precipitation of the oxalate from fairly strong (up to 1M) ammonium citrate or ammonium lactate solution. For the lighter rare earths, this presents no difficulty, but for the Ho-Lu group the rare-earth oxalate's solubility may easily lead to undesirable losses. Under these conditions, the authors have found that the heavy rare earths may be recovered more efficiently by precipitation as the 8-hydroxyquinolates.

Crouthamel and Martin have studied the solubility of ytterbium oxalate and complex ion formation in oxalate solutions[96] and found that their results could be explained by the existence of $Yb(C_2O_4)^+$ and $Yb(C_2O_4)_2^-$ complex ions. Experiments[97] with Nd disclosed the existence of similar complexes although the total neodymium concentration in solution was approximately fifty times less than the Yb. With Ce^{+3},[97] however, it was necessary to postulate the existence of a $Ce(C_2O_4)_3^{-3}$ complex in addition to the $Ce(C_2O_4)^+$ and $Ce(C_2O_4)^-$ complexes in order to explain the data. Feibush, Rowley, and Gordon[131] have used the same techniques to study the yttrium oxalate system and they, too, require that the $Y(C_2O_4)_3^{-3}$ complex be formed in order to explain their results. No explanation is given for this difference in behavior between Yb-Nd and Y-Ce^{+3}, but there seems no question that the complexes exist. An interesting consequence of these experiments is that they show that the total concentration in solution of those rare earths which form the trioxalate complex is increasing with the 3/2 power of the oxalate concentration while those which form only the dioxalate increase with the 1/2 power (Figs. 12, 13). If this behavior extends into more concentrated

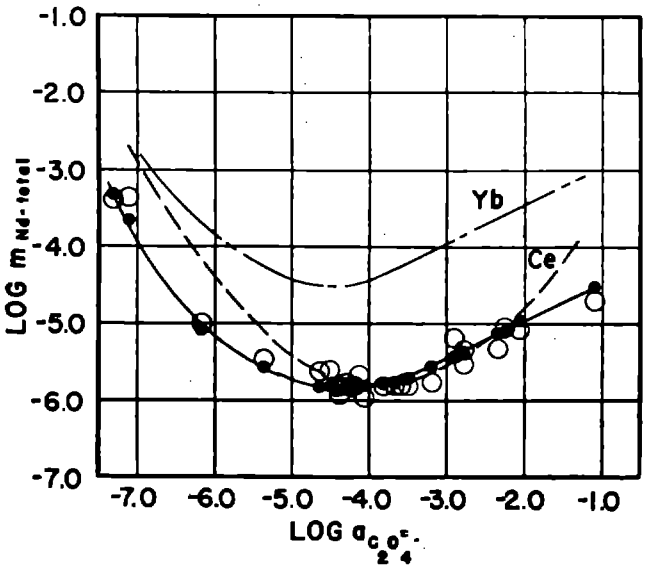


Fig. 12. Total Yb, Ce^{+3}, and Nd concentrations in buffered oxalate solutions. Yb and Ce curves are labeled, solid curve and experimental points are for Nd (96)

oxalate solutions some very interesting reversals of the order of solubility may be expected among the rare-earth group of elements.

Ce^{+4} oxalate is considerably more soluble than the trivalent rare-earth oxalates. Ryabchikov and Vagina[399] report that the bright orange ceric oxalate complex is reasonably stable in aqueous solution at room temperature but decomposes on heating, with the formation of a cerous oxalate precipitate. In addition, they have used the high ceric oxalate solubility to separate cerium from a mixture of rare earths with 97-98% yields of 99.9% pure CeO_2.

IV. 3A-5. 8-Hydroxyquinolate

In ammoniacal solution, 8-hydroxyquinoline may be used as a quantitative precipitant for the rare-earth elements. Very little quantitative solubility data are available but Eswaranarayana and Raghava Rao[128] have used the reagent for the determination of Ce^{+3} and La^{+3}, and Pokras and Bernays[367, 368] have used it for Sc^{+3}.

The precipitation is fairly sharply dependent on pH, as shown by the Eswaranayana and Raghava Rao data in Fig. 14, and most precipitations are carried out in slightly ammoniacal solution. Pokras and Bernays indicate that there is no precipitation of scandium at pH 3.90 and essentially complete precipitation at pH 5.72, but they give no data for intermediate pH's.

8-hydroxyquinoline is certainly not a selective precipitant for the rare-earth elements.[274] The precipitate is flocculent and often hard to wash, and

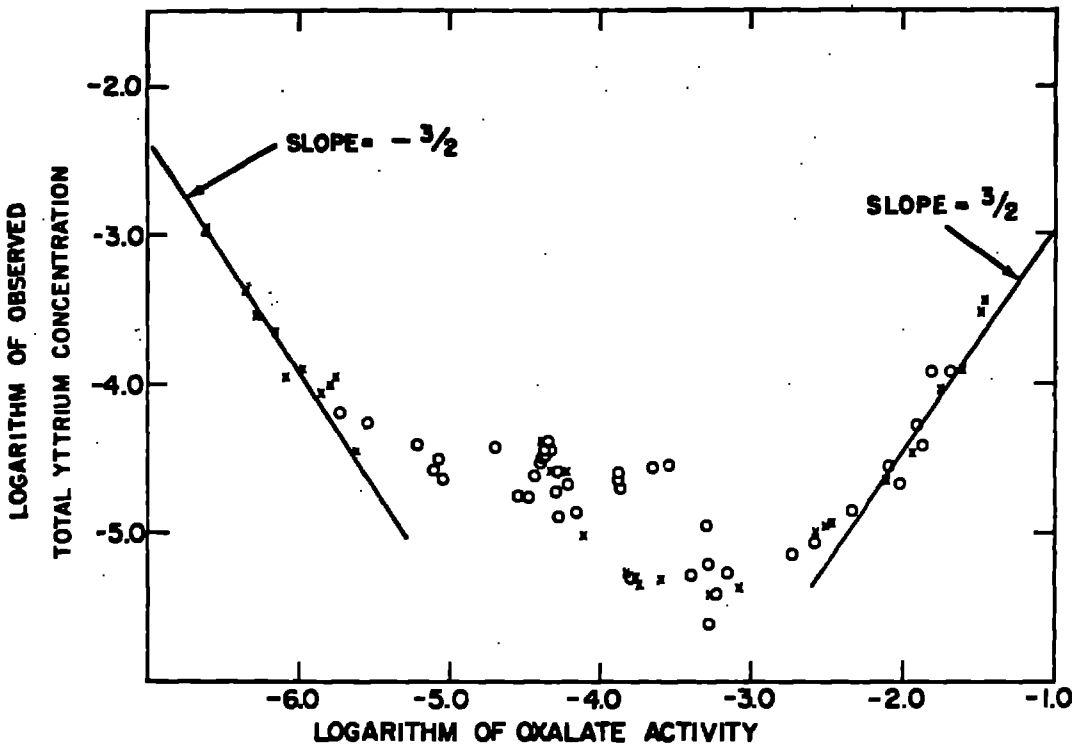


Fig. 13. Plot of logarithm of observed yttrium concentration vs logarithm of oxalate ion activity (131)

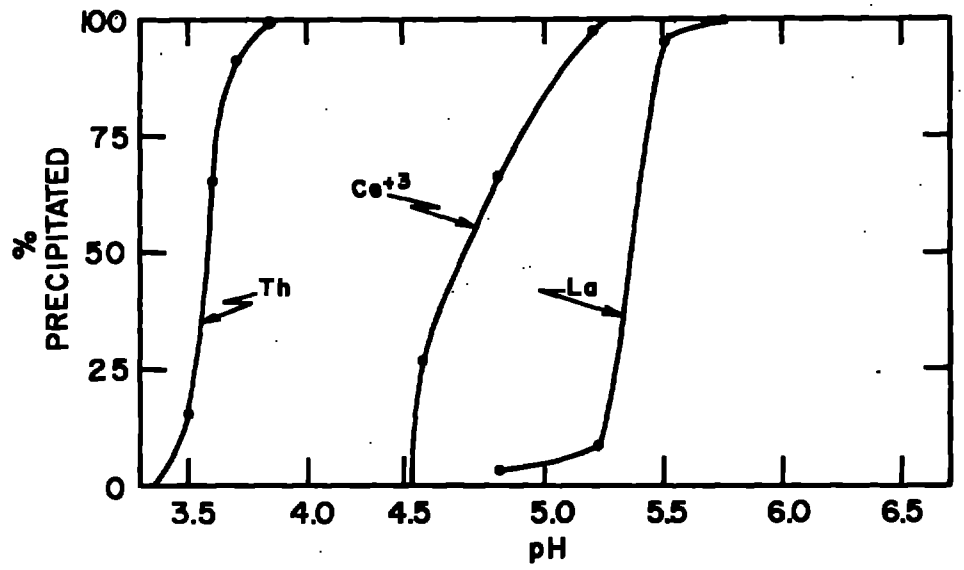


Fig. 14. Precipitation of thorium and rare earth - 8-hydroxyquinolates vs pH (128)

therefore its use as a gravimetric compound is open to some question. It is of value in spite of these drawbacks, since it is a more sensitive reagent for the rare earths than other precipitants (see Section IV. 3A-13) and may be used to recover very small amounts of material from solution. The authors, for example, have used 8-hydroxyquinoline to precipitate $\ll 0.1$ mg/ml of Lu and Yb from 1M ammonium lactate solutions with essentially complete recovery of the rare earths. Under the same conditions, oxalate and hydroxide gave no precipitate whatever.

IV. 3A-6. Ammonium Tartrate

Ammonium tartrate is often used as a precipitant to separate scandium from a large number of other elements. Fischer and Bock[140] state that in an ammoniacal solution containing an excess of ammonium tartrate the solubility of scandium ammonium tartrate is approximately 3 to 4 mg Sc_2O_3/liter soln. Fischer, Steinhauser and Hohmann[139] have extended the Fischer and Bock study and show that tartrate may be used to separate scandium from very large excesses of Y, Fe, Mn, Ti, Mg, Ca, Al, Cu, Cd, Zn, Pb, Ga, Ge, Sn, Nb, Cr, V, Mo, and Ni. They used solutions which were either 10% or 20% in ammonium tartrate and 0.2N to 1.5N in NH_4OH. No specific solubility data are available on the ammonium tartrates of other rare earths, but according to Meyer[310] the ceric earths are quite soluble and the yttrium earths difficulty soluble. The data of reference 139 indicate that yttrium ammonium tartrate is at least as soluble as 0.5 mg Y_2O_3/ml 10 to 20% ammonium tartrate soln. It is reasonable to expect the heaviest rare-earth tartrates to be less soluble than yttrium, so that they might well coprecipitate with scandium if they are present in any significant amount.

IV. 3A-7. Complex Cyanides

The rare earths are reported to form quite insoluble complex cyanides.[495] Most of the work has been carried out with the ferrocyanide, ferricyanide, and cobalticyanide salts.[495, 547] The insoluble rare-earth salts are quite complex in that their compositions and solubilities are functions of the cation as well as the anion of the precipitant. Thus Tananaev and Seifer[474] report that in the $Ce(NO_3)_3$-$Na_4(Fe(CN)_6)$ system, $Ce(Fe(CN)_6)_3$ precipitates initially; but with an excess of reagent $Na_4Ce_8(Fe(CN)_6)_7$ precipitates (solubility 2.1×10^{-4} mole/liter). In the $Y(NO_3)_3$-$K_4(Fe(CN)_6)$ system, $K_4Y_8(Fe(CN)_6)$-$3OH_2O$ precipitates (solubility 6.2×10^{-6} mole/liter); but in the $Y(NO_3)_3$-$Rb_4(Fe(CN)_6)$ system, $RbY(Fe(CN)_6)$-$2H_2O$ is the precipitate (solubility 1.8×10^{-4} mole/liter); and in the $Y(NO_3)_3$-$Li_4(Fe(CN)_6)$ and $Y(NO_3)_3$-$Na_4(Fe(CN)_6)$ systems the authors report that there is no ferrocyanide precipitate at all.

While the complex rare-earth cyanides appear to be quite insoluble, their use has been restricted mainly to fractional precipitation separations, especially of the yttrium earths,[495] and the authors know of no cases where they have been used in radiochemical separations of any kind.

IV. 3A-8. Phosphate and Related Anions

The rare-earth phosphates are quite soluble in acid solution. As the pH is increased, however, solubility decreases, and in solutions above pH 4 to 5 precipitation is essentially complete. A fairly large number of elements also precipitate under these conditions[274] and there are indications of fairly large differences of solubility of individual members of the rare-earth group.[279] No precise data are available on the rare-earth phosphate solubility vs solution pH, and the use of phosphate either as a quantitative gravimetric precipitant or as a desirable precipitant to separate the rare earths from other elements is open to some question.

Scandium forms useful insoluble salts with several phosphate relatives. Beck[22] has reported that scandium pyrophosphate is very sparingly soluble, even in mineral acids. In mineral acids, too, the scandium salts of aneurin pyrophosphate (cocarboxylase) and phytic acid ($C_6H_6(OPO(OH)_2)_6$) are quite insoluble, and the scandium salt of adenosin triphosphate is insoluble in 30% acetic acid. Zr also precipitates under each of these conditions, but Mg, Ca, Ba, Al, Y, Th, Cu, Hg, Tl, Cr, Mn, and Fe do not.

Vickery[508] has published an excellent review of the precipitation and extraction reactions of scandium which gives more precise data than are available anywhere else in the literature. Table 4 is reproduced from his article and indicates the fraction of scandium that may be precipitated under optimum conditions with a large number of reagents. For specific data as to the optimum conditions in each case, the original article should be consulted.

Bomberger[40] has reported that hypophosphorous acid may be used as a gravimetric reagent for scandium. The precipitation is essentially quantitative (~99.9%) when the initial precipitate is digested over steam for one hour. Optimum conditions are in the area of 1N HCl-0.5N H_3PO_2, but considerable latitude is possible with small loss in efficiency. Any substance that oxidizes hypophosphorous acid under hot, acid conditions, or any one of a fairly long list of elements (Zr, Hf, Th, Ta, Ca, Ag, Au, Hg, Bi, Sb, As, Sn, Se, Te, Pd, Al, Ga, In, Y, V, Cr, Mo, U, F, Fe, Co, and Pt), interferes with the scandium hypophosphite precipitation, so the reagent is best used as a final precipitant in a solution which contains only scandium.

IV. 3A-9. Iodate

Ce^{+4} forms an insoluble ceric iodate[48] which permits easy and rapid

Table 4. Precipitation of scandium by various precipitants. Tabulated data are % Sc precipitated under optimum conditions (508)

Precipitant	Mg. of Sc_2O_3 per ml.					
	1	5	10	50	75	100
NaOH	80	90	—	98	98	—
KOH	80	—	100	—	—	—
NH_4OH	60	69	—	82	—	85
Na_2CO_3	Nil	Nil	10	—	—	16
K_2CO_3	50	—	72	—	85	—
$(NH_4)_2CO_3$	Nil	Nil	Nil	10	—	12
$H_2C_2O_4$	Nil	12·5	27	—	37	52
$Na_2C_2O_4$	Nil	—	—	25	—	61
$K_2C_2O_4$	Nil	—	20	—	—	43
$(NH_4)_2C_2O_4$	Nil	Nil	Nil	—	16	—
HF	90·5	—	95	94	—	96
NaF	35	42	—	55	—	72
KF	86	—	—	90	92	92
NH_4F	Nil	Nil	Nil	—	—	—
H_3PO_4	Nil	—	—	—	—	Nil
NaH_2PO_4	90	90	—	95	—	97
Na_2HPO_4	99	—	100	100	—	100
Na_3PO_4	53	—	76	—	82	84
$K_2H_2P_2O_7$	95	—	97	—	99	—
$Na_2H_2P_2O_7$	96	—	—	98	—	99
Cocarboxylase	93	93	—	98	—	99
Phytin	99	100	—	100	—	100
Na_2SO_4	Nil	—	—	—	Nil	— *
K_2SO_4	66	—	73	—	81	— *
$(NH_4)_2SO_4$	Nil	Nil	—	Nil	—	Nil *
AcOH	Nil	Nil	32	—	—	63
NaOAc	66	70	—	74	—	72
NH_4OAc	Nil	—	Nil	—	Nil	—
Tartaric acid	Nil	—	50	—	63	—
Na K tartrate	Nil	—	—	Nil	—	—
$(NH_4)_2$ tartrate	81	92	—	96	99	—
Citric acid	—	30	—	39	—	42
KIO_3	Nil	Nil	—	—	—	Nil
$Na_2B_4O_7$	93·5	—	—	99	—	99
Tannin	85	—	86	—	90	—
Oxine	85	93	—	99·3	—	—
Alizarin	89	91	99	—	—	100

* In the presence of mixed lanthanons.

Precipitation of $Sc(OH)_3$ *in presence of* NH_4Cl (*concn., 50 mg. of* Sc_2O_3 *per ml.*).

NH_4Cl concn. (mg./ml.)	5	15	25	50
Pptn. (%) by NaOH	96	85	79	63
,, KOH	95	87	75	60
,, aq. NH_3	89	75	62	45

Inhibition of $Sc(OH)_3$ *precipitation* (50 *mg. of* Sc_2O_3 *per ml.*).

Hydroxy-acid concn. (%)	1	5	15	30
Pptn. (%) by NaOH (citrate)	80	52	27	15
,, ,, (tartrate)	86	49	22	19

separation of cerium from the other rare earths. The precipitation is usually carried out in approximately 4M HNO_3 solutions. Zr^{+4} and Th^{+4} iodates precipitate under the same conditions and a most effective radiochemical separation is obtained by reducing cerium with H_2O_2, scavenging the solution with zirconium iodate, oxidizing Ce^{+3} with bromate, and precipitating ceric iodate.

Venkataramaniah and Raghavarao[494] have reported an interesting procedure for separating Ce^{+4} from the other rare earths and thorium by precipitating ceric periodate. The precipitation is carried out by adding a 1:5 HNO_3 solution saturated with potassium periodate to a 1:5 HNO_3 solution containing Ce^{+4} and digesting in a boiling water bath for 10 to 15 min. Precipitation is quantitative and the salt may be dried at 100-110°C and weighed as $CeHIO_6 \cdot H_2O$. Neither Th^{+4} nor the other rare earths precipitate under these conditions.

IV. 3A-10. Cupferron

Cupferron and neocupferron form insoluble salts with the rare-earth elements which may be of value in quantitative determination of these elements.[372] The precipitates are somewhat soluble below pH 2 and the optimum pH for precipitation seems to be about 3.5. Significant amounts of the precipitant are occluded in the rare-earth salts so it is necessary to ignite the cupferrate to the oxide to get the best results; but ignition proceeds smoothly, and final results are comparable in accuracy to those obtained by the oxalate method. The reagents are far from selective for the rare earths,[274] however, and care must be taken that there are no interfering cations present when the rare earths are precipitated.

Sinha and Shome[441] report that Th^{+4} and Ce^{+3} may be precipitated quantitatively by n-benzoylphenylhydroxylamine and determined by ignition to the oxide. The authors do not mention the other rare earths but presumably they behave very much like Ce^{+3}.

IV. 3A-11. Chloride

Fischer, Wernet, and Zumbusch-Pfisterer[138] have reported that the rare earths are relatively insoluble in saturated HCl solution (24 mg Y_2O_3/100 ml at 0°C) and much less soluble in saturated HCl – diethyl ether (1.5 mg Y_2O_3/100 ml 1:1 soln. at 0°C). Scandium is considerably more soluble in each of these cases (> 1.5 g Sc_2O_3/100 ml HCl at 0°C; > 4 g Sc_2O_3/100 ml HCl – ether at 0°C) and the authors suggest that this might be a useful means of separating Sc – rare-earth mixtures under some circumstances.

IV. 3A-12. Miscellaneous Precipitants

Takashima[473] reports that scandium may be determined gravimetrically

as the hexamminecobalt fluoscandate $[Co(NH_3)_6][ScF_6]$. Precipitation is carried out in a pH 3 to 4 solution and the precipitate is dried at 110°C. The author reports that 0.5 to 5 mg of scandium can be determined with an error of less than 3%.

Reddy, Sarma, and Raghava Rao[385] report that La may be separated from the rare earths excluding cerium by controlled precipitation of lanthanum chromate.

IV. 3A-13. Sensitivity of Various Precipitants

In radiochemical investigations it is often desirable to know the smallest amounts of rare-earth carrier that may be precipitated in a given set of conditions. Relatively few articles are available which make a direct comparison of the sensitivity of various precipitants to the rare-earth elements. Wendlandt and Hayes[521] have compared the oxalate and cupferrate sensitivity of the light rare earths and Wendlandt and Sewell[552] have extended the study to several salts of the heavy rare earths. Their data are combined in Table 5 and serve to indicate the limits of precipitation for each of these reagents under optimum conditions. Only four reagents have been compared in Table 5; of these, 8-hydroxyquinoline is the most sensitive and oxalic acid the least sensitive precipitant for the rare earths.

Table 5. Sensitivity of the rare earths to various precipitants (521, 552)

	$\mu g\ M^{+3}$ per ml			
Metal Ion	Oxalic Acid	Cupferron	8-Hydroxyquinoline	2-Methyl 8-Hydroxyquinoline
La	6.3	2.4		
Ce^{+3}	6.4	1.6		
Pr	6.4	1.6		
Nd	6.6	2.5		
Sm	6.9	5.1		
Eu	35	5.2	1.7	17
Gd	17.8	17.8		
Tb	36	7.1	1.4	7.1
Dy	19	7.4	1.1	7.4
Y	10.2	10.2		
Ho	38	13	3.8	13
Er	57	17	3.8	9.5
Yb	40	30	4.0	20

IV. 3B. COPRECIPITATION

Coprecipitation is a difficult subject to discuss coherently under the best of circumstances. Discussion of the rare earths is doubly difficult, of course, since they will "coprecipitate" one with another in almost all their precipitation reactions. One may always use one rare earth as a carrier to coprecipitate another, and the variation in chemical behavior within the rare-earth group permits some selectivity as to the carrier efficiency (e.g., one would expect Yb to be a better carrier for Lu than La). But too close a similarity in chemical behavior may sometimes introduce as many difficulties as it solves (e.g., the Lu-Yb separation is not an easy one).

For the purposes of this section, however, let us assume that the rare earths behave as a single element and divide the subject into two parts: co-precipitation of the rare earths with other precipitates, and coprecipitation of other elements with rare-earth precipitates.

In general, it is reasonable to expect that the rare earths will coprecipitate with the insoluble salt of any anion with which they are normally insoluble. Thus, ferric hydroxide will coprecipitate carrier-free rare earths without difficulty, or the rare earths may be carried on calcium oxalate precipitates.[380, 381] Brezhneva et al.[45] studied the carrying of cerium and of yttrium on calcium oxalate at pH 4 to 5 as a function of oxalate concentration. They found that 0.075 molar/liter of calcium was necessary for optimum carrying. Both lanthanides show a maximum in the amount carried down at a particular optimal oxalate concentration (see Fig. 15), the decrease with increasing oxalate at high oxalate concentration being attributed to the formation of oxalate complexes as proposed by Crouthamel and Martin.[96, 97]

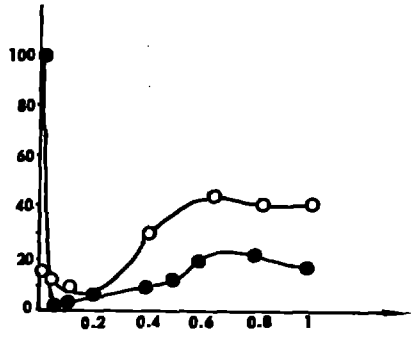


Fig. 15. Coprecipitation of cerium and yttrium with calcium oxalate at various total concentrations of oxalate. The equilibrium concentration of cerium and yttrium is shown as a percentage along the ordinate axis, and the excess concentration of oxalate in g eq/l along the abscissa axis (45)
(● = Cerium, O = Yttrium, pH of solution: 4-5)

In 4M HNO_3, less than 1% of rare-earth activities carry on thorium iodate precipitates,[434] but McLane and Peterson[303] have shown that in solutions of low ionic strength Ac may be carried completely by zirconium iodate. Presumably the carrying efficiency for the entire rare-earth group would be quite high under the same conditions. In the same paper McLane and Peterson indicate that Ac may be carried on either bismuth phosphate or barium sulphate, and Rogers and Watrous[390] report that Ac may be carried quite efficiently on lead sulfate, but few data are available on the behavior of the rest of the rare-earth group in these systems.

Conversely, when the rare earths are precipitated it is reasonable to expect that cations which form insoluble or moderately soluble salts with the precipitating anion will be coprecipitated. Thus, the rare-earth hydroxides will carry a whole host of elements which are insoluble in basic solution, or the rare-earth oxalate will coprecipitate calcium. These are rather obvious events, of course, and the sort of thing that radiochemists accept as routine. Perhaps that is why no articles on this specific aspect of rare-earth radiochemistry have appeared in the literature. It may be useful, however, to point out that not all of the coprecipitation reactions are self-evident. The authors have found, for instance, that Ba and Zr have some tendency to coprecipitate with the rare-earth fluorides. Gest, Burgus, and Davies[171] have shown that the Zr coprecipitation is very sharply dependent on the Zr concentration, and Gest, Ballou, Abraham, and Coryell[170] have shown a somewhat lesser concentration dependence for Ba. Radiochemists, therefore, should not be too surprised when unexpected elements sometimes tag along in their rare-earth chemistry.

IV. 3C. PYROLYSIS

IV. 3C-1. Oxalate

For any gravimetric determination of the rare earths, precipitates must be dried, and the obvious figure of merit for this operation is the temperature range over which a salt of known composition is stable. Since the oxalates are probably used more often than any other salt in the gravimetric determination of the rare earths, it is perhaps appropriate that their pyrolitic behavior has been investigated more thoroughly than other rare-earth salts. The curve for the thermal decomposition of $Nd_2(C_2O_4)_3 \cdot 10H_2O$, which has been reproduced from an article by Caro and Loriers,[70] is shown in Fig. 16 and may be considered as fairly typical of all the rare-earth oxalates. The decahydrate begins losing water steadily at about 50°C and the sample decomposes continuously until Nd_2O_3 is formed at about 700°C. There are no level portions of the curve which denote a stable, weighable intermediate compound, and the usual practice is to decompose the oxalate completely and weigh as the

oxide. Wendlandt[525, 526] has also studied the pyrolysis of the rare-earth oxalates and, since his curves are in a concise form, his data are reproduced in Figs. 17-20 and Table 6. The most obvious feature of the curves is that there are so few weighable intermediate rare-earth oxalate compounds. Where these exist at all, the temperature range for stability is fairly small, so some care must obviously be taken if these intermediate salts are to be weighed accurately. Above 800°C, however, all of the oxalates are completely decomposed to oxides and may be weighed accurately. It should perhaps be noted that CeO_2 is formed at 360°C, much lower than the other rare-earth oxides.

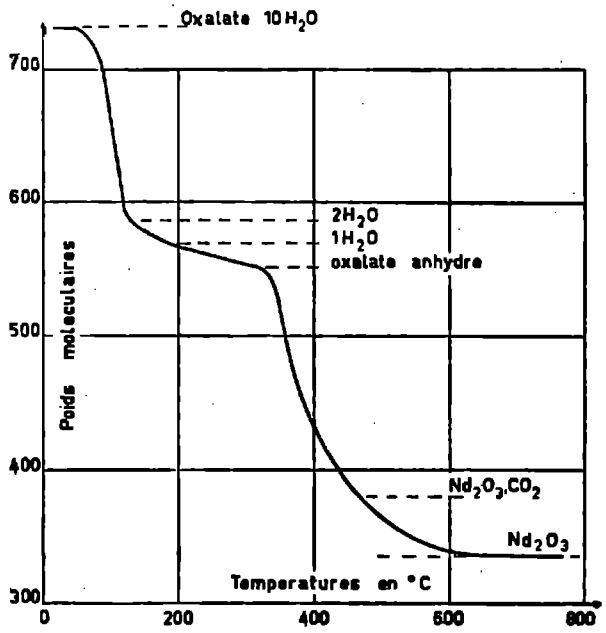


Fig. 16. Thermolysis curve of $Nd_2(C_2O_4)_3 \cdot 10H_2O$ (70)

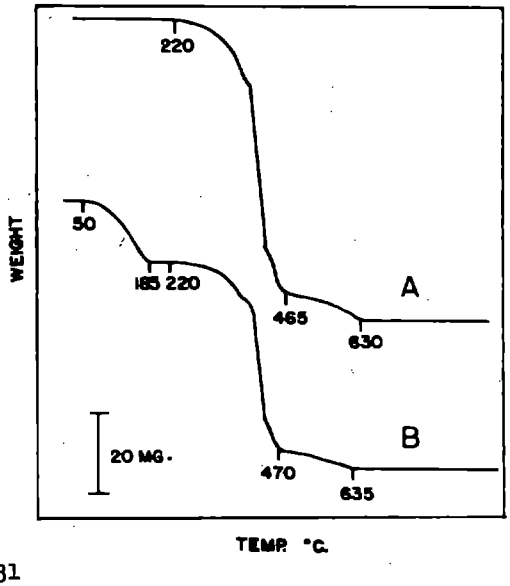


Fig. 17. Thermal decomposition curves of scandium oxalate. A. Scandium oxalate 2-hydrate. B. Scandium oxalate 6-hydrate (525)

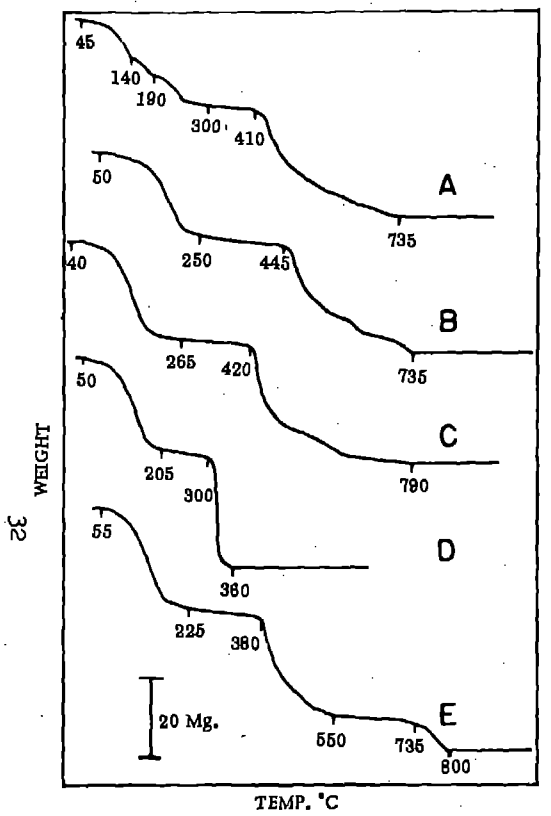


Fig. 18. Thermal decomposition curves of rare-earth metal oxalates. A. Samarium oxalate $10H_2O$. B. Neodymium oxalate $10H_2O$. C. Praseodymium oxalate $10H_2O$. D. Cerium oxalate $10H_2O$. E. Lanthanum oxalate $10H_2O$ (525)

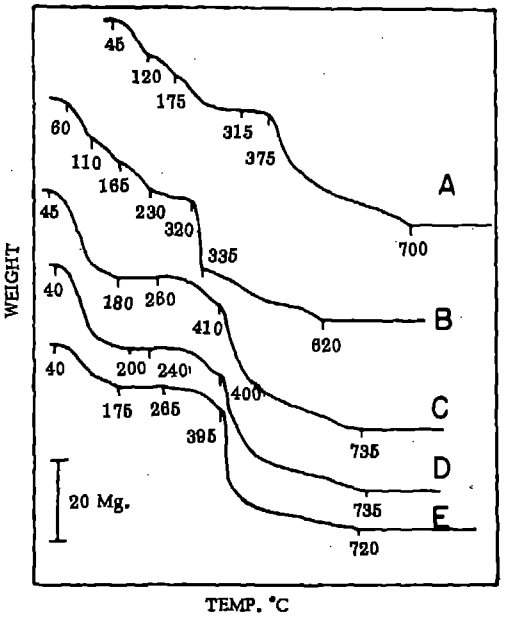


Fig. 19. Thermal decomposition of yttrium and rare-earth metal oxalates. A. Gadolinium oxalate 10-hydrate. B. Europium oxalate $10H_2O$. C. Yttrium oxalate $9H_2O$. D. Holmium oxalate $10H_2O$. E. Erbium oxalate $6H_2O$ (525)

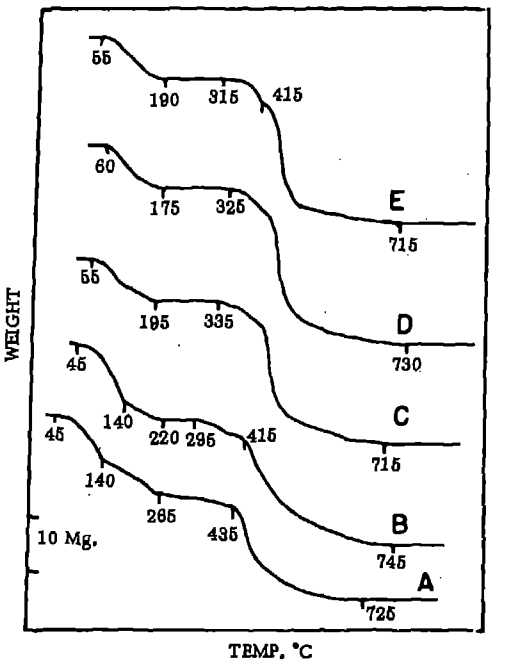


Fig. 20. Thermal decomposition curves of rare-earth metal oxalates. A. Terbium oxalate $10H_2O$. B. Dysprosium oxalate $10H_2O$. C. Thulium oxalate $5H_2O$. D. Ytterbium oxalate $5H_2O$. E. Lutetium oxalate $6H_2O$ (526)

Table 6. Decomposition temperatures of rare-earth metal oxalates (526)

Rare Earth Metal	Temp., ° C.	Transition
Lanthanum	55–380	10-hydrate → anhydrous
	380–550	Anhydrous → $La_2O_3.CO_2$
	735–800	$La_2O_3.CO_2$ → oxide
Cerium	50–360	10-hydrate → oxide
Praseodymium	40–420	10-hydrate → anhydrous
	420–790	Anhydrous → oxide
Neodymium	50–445	10-hydrate → anhydrous
	445–735	Anhydrous → oxide
Samarium	45–300	10-hydrate → anhydrous
	410–735	Anhydrous → oxide
Europium	60–320	10-hydrate → anhydrous
	320–620	Anhydrous → oxide
Gadolinium	45–120	10-hydrate → 6-hydrate
	120–315	6-hydrate → anhydrous
	375–700	Anhydrous → oxide
Terbium	45–140	10-hydrate → 5-hydrate
	140–265	5-hydrate → 1-hydrate
	265–435	1-hydrate → anhydrous
	435–725	Anhydrous → oxide
Dysprosium	45–140	10-hydrate → 4-hydrate
	140–220	4-hydrate → 2-hydrate
	295–415	2-hydrate → anhydrous
	415–745	Anhydrous → oxide
Holmium	40–200	10-hydrate → 2-hydrate
	240–400	2-hydrate → anhydrous
	400–735	Anhydrous → oxide
Erbium	40–175	6-hydrate → 2-hydrate
	265–395	2-hydrate → anhydrous
	395–720	Anhydrous → oxide
Thulium	55–195	5-hydrate → 2-hydrate
	335–730	2-hydrate → oxide
Ytterbium	60–175	5-hydrate → 2-hydrate
	325–730	2-hydrate → oxide
Lutetium	55–190	6-hydrate → 2-hydrate
	315–715	2-hydrate → oxide
Yttrium	45–180	9-hydrate → 2-hydrate
	260–410	2-hydrate → anhydrous
	410–735	Anhydrous → oxide
Scandium	50–185	6-hydrate → 2-hydrate
	220–635	2-hydrate → oxide

IV. 3C-2. 8-Hydroxyquinolate and Related Anions

The rare-earth—8-hydroxyquinolates differ from the oxalates in that they are stable at fairly high temperatures. Wendlandt's data[518] for several of the rare earths are reproduced in Table 7 and Fig. 21.

Table 7. Decomposition temperatures for the rare-earth 8-quinolinol chelates (518)

$M(C_9H_6NO)_3$	Stage I °C	Stage II °C	Stage III °C
Lanthanum	360	420-510	800
Cerium (III)	350	---	420
Praseodymium	280	320-520	575
Neodymium	250	330-510	730
Samarium	260	410-500	700
Gadolinium	250	400-525	755
Yttrium	175	370-525	740

In Table 7, the decomposition is classified in three stages: (I) A small loss of weight (about 1%) in the temperature range 250-300°C; (II) The oxidation of organic matter in the temperature range 350-525°C, and (III) The formation of the oxide in the temperature range 700-800°C.

Only seven of the rare earths are represented in Fig. 21, of course, and it is natural to expect that the remaining rare earths will behave in pretty much the same manner as those shown. Pokras and Bernays,[367] however, report that scandium 8-hydroxyquinolate loses measurable amounts of weight when heated at 110°C and very large amounts when heated for long periods at 165°C, so it may be wise to ignite the heavy rare-earth oxinates to oxides until such time as their decomposition behavior is determined.

Wendlandt has also studied the thermal decomposition of substituted rare-earth 8-hydroxyquinolates,[522, 523] the data for which are shown in Figs. 22-27.

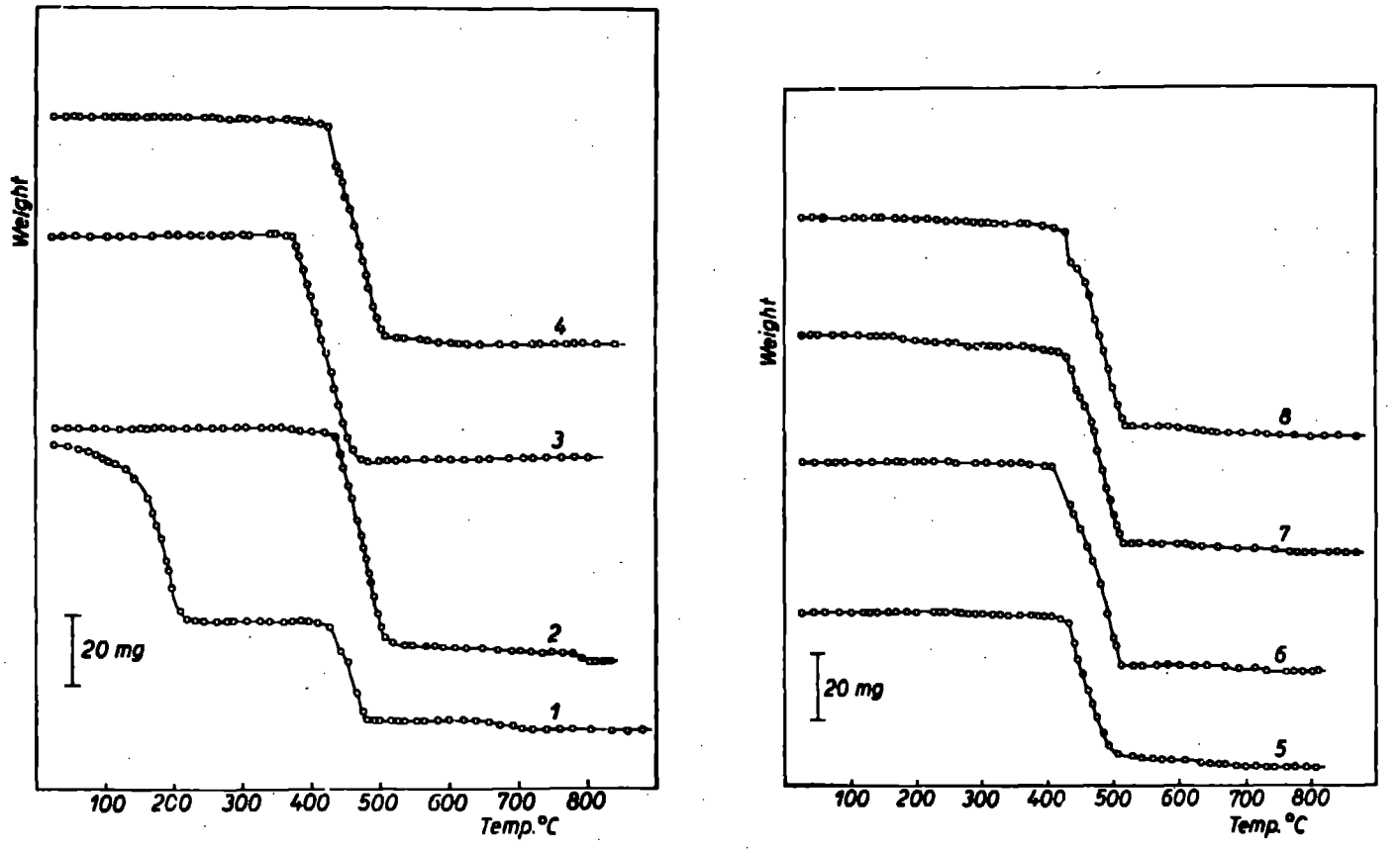


Fig. 21. Thermolysis curves of the 8-quinolinol chelates of the rare-earth metals (518): 1. Lanthanum + coprecipitated oxine, 2. Lanthanum, 3. Cerium (+3), 4. Praseodymium, 5. Samarium, 6. Neodymium, 7. Yttrium, 8. Gadolinium.

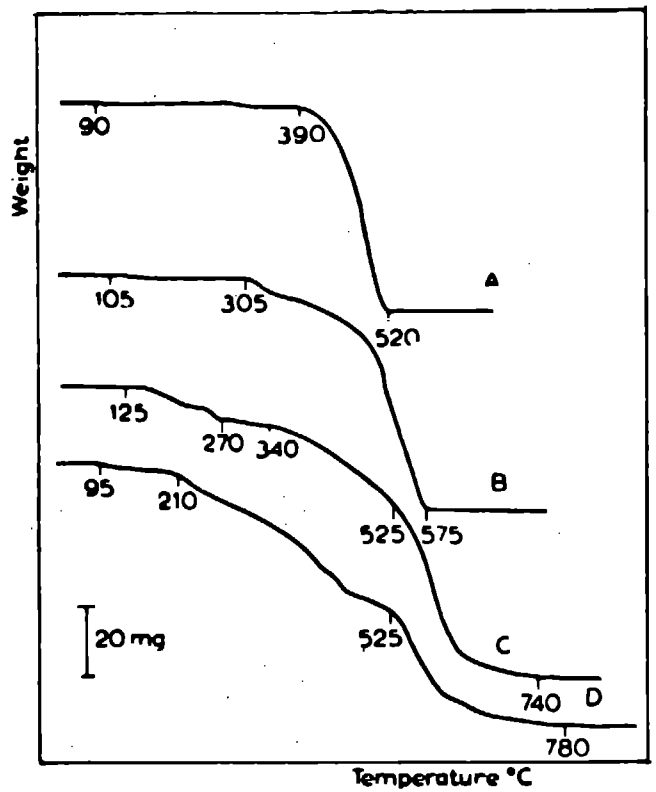


Fig. 22. Thermal decomposition curves of the rare-earth metal chelates (523): A. Cerium (+4) 5, 7 dibromo-8-quinolinol; B. Cerium (+4) 5, 7 dichloro-8-quinolinol; C. Lanthanum 5, 7, dibromo-8-quinolinol; D. Lanthanum 5, 7-dichloro-8-quinolinol.

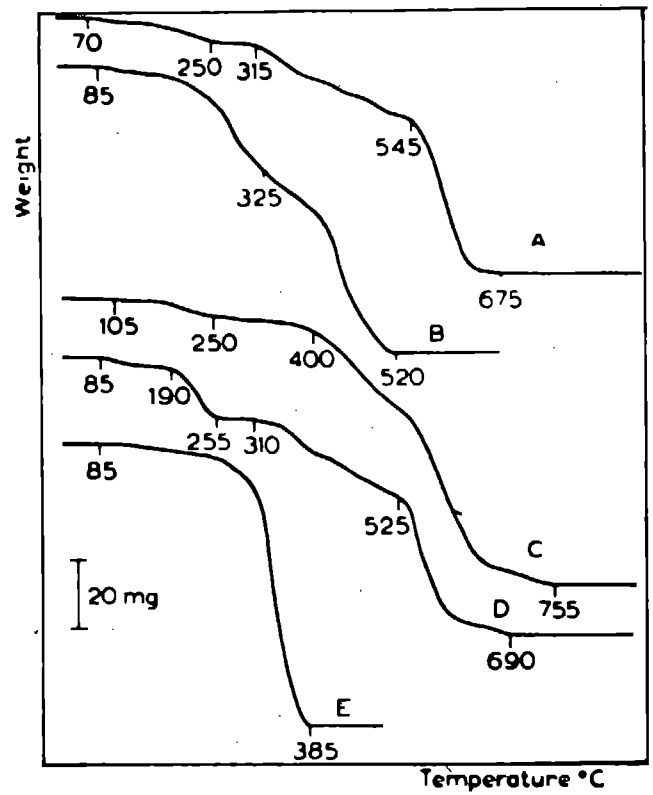


Fig. 23. Thermal decomposition curves of the rare-earth metal chelates (523): A. Neodymium 5, 7-dichloro-8-quinolinol; B. Praseodymium 5, 7-diiodo-8-quinolinol; C. Praseodymium 5, 7-dibromo-8-quinolinol; D. Praseodymium 5, 7-dichloro-8-quinolinol; E. Cerium (±4) 5, 7-diiodo-8-quinolinol.

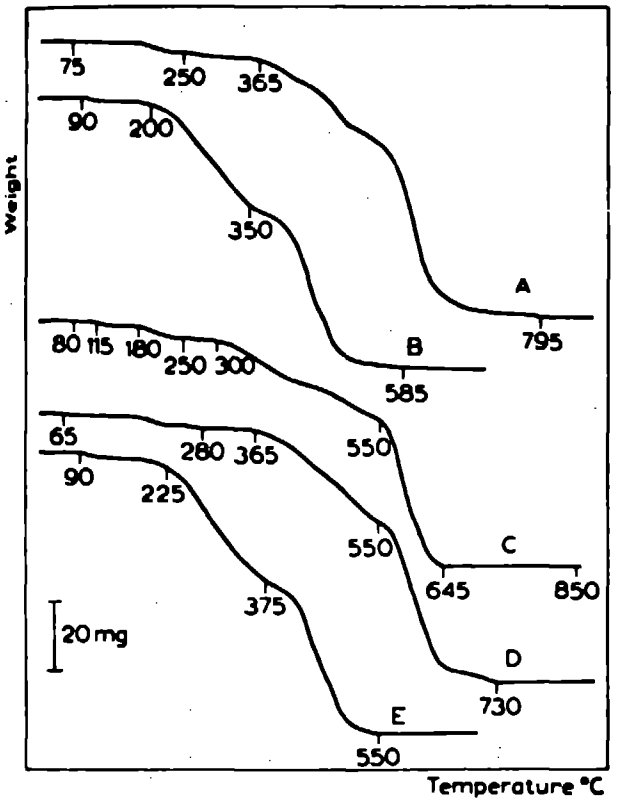


Fig. 24. Thermal decomposition of the rare-earth metal chelates (523): A. Samarium 5, 7-dibromo-8-quinolinol; B. Samarium 5, 7-diiodo-8-quinolinol; C. Samarium 5, 7-dichloro-8-quinolinol; D. Neodymium 5, 7-dibromo-8-quinolinol; E. Neodymium 5, 7-diiodo-8-quinolinol.

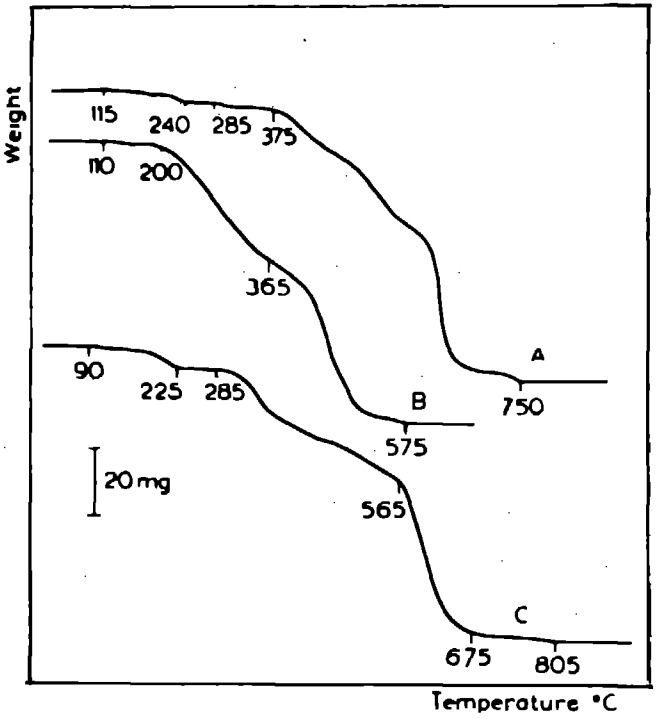


Fig. 25. Thermal decomposition curves of yttrium chelates (523): A. Yttrium 5, 7-dibromo-8-quinolinol; B. Yttrium 5, 7-diiodo-8-quinolinol; C. Yttrium 5, 7-dichloro-8-quinolinol.

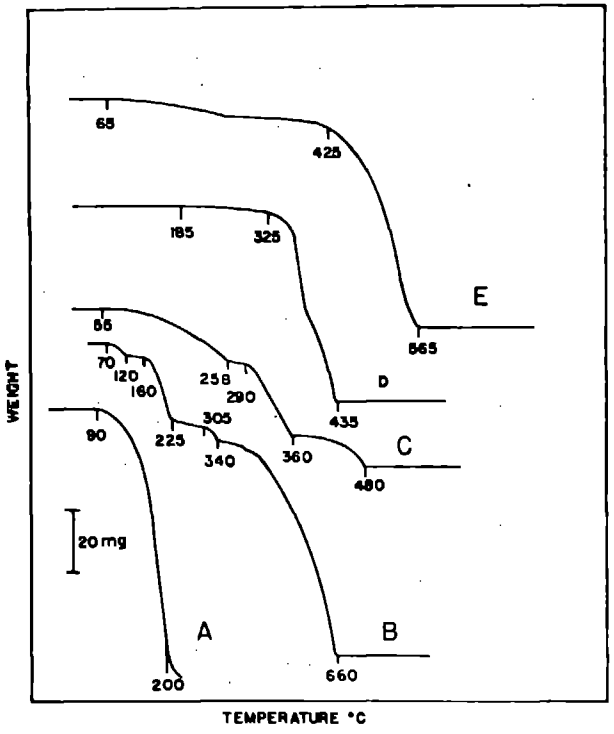


Fig. 26. The thermal decomposition curves of the chelating agent and metal chelates (522): A. 2-methyl-8-quinolinol; B. Scandium 2-methyl-8-quinolinol; C. Uranium (+6) 2-methyl-8-quinolinol; D. Thorium 2-methyl-8-quinolinol; E. Yttrium 2-methyl-8-quinolinol.

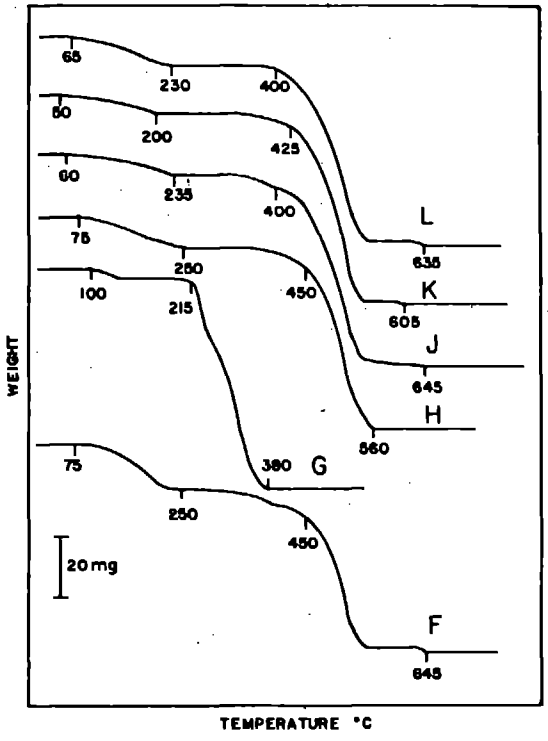


Fig. 27. The thermal decomposition curves of the rare-earth chelates (522): F. Lanthanum 2-methyl-8-quinolinol; G. Cerium 2-methyl-8-quinolinol; H. Praseodymium 2-methyl-8-quinolinol; I. Neodymium 2-methyl-8-quinolinol; J. Samarium 2-methyl-8-quinolinol; K. Gadolinium 2-methyl-8-quinolinol.

IV. 3C-3. Cupferrate and Neocupferrate

Wendlandt[515, 516, 529] has studied the thermal decomposition of the rare-earth cupferrates and neocupferrates, data for which are reproduced in Figs. 28 and 29.

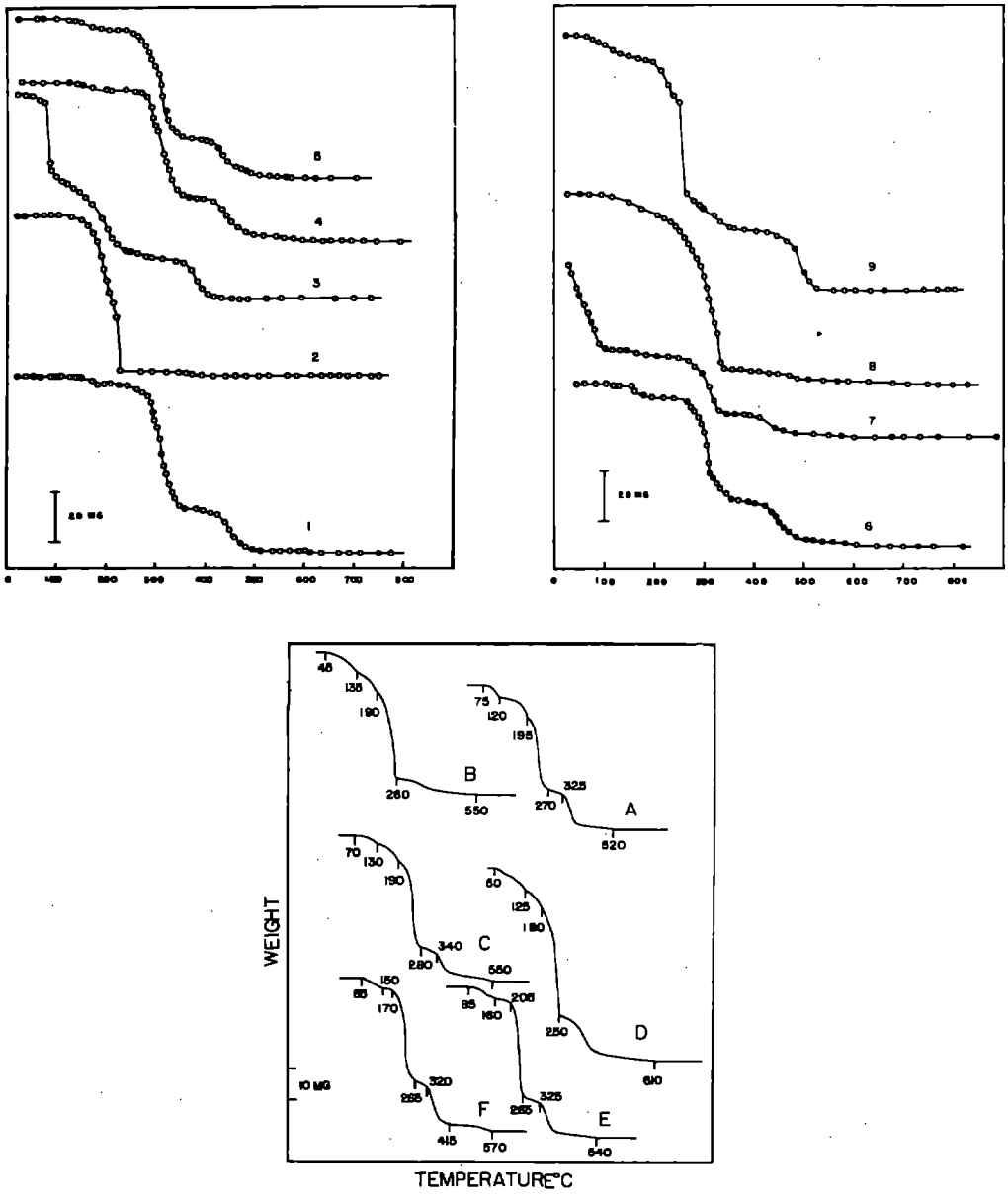


Fig. 28. Pyrolysis curves of scandium, yttrium, and rare-earth cupferrates. 1. Lanthanum, 2. Cerium (III), 3. Cerium (IV), 4. Praseodymium, 5. Neodymium, 6. Samarium, 7. Gadolinium, 8. Yttrium, 9. Scandium, A. Ytterbium, B. Erbium, C. Dysprosium, D. Holmium, E. Terbium, F. Europium.

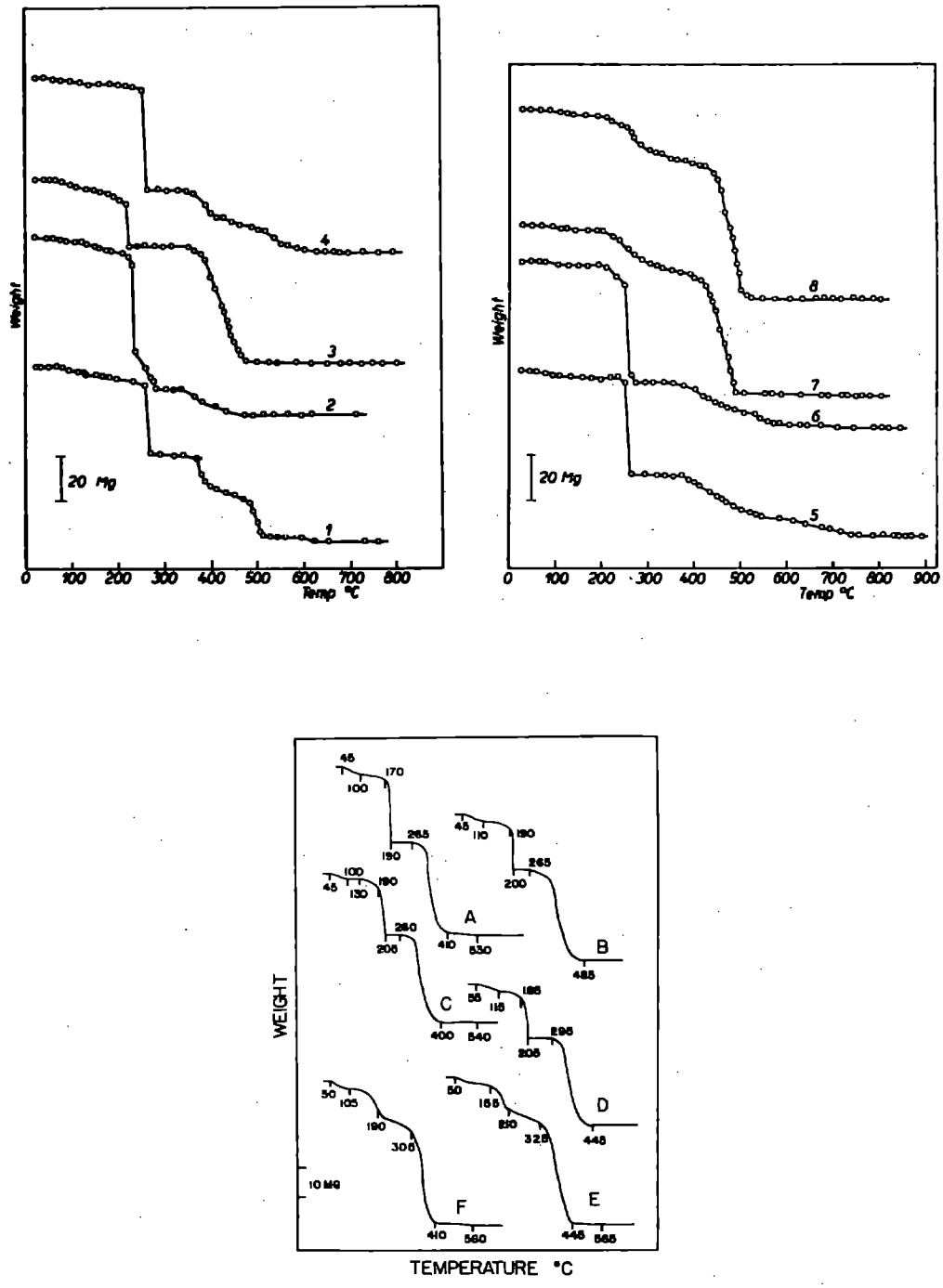


Fig. 29. Pyrolysis curves of yttrium and rare-earth neocupferrates. 1. Lanthanum, 2. Cerium (III), 3. Cerium (IV), 4. Praseodymium, 5. Neodymium, 6. Samarium, 7. Gadolinium, 8. Yttrium, A. Erbium, B. Ytterbium, C. Dysprosium, D. Holmium, E. Terbium, F. Europium.

IV. 3C-4. Other Anions

Wendlandt has studied the thermal decomposition of the rare-earth chlorides[524, 527] and fluorides,[528] and Chretien and Capestan[78] have studied the sulfamates, but since these salts are not used for gravimetric determinations their pyrolysis curves will not be reproduced here.

IV. 4. SPECTROPHOTOMETRY, TITRATION, AND COLORIMETRY

IV. 4A. SPECTROPHOTOMETRY OF SIMPLE IONS

Thirteen of the fifteen lanthanide elements possess the interesting property of showing light absorption bands in solutions of their simple salts. These bands are relatively narrow and are very useful for qualitative and quantitative estimation of individual rare earths. Lanthanum, lutetium, and yttrium do not exhibit any usable absorption bands, and may not be determined by this method.

A fairly large number of papers on the spectrophotometric measurement of the rare earths have appeared in the literature, perhaps the best of which have been published by Stewart and Kato,[462] Moeller and Brantley,[314] Rodden,[388, 389] Holleck and Hartinger,[203] and Banks and Klingman.[14]

Figures 30-33 have been reproduced from the paper by Stewart and Kato[462] and indicate the useful peaks for all of the rare earths in the visible, infrared, and ultraviolet regions. Wavelength positions and molecular extinction coefficient values for "index peaks" which have been recommended by Stewart and Kato for determining the rare earths are shown in Table 8. Where more than one peak is listed for a given element, the "primary," or most highly recommended, peak is listed first. It is apparent that there are interferences for each of the peaks listed in Table 8. For detailed information on the extent of each interference the original paper should be consulted.

Additional data on the absorption spectra of the rare earths may be obtained from papers by Prandtl and Scheiner[377] (all the rare earths), Wylie[540] (Pr, Nd, Sm), Jorgensen[223] (Dy, Ho, Er), and Onstott and Brown[346] (Tb).

Promethium, of course, is seldom encountered in sufficient amounts to measure spectrophotometrically. Stewart,[459] however, has measured its absorption spectra and has shown it to be quite complicated.

Butement[65] has studied the absorption and fluorescence spectra of bivalent samarium, europium, and ytterbium. The spectra for each of these species are simpler than the spectra for the corresponding trivalent ion, but no attempt to use the absorption peaks for analysis is reported.

Although the simple salts of yttrium and lanthanum cannot be determined by absorption spectra, other techniques have proven useful. Legrand and Loriers[267] have published a paper which indicates that x-ray fluorescence

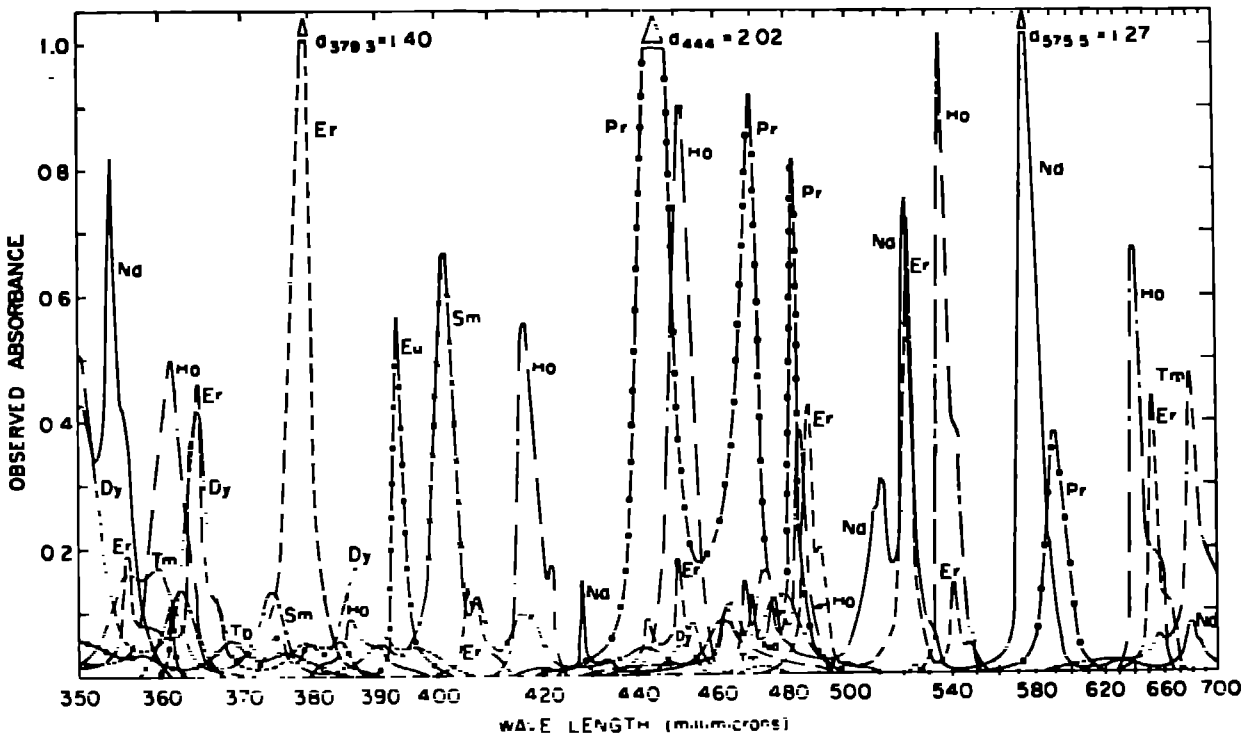


Fig. 30. Absorption spectra of all rare earths in visible range (462)

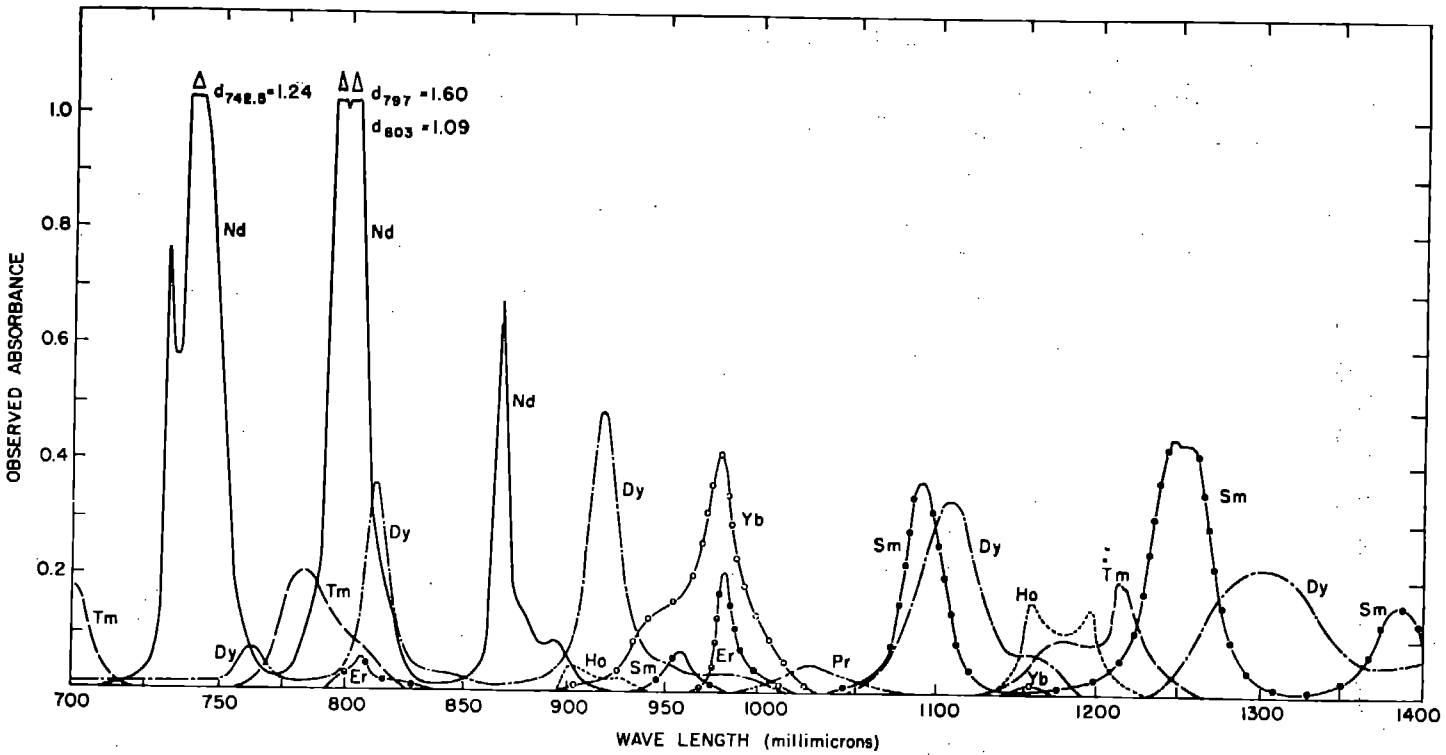


Fig. 31. Absorption spectra of all rare earths in near-infrared (462)

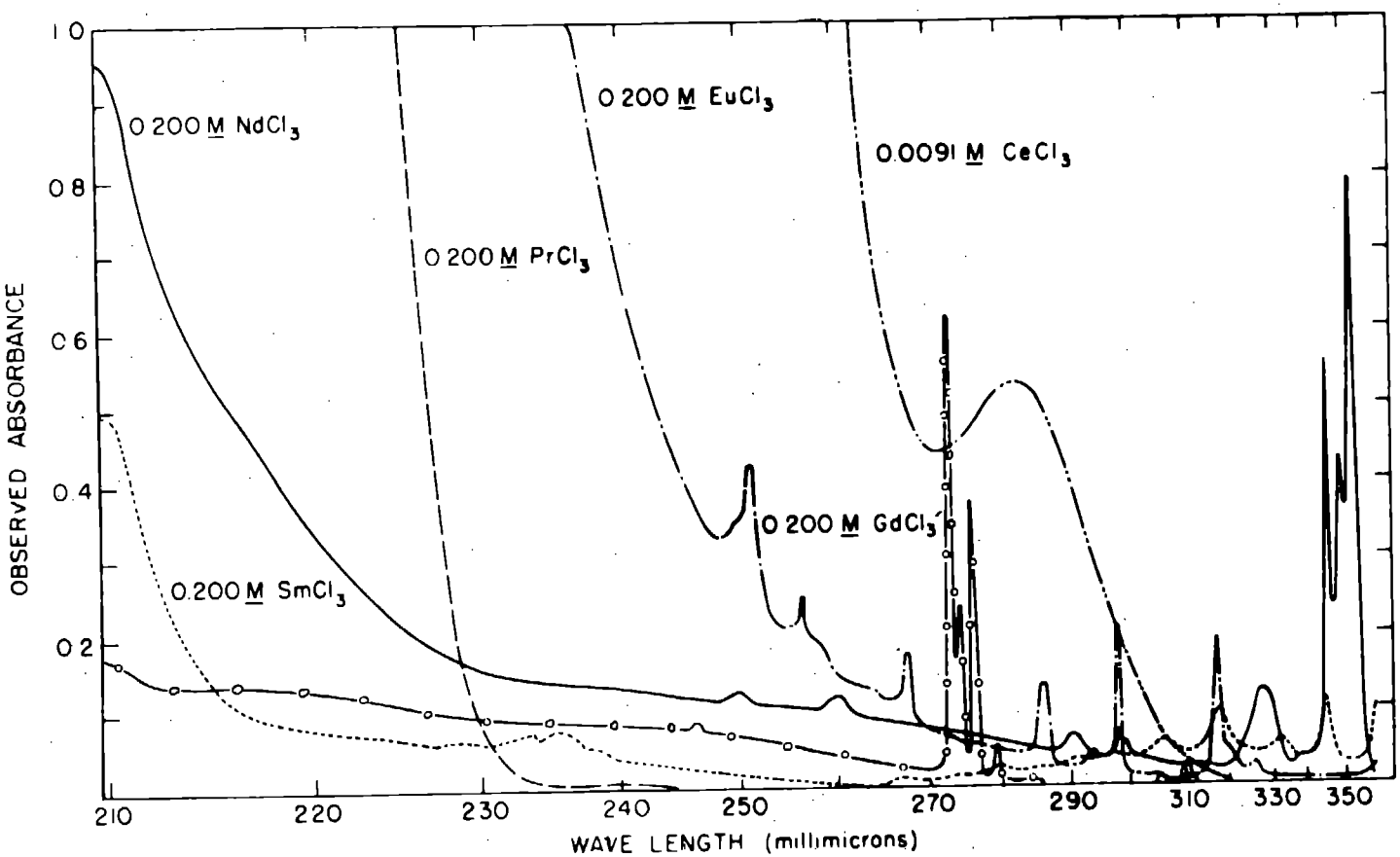


Fig. 32. Absorption spectra of light rare earths in ultraviolet range (462)

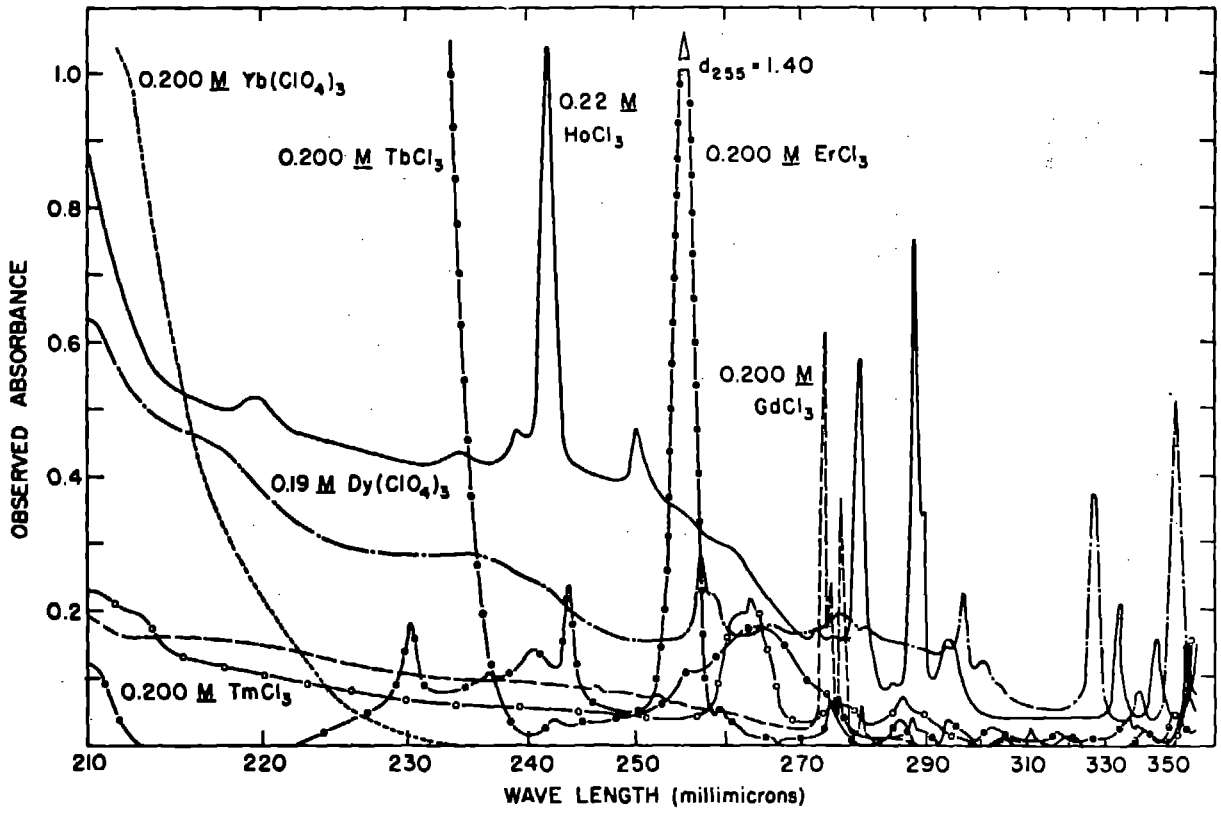


Fig. 33. Absorption spectra of heavy rare earths in ultraviolet range (462)

Table 8. Index peaks, extinction coefficients, and interfering rare-earth elements in the spectrophotometric determination of individual rare earths (462)

Element	λ-max (mμ)	ε	Interfering Element
Ce	253	755	Most elements interfere. (See
	296	26	refs. 462, 178.)
Pr	444.0	10.1	Sm, Ho, Er
	482.5	4.1	Nd, Sm, Ho, Er
	590	1.95	Nd
Nd	575.5	6.34	Pr
	742.5	6.22	Dy
	868	3.10	Dy
	522.3	2.74	Er
Sm	401.6	3.30	Eu, Dy
	1250	2.19	Dy, Tm
	1095	2.00	Dy (See ref. 326.)
Eu	394.3	2.90	Sm, Dy, Ho
Gd	272.7	3.16	See ref. 462.
	275.6	1.90	" " "
Tb	219	374	Eu, Pr, Ce (See ref. 462.)
Dy	911	2.40	Yb, Ho
	1102	1.80	Sm
Ho	536.5	4.55	Er
	416.1	2.52	Sm
	641	3.04	Er, Tm
Er	523.5	3.55	Nd
	379.3	6.66	Nd
	654	2.04	Ho, Tm, Nd
Tm	682.5	2.36	Nd
	781	1.00	Nd, Dy
Yb	973	2.10	Er, Dy
	950	0.77	Dy, Sm

techniques may be used to measure yttrium quantitatively in the presence of other rare earths; and Menis, Rains, and Dean[546] report that flame spectrophotometric methods may be used for quantitative determination of lanthanum.

IV.4B. TITRATION AND COLORIMETRY

Titration has proven to be a very useful method for quantitative determination of the rare-earth elements. Most published procedures involve addition of a standard solution of a strong complexing agent such as ethylene-

diaminetetraacetic acid (EDTA) to a rare-earth solution. The end point at which all of the rare earth has been complexed is identified by a change of indicator color in the solution. The change in color is often followed spectrophotometrically for the best results but this is not always necessary.

Typical EDTA titration papers have been published by Brunisholz and Cahen,[56] who used a mixed alizarin sulfonate-methylene blue indicator; by Flaschka,[145] and Wunsch,[539] who used eriochrome black T; by Fritz and Pietrzyk,[158] who titrated scandium with copper as an indicator; by Jenickova, Suk, and Malat,[219] who used brompyrogallol red for the rare earths; by Cheng,[75] Cheng and Williams,[74] and Flaschka and Abdine,[146] who used 1-(2-pyridyl-AZO)-2 naphthol (PAN) as indicator for scandium and the rare earths; by Crouch and Swainbank,[92] who used xylenol orange as an indicator in an ultra-micro method for the estimation of the rare earths; by Bril, Holzer, and Rethy,[47] who used alizarin red S in a simultaneous determination of thorium and rare earths in their mixtures; and by Frum,[160] who used monochrome Bordeaux C to detect La^{+3} in the presence of Ce^{+3} and Ce^{+4}. Hall, Gibson, Wilkinson, and Philips[186] have published a procedure which involves titration with EDTA and conductometric determination of the end point, while Hara and West[190] have used high-frequency titrations.

Perhaps the best volumetric method for measuring the rare earths involves the use of arsenazo (3-(2 arsonophenylazo)-4, 5 dihydroxy-2, 7 naphthalene disulfonic acid, trisodium salt) as an indicator, a procedure first developed by Kuznetsov.[253] This reagent may be used as complexing agent for direct colorimetric determination of the rare earths[155, 15, 252] or in conjunction with EDTA titration.[156]

The rare earth-arsenazo color intensity increases as the temperature is increased, and Kuznetsov and Petrova[254] have measured small amounts of rare earths at elevated temperatures in the presence of Th with greater accuracy than is possible at ordinary temperatures.

A close relative of arsenazo is 2(0-arsonophenylazo)-1, 8-dihydroxy-3, 6 naphthalene disulfuric acid (neothorone), which has been used by Shibata, Takeuchi, and Matsumas[437] to measure lanthanum colorimetrically.

These references do not exhaust all of the reports which have been published on EDTA titration of the rare earths. A much more thorough coverage of the entire subject of EDTA titration has been written by Barnard, Flaschka, and Broad[18] and their series of review articles should be consulted for additional references.

Papers on the direct colorimetric determination of the rare earths have also been published by Holleck, Eckardt, and Hartinger[204] who found sulfosalicylic acid and aurin tricarboxylic acid to be the best color-forming reagents for spectrophotometric determination of the rare earths. Rinehart,[387]

however, has found alizarin red S to be quite satisfactory for the rare earths and yttrium; Eberle and Lerner[122] have used the same reagent for quantitative determination of scandium; Bergstresser[25] has used 8-hydroxyquinoline for colorimetric determination of lanthanum in plutonium with good results, and Alimarin, Przheval'skii, Puzdrenkova, and Golovina[6] have used the same reagent for Ce^{+3} and Ce^{+4}.

Vanossi[493] has reported a colorimetric procedure for scandium which involves the use of carminic acid in acetic acid solution and claims a sensitivity of 1 μg Sc for the method, while Biryuk and Nazarenko[30] have used derivatives of 2:3:7 trihydroxy-6 fluorone to detect 0.04 to 2 μg of scandium per ml, and Korenman, Gunina, and Trifonova[242] have studied the color reaction of scandium with hydroxyanthraquinone and 1, 1 dihydroxyazo dyes.

Popa, Negoiu, and Baiulescu[370] have developed a procedure for determining Ce^{+4} in the presence of trivalent lanthanide elements which uses O-dianisidine in 20% H_2SO_4 solution.

Goto and Kakita[176] have extracted the cerium-methylene blue complex into organic solvents and determined the cerium concentration colorimetrically.

The titration procedures described above may be used for fairly large samples of rare earths, of course, but perhaps the main advantage of both the titration and colorimetric procedures is that they may be used to determine very small amounts of rare earths with good precision. Many of the procedures were designed specifically to measure microgram quantities of these elements and seem to do so very nicely.

IV.5. COMPLEX IONS AND CHELATE COMPOUNDS

IV.5A. INTRODUCTION

Although the rare earths have been known for a great many years, until comparatively recently most published articles have been concerned primarily with relatively simple salts of these elements. With the advent of ion-exchange resins and liquid-liquid extraction procedures, however, a considerable literature on the formation of complex salts and chelate compounds of the rare-earth elements began to appear and at present there is information available on a very large number of these species. Terent'eva[477] has published a masterful review of this aspect of rare-earth chemistry and this section will, to a great extent, consist of a translation of that paper, supplemented where necessary by additional or more recently published data.

Many methods are known for disclosing complex compounds of rare-earth elements in solution. For example, the distribution of ions of rare-earth elements between ion exchangers and aqueous solutions containing different complexing agents makes it possible to discern the comparative structures of complex compounds. Comparison of the results of polarographic re-

duction of Eu^{+3}, in the presence and absence of different ions, indicates formation of complex compounds. Transfer of the rare earths from the aqueous to the organic phase in the presence of β-diketones, tributyl phosphate, and other agents, indicates formation of complexes. A change in the transport number, and in the electroconductivity, confirms the formation of complex compounds. Rare-earth transfer to the anode during electrolysis in the presence of organic anions indicates formation of negatively charged complex ions, while the change in spectral characteristics of rare-earth elements in the presence of complexing agents likewise indicates complex formation. The absence of a characteristic reaction under conditions where the rare earths normally are precipitated may be used as a simple indication of the presence of complexes; the sensitivity of this method decreases with increasing solubility of the rare-earth salt in the order $F^- > C_2O_4^= > OH^- > Fe(CN)_6^{-4}$.

Although a large number of complex compounds of the rare earths are known, these elements are notably more reluctant to form complex species than, for instance, are the transition elements. Moeller[316] attributes this reluctance to a combination of (1) electronic configurations unfavorable to the orbital hybridizations necessary for covalent bond formation and (2) comparatively large size which precludes the development of many very strong electrostatic or ion-dipole attractions. The main differences between individual rare earths lie in the number of 4f orbital electrons and Moeller assumes that, since the 4f electrons are shielded by 5s and 5p orbitals, any covalent bonding must involve higher energy orbitals such as 5d, 6s, 6p, etc., and not the 4f electrons. Terent'eva[477] disagrees with this assumption on the grounds that the very large number of complex compounds now known could not all involve ionic bonding or covalent bonding with high-energy orbitals. The nature of these bonds has obviously not been determined to everyone's satisfaction, and a considerable amount of work needs to be done in this field. Meanwhile, apparently contradictory evidence continues to appear. Gulyas[181] classifies the rare earth-acetylacetone complex bond as a covalent type with higher d, s, and p orbital electrons because the 4f electrons are not involved; but Jones[222] concludes that rare-earth bonding with ethylene-diamine-tetraacetic acid (EDTA) is ionic in nature by analogy with the alkali and alkaline-earth-element complexes.

Whatever the final disposition of this question, however, it is plain from the following survey that the number of complex rare-earth compounds is rather high. In the first part of the survey are presented the complex compounds with salts of inorganic acids and ammonia, while in the second (and considerably broader) part are the complex compounds with organic additives.

IV. 5B. COMPOUNDS WITH INORGANIC ADDITIVES

IV. 5B-1. Sulfates

The sulfates of alkaline metals can play a significant role in separating a mixture of rare-earth elements into subgroups. In the interaction of the sulfates of potassium and sodium with the salts of the rare-earth metals, there are formed somewhat insoluble sulfates of the type $Me_2(SO_4)_3 \cdot nH_2O$, where n = 5, 8, 9. Upon addition of an excess of reagent, the sulfates of the elements of the yttrium subgroup dissolve and sulfates of the elements of the cerium subgroup remain in suspension (the sulfates of the intermediate elements possess intermediate solubilities).

The solubility of the sulfates of the elements of the yttrium subgroup, in a solution of alkali metal sulfates, may be explained by the formation of complex compounds of the type $Me^I_3[Me(SO_4)_3]$ or $Me^I[Me(SO_4)_2]$, where Me^I = K, Na, NH_4. This hypothesis is supported by the fact that a solution containing the ions Y^{3+} and an excess of SO_4^{2-} ions does not show an yttrium reaction with $K_4[Fe(CN)_6]$; upon addition of $(NH_4)_2C_2O_4$, the yttrium oxalate does not precipitate but causes only an opalescence.

Various authors[228] have noted a tendency toward formation of complex sulfates even by such a basic element as lanthanum. It has been discovered that when a mixture of a concentrated solution of $La(NO_3)_3$ stands with concentrated H_2SO_4, $H_3[La(SO_4)_3]$ is precipitated in the form of fine-grained spicules.

Korenman,[240] in determining the solubility of oxalates of rare-earth elements in acids, found that their greater solubility in H_2SO_4 than in HCl indicates formation of complex sulfates.

From the pH value of saturated solutions of oxalates in H_2SO_4, and the total concentration of $C_2O_4^{2-}$ (or Me^{3+}) in these solutions, he calculated the constants of instability for complex ions of type $MeSO_4^+$. Kuntz,[249] studying the oxidation-reduction potentials of the Ce^{3+}/Ce^{4+} systems in sulfuric acid solution, discovered the appearance of complex-formation between the ions SO_4^{2-}, HSO_4^-, and Ce^{4+}, while Hardwick and Robertson[192] have shown that ceric ion associates with sulfate to form successively $Ce(SO_4)^{++}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{-2}$.

Newton and Arcand[336] and Fronaeus[159] have studied the Ce^{+3}-$SO_4^=$ system and Fronaeus has shown that the mono-, di-, and tri-sulfato complexes of this ion also exist.

IV. 5B-2. Sulfites

During interaction of the salts of elements of the cerium subgroup with K_2SO_3, precipitates of colloidal character are formed which in the course of

time convert to spheroidal crystals. The salts of yttrium and erbium initially also make colloidal suspensions; with further addition of K_2SO_3 the precipitate is dissolved, which can be explained by formation of the complex compounds $[Me(SO_3)_3]^{3-}$. Upon standing out of solution for extended times they become very coarse crystals, in the form of plates, and druse which seems to be associated with the decomposition of the complex compound.

Complex sulfites have been studied by Vickery.[504] While studying the titration of $Me(OH)_3$ with H_2SO_3, he discovered that at the ratio of $Me:SO_3 = 1:3$ a compound is formed having the composition $H_3[Me(SO_3)_3]$. Spectrophotometric study of the "bisulfite" solution indicated that this compound has a structure close to the structures of solutions of complex compounds of lanthanides with "complexons." The maximum change in the spectrum, in comparison with the spectra of solutions of simple salts of rare-earth elements, is found at pH 5.5 to 6.1. During titration of the "bisulfite" solution of a rare-earth element at pH 3.8 by NaOH, a sediment is precipitated whose makeup is $Na_3[Me(SO_3)_3]$. Upon further titration the $SO_3^=$ ions are displaced by OH^- ions and become first $Na[Me(SO_3)_2(OH)_2]$, then $Na_3[Me(SO_3)(OH)_4]$, and finally precipitate $Me(OH)_3$. The existence of the complex anion $[Me(SO_3)_3]^{3-}$ is confirmed by experiments with anion-exchange resins. Three Cl^- ions of the anion exchanger (RCl) are displaced by the one ion $[Me(SO_3)_3]^{3-}$:

$$3RCl + H_3[Me(SO_3)_3] \rightarrow 3HCl + R_3[Me(SO_3)_3].$$

Solutions of the complex compound $H_3[Me(SO_3)_3]$ are easily oxidized by oxygen to sulfates:

$$4H_3[Me(SO_3)_3] + 3O_2 \rightarrow 2Me_2(SO_4)_3 + 6SO_2 + 6H_2O.$$

The oxidation proceeds without intermediate formation of simple sulfites. As Vickery noted, in contrast to other complex compounds of rare-earth elements, the stability of the complex sulfites decreases with increase of the atomic number of the rare-earth element. According to speed of oxidation, the yttrium compound takes an intermediate position between the compounds of neodymium and samarium. The ability of complex sulfites gradually to be oxidized by oxygen is utilized for separating mixtures of rare-earth elements.

Mayer and Schwartz[296] have studied the $Ce^{+3} - SO_3^=$ system using cation-exchange resins and give a dissociation constant of 1.1×10^8 for the reaction

$$Ce^{+3} + HSO_3^- = CeSO_3^+ + H^+.$$

IV.5B-3. Thiosulfates

When mixing concentrated solutions of the salts of rare-earth elements

and the thiosulfate of sodium, there are formed thiosulfates of the rare-earth elements of composition $Me_2(S_2O_3)_3$. Being moderately soluble in water, they are precipitated as well-formed crystals having the colors characteristic of the ions of rare-earth elements. Upon ignition[394] they are changed into products of composition $Me_2O(SO_3)_2$. The thiosulfate of cerium, upon ignition, forms CeO_2 which is not soluble in concentrated salt solutions. These characteristics are used for separation of cerium from residual rare-earth elements. When dissolving thiosulfates of rare-earth metals in excess thiosulfates of alkaline metals, the complex compounds $Na_5[Me(S_2O_3)_4]$ and $K_3[Me(S_2O_3)_3]$ result, a fact which has been established by the electroconductivity method.[110]

IV. 5B-4. Halides

Simple fluorides seem to be one of the most difficult-to-dissolve salts of rare-earth elements. However, Dergunov,[103] by studying diagrams of the fusibility of mixtures of rare-earth fluorides and alkaline metals, succeeded in tracing the complex fluorides $K[LaF_4]$ and $Na[LaF_4]$, and likewise $M_3[MeF_6]^{3-}$ (where M = K, Rb, and Cs), which are soluble in dilute acids.

Other researchers[363] have also noted that when dissolving PrF_3 in a melt of KHF_2, a complex fluoride of praseodymium is formed which is soluble in dilute acid salts.

Scandium is considerably more soluble in aqueous fluoride solution than are the other rare earths. Kury, Paul, Hepler, and Connick[251, 352] report the existence of ScF^{++}, ScF_2^+, ScF_3(aq), and ScF_4^- species and give the equilibrium quotients at 25°C for the reactions:

$$Sc^{+3} + F^- = ScF^{+2} \qquad K_1 = 1.2 \times 10^7$$

$$ScF^{+2} + F^- = ScF_2^+ \qquad K_2 = 6.4 \times 10^5$$

$$ScF_2^+ + F^- = ScF_3(aq) \qquad K_3 = 3.0 \times 10^4$$

$$ScF_3(aq) + F = ScF_4 \qquad K_4 = 7 \times 10^2$$

There is nothing conclusive in the literature on complex halides of trivalent rare-earth elements of the type $[MeCl_6]^{3-}$. There is information[323] on separation of hexachlorocerium acid of tetravalent cerium: $H_2[CeCl_6]$. A suspension of pure dry cerium oxide in anhydrous dioxane was treated with dry gaseous HCl over the course of several hours. The solution colored quickly to an orange-red hue and the temperature rose to 50°C. After separation of the yellow-colored sedimentation it was maintained for 24 hours at 2-3°C. Spicule-shaped crystals of orange-red hue evolved. The crystals were removed, scrubbed with dioxane and then with a petroleum ether, and dried in a stream of dry air. Data of analysis corresponded to the formula $H_2[CeCl_6] \cdot 4C_4H_8O_2$. A double salt with pyridine $H_2[CeCl_6] \cdot (C_5H_5N)$ was

obtained from a solution of these crystals in methanol.

Further evidence for the extreme reluctance of the rare earths to form chloride complexes is provided by Diamond, Street, and Seaborg[104] and Hulet, Gutmacher, and Coops,[209] who show that even in very concentrated HCl or LiCl the formation of rare-earth chloride complexes is slight.

IV. 5B-5. Nitrates

The nitrates of rare-earth elements give (with alkaline nitrates, alkaline earth, and some other elements) well-crystallized double salts — for example, with magnesium, $Mg(NO_3)_2 \cdot Me(NO_3)_3 \cdot 24H_2O$. D.I. Mendeleyev in 1873 first used the crystallization of double nitrates of ammonia for separation of La from "Di." These salts are still used today for preparatory separation of elements of the cerium subgroup. Double nitrates, found in aqueous solution, display a complex character. In the presence of a large surplus of NO_3^-, the rare-earth elements of the yttrium subgroup yield, upon addition of $(NH_4)_2C_2O_4$, an oxalate precipitate only after standing for some time. One may suppose that the complex ions $[Me(NO_3)_6]^{3-}$ exist in the solution.

According to the data of Noyes and Garner,[343] in aqueous nitric acid solutions of $Ce(NO_3)_4$ there exists an excess of NO_3^- ions, forming the complex ions $[Ce(NO_3)_6]^{2-}$. The existence of the latter is demonstrated by the fact that, during electrolysis of a solution of Ce^{4+} salts in 6N HNO_3, cerium appears in the anode region. The expressed hypothesis was supported by data published later by other authors.[433, 235] The capability to give similar complex compounds is widely used today for separation of cerium from other rare-earth elements. Cerium is extracted by ethyl ether from nitric acid, in the form of a complex acid $H_2[Ce(NO_3)_6]$.

In 1956 an article was published[304] on extraction of the double salts of La, Ce, Pr, and Nd with the nitrate of triphenylbenzylphosphonium. These salts are crystalline substances, easily soluble in organic solvents. They are hydrolyzed in aqueous solutions. On the basis of analytical data the author presented their formula in the form: $[(C_6H_5)_3(C_2H_5CH_2)P] \cdot [Me(NO_3)]_5$ (where Me = La, Ce, Pr, Nd).

Miss L.O. Tuazon[551] has shown that even in relatively dilute nitrate solution Ce(+4) forms a $Ce(NO_3)(OH)^{+2}$ complex and, to a lesser extent, $Ce(NO_3)_2^{+2}$.

IV. 5B-6. Nitrites

Nitrites of the type $Cs_2Na[Me(NO_2)_6]$ (where Me = La, Ce, Pr, Y) were prepared by Ferrari et al.[133] by slowly diffusing an aqueous solution of $CsNO_3$ through a parchment membrane into solution consisting of $Me(NO_3)_3 \cdot 6H_2O$

and $NaNO_2$. The compound isolated by the authors, $Cs_2Na\,[La(NO_2)_6]$, appeared as faintly greenish, almost colorless crystals.

IV.5B-7. Carbonates

When CO_2 is passed into a suspension of hydroxides of rare-earth elements, crystalline carbonate is obtained. Under the action of a saturated solution of K_2CO_3 on the solution, the salts of the cerium group of elements secrete a slimy residue which, in the course of further addition of reagent, is dissolved with formation of a complex compound which is not decomposed by the action of $(NH_4)_2C_2O_4$. If a more dilute carbonate solution is added, a residue is obtained which is not soluble in an excess of reagent. The solubility of carbonates in a saturated solution of K_2CO_3 increases with the increase in atomic number of the rare-earth elements. The composition of the complex carbonates soluble in water seems to be $K_3\,[Me(CO_3)_3]$. Fischer[142] used carbonates for fractionally separating mixtures of rare-earth elements. Axelrod[11] has completed a Ph.D. thesis on "Studies of the Rare-Earth Carbonates" in which he prepared various forms of the rare-earth carbonates by hydrolysis of trichloroacetate or urea solutions containing fairly high concentrations of the rare-earth elements.

IV.5B-8. Chromates

A spectrophotometric study[484] was made of a 1M solution of $HClO_4$ containing Ce^{4+} and Cr^{6+} (at 25°C). It was found that a complex compound exists in the solution containing 1 Ce^{4+} ion to 1 Cr^{6+} ion.

IV.5B-9. Phosphates

Serebrennikov[432] reports that, during conductometric titration of a 0.1N solution of $(NH_4)_2\,[Ce(NO_3)_6]$ by a 0.1N solution of $Na_4P_2O_7$, he noted in the solution a complex compound of Ce^{4+} with the pyrophosphate ion: $Na_4\,Ce(P_2O_7)_2$. The author explained the composition of this compound by the fact that, in it, the pyrophosphate ion exhibits a coordination capacity of three (which appears somewhat unexpected).

Addition of sodium phosphate (and polyphosphates) to an aqueous rare-earth solution adjusted to pH 4.5 results in the precipitation of normal phosphates (and polyphosphates) corresponding to the formulae $R(PO_4)$, $R_4(P_2O_7)_3$, and $R_5(P_3O_{10})_3$.[66] At higher concentrations of pyrophosphates and triphosphates, Giesbrecht and Audrieth[173] have shown that soluble species exist in which the ratio of rare-earth metal ion to triphosphate is 1:2 (they postulate an anionic complex with the formula $[Na_4(RE)(P_3O_{10})_2]^{3-}$ as one possibility).

Genge and Salmon,[169] using elution of cations from ion-exchange resin solumns as a criterion, conclude that scandium has a somewhat greater tendency to form complexes with orthophosphoric acid than do the other rare earths.

IV. 5B-10. Heteropoly Compounds

The known[17] compounds are Me^{I}_{8} $[Ce(Mo_2O_7)_6] \cdot 8H_2O$ and Me^{I}_{8} $[Ce(W_2O_7)_6] \cdot 8H_2O$, where Me^{I} = K, Na, NH_4. The first of these was obtained in the form of yellow crystalline sediment upon drop-by-drop addition of a normal solution of ammonium molybdate into a boiling mixture of $(NH_4)_2$ $[Ce(NO_3)_6]$. A double salt of composition $(NH_4)_6H_2$ $[Ce(Mo_2O_7)_6]$ was precipitated from the sulfuric acid solution. Ammonium ions, being located on the exterior sphere of the polycerium molybdate, are capable of interchanging with other cations — frequently for Ag^+ and ions of trivalent rare-earth elements. The resulting compounds are difficult to dissolve in mineral acids.[432] Their complex character is emphasized by the fact that they do not produce a reaction in Ce^{4+} with hydrogen peroxide; oxalic acid changes this compound into cerium oxalate incompletely and only after boiling.

Komarovskii and Korenman[239] produced a compound of the type $(NH_4)_3$ $[MeMo_7O_{24}] \cdot 12H_2O$ (where Me = La or Ce).

IV. 5B-11. Ammoniates

Complex ammoniates of rare-earth elements can be produced[80, 125, 21] in a medium of liquid ammonia, or by means of uninterrupted hours-long passage of a stream of ammonia through a solution of $Me(NO_3)_3$ with a somewhat raised temperature (~40°). A crystalline substance of composition Me $[(NH_3)_6]$ NO_3 is produced.

In 1955 Popov and Wendlandt[371] discovered a barely stable complex compound of divalent samarium with ammonia. A batch of dehydrated $SmCl_3$ was placed in a porous glass filter, in a special closed system, and cooled by solid CO_2. The surface of the batch was covered with a solution of sodium and liquid ammonia, and for several minutes the solution was filtered. The sodium residue was removed by repeated scrubbing with ammonia. The reaction product, a solid substance of a red-brown color, was heated to room temperature in atmospheric nitrogen. In air it rapidly lost the ammonia, and this guaranteed, apparently, that it was connected with the oxidation of Sm^{2+} to Sm^{3+} and the breakdown of the complex ammonia. One may assume that the compound had a composition of $[Sm(NH_3)_4]$ Cl_2; however, because of insufficient stability it could not be analyzed.

Vickery[506, 507] has convincingly demonstrated the existence of a hexammino scandium cation in aqueous solution. The stability of the complex is sufficiently great so that the precipitation of scandium as oxalate or hydroxide from solutions containing ammonium ion is seriously interfered with.

IV. 5C. COMPOUNDS WITH ORGANIC ADDITIVES

IV. 5C-1. Carboxylic Acids

In the domain of organic substances, acids seem to be one of the strongest complex-forming agents for rare-earth elements. It is noteworthy that the structure of the resultant complex compounds depends in a significant degree on the structure of the acid; i. e., on length of hydrocarbon chains, basicity, and relative position of functional groups.

Simple carboxylic acids do not present special interest. The first members of this series, although they do form complex compounds, exhibit insignificant stability in solution; and acids with a hydrocarbon chain of 10 to 15 atoms produce only salts difficult to dissolve in water. We will mention only a few of their representatives.

IV. 5C-1(a). Acetic Acid, $CH_3 - \overset{O}{\overset{\|}{C}} - OH$. Ammonium acetate produces complex compounds, but they are unstable and exist only in a significant excess of reagent. In these circumstances the complex compounds are not broken down under the action of $K_4[Fe(CN)_6]$. Weinlandt and Henrichson[514] found that upon addition of nitric acid to cerium acetate solution, a complex cationic species is formed containing three atoms of cerium and three radicals of acetic acid: $[Ce_3(CH_3COO)_3](NO_3)_6 \cdot 13H_2O$. There were also precipitated complex compounds in which the anion consisted of perchlorate, chromate, or picrate.

Canneri[69] produced complex cerium acetates in which three supplementary valencies in the inner sphere were taken by three molecules of urea: $[Ce(CH_3COO)_3] \cdot 3CO(NH_2)_2]$.

In 1950, Vickery[497] discovered complex compounds having, in their inner spheres, acetate ions and molecules of ammonia: $[Me_3(CH_3COO)_3 \cdot (NH_3)_3](SO_4)_3 \cdot xH_2O$ (where Me = Pr, Nd, Sm). He did not succeed in forming similar compounds for La, Ce^{3+}, and Ce^{4+}. The complexes were produced during fractional crystallization of the double sulfates of rare-earth elements from an ammonium-acetate solution in the presence of H_2SO_4 and HCl; the emergence of similar complex compounds interrupted the normal course of crystallization. Solutions of this compound with neodymium, according to the observations of the author, exhibited a blue fluorescence under a mercury lamp – a characteristic which may be utilized for qualitative determination of neodymium.

Seaton[428] has made a very thorough investigation of the behavior of neodymium and, to a lesser extent, yttrium in acetic acid solution; and Sonesson[444] has determined the complexity constants of the acetate complexes of La^{+3}, Ce^{+3}, Nd^{+3}, and Gd^{+3}.

The study of the characteristics of acetate complexes has practical interest. For example, when precipitating various rare-earth elements by electrolytic methods in acetic acid, knowledge of the composition of the resultant compounds, and their composition as a function of the pH of the solution, aids in the correct choice of electrolytical conditions.[398]

IV. 5C-1(b). Stearic Acid, $CH_3(CH_2)_{16} - \overset{O}{\overset{\|}{C}} - OH$. Rare-earth elements with this acid create only salts poorly soluble in water.

IV. 5C-1(c). Oxalic Acid, HOOC – COOH. The introduction of a second COOH-group into a molecule of a restricted acid, especially in the α-position, increases stability of the complex compound.[480] With increase of space between the COOH groups, the tendency toward complex-formation diminishes. For example, at a distance of only 7 to 8 atoms of carbon between carboxyl groups, complex compounds are no longer formed with elements of the yttrium subgroup.

The first member of the series of dibasic carboxylic acids – oxalic acid – forms a somewhat stable complex compound with succeeding members of the group of rare-earth elements. This explains their loss when precipitating a mixture of these elements with ammonium oxalate. Complex compounds are formed which appear to have the composition $(NH_4)_3[Me(C_2O_4)_3]$.

Orlov,[348] studying oxalates of rare-earth elements, found that cerium in higher valencies is capable of forming complex oxalates. This characteristic has often been utilized[399] for separating out cerium from a mixture with other rare-earth elements. The oxalate mixture is dissolved in hot H_2SO_4, diluted with water, and poured into a great abundance of ammonium oxalate. The solution takes on a dark orange color as a result of the formation of a complex cerium oxalate, and all the remaining elements of this group are precipitated in the residue which contains an insignificant admixture of trivalent cerium. This residue is rapidly filtered out; Ce^{4+} remains in the solution and appears to have the form of a complex compound of type $(NH_4)_2[Ce(C_2O_4)_3]$ or $(NH_4)_4[Ce(C_2O_4)_4]$. When standing, the filtrate loses color due to reduction of the cerium which in the residue has become $Ce_2(C_2O_4)_3$. To speed the process of reduction of the cerium, Na_2SO_3 is added to the solution and the mixture is heated.

Crouthamel and Martin[96, 97] have proven the existence of complexes of the form $RE(C_2O_4)^+$ and $RE(C_2O_4)_2^-$ for Yb and Nd, and, in addition to the mono- and di-oxalate complexes, a species of the form $RE(C_2O_4)_3^{-3}$ for Y and Ce^{+3}.

Brezhneva and co-workers[45] studied the carrying of cerium and yttrium on calcium oxalate. They found that at high oxalate concentrations the ef-

ficiency of carrying decreased with increasing oxalate concentration. This effect they ascribe to the formation of complex oxalates.

Vickery[507] has reported the preparation of an anionic scandium oxalate complex that would not stick to cation exchange resins but he gives no formula; presumably it is $Sc(C_2O_4)_3^{-3}$.

IV.5C-1(d). Malonic Acid, $HOOC - CH_2 - COOH$. When mixing solutions of ammonium malonate and salts of cerium group elements (La, Ce, Pr), a powdery residue rapidly precipitates which is soluble in an excess of reagent. However, after 20 to 30 minutes well-formed spicule-shaped crystals are deposited from the transparent solution and joined in a druse reminiscent of needles and spheres. The transparent solution (until precipitation of the crystalline residue) produces a negative reaction on an ion of the rare-earth element with the solution $K_4[Fe(CN)_6]$, which indicates the formation of a complex compound.

During interaction of yttrium and erbium salts with ammonium malonate, no precipitate is formed. Addition of solutions of $K_4[Fe(CN)_6]$ or NH_4OH does not induce deposit of a precipitate; KOH precipitates $Er(OH)_3$, but it does not precipitate $Y(OH)_3$. Addition of $(NH_4)_2C_2O_4$ immediately deposits the precipitate of the oxalates of both elements. Introduction into the solution of a significant excess of ammonium malonate does not strengthen the complexes. It is interesting to note the fact that with the passing of time crystals begin to deposit from the transparent solutions. Chemical analysis shows these residues to be of the general formula $Me(C_3H_2O_4)\cdot nH_2O$, i.e., a simple malonate of rare-earth elements. Gelles and Nancollas[167] have studied solutions of malonates of rare-earth elements by electrochemical methods and have come to the conclusion that the subject elements definitely form complex malonates. As one of the possible formulas for these compounds the authors consider $[MA]^+$ (where A^{2-} is the anion of the malonic acid).

IV.5C-1(e). Succinic Acid, $HOOC - (CH_2)_2 - COOH$. When pouring together a solution of ammonium succinate and solutions of the salts La, Ce, and Pr, an amorphous residue is deposited which then dissolves. With a longer period, crystals begin to precipitate in the form of spicules. If an excess of a salt of a rare-earth element is added to the ammonium succinic acid solution, there is an immediate deposition of a hard-to-dissolve precipitate. For elements of the yttrium subgroups (Y, Er), a somewhat different result is obtained. When flowing a solution of succinic acid in excessive quantity into a solution containing yttrium or erbium salt, initially no residue is deposited and the solution remains transparent. When experimenting with this solution in NH_4OH and $(NH_4)_2C_2O_4$, the characteristic residues of hydroxides and oxalates of

these elements are rapidly deposited; under the action of $K_4[Fe(CN)_6]$, the residue is precipitated – not immediately, but after a few minutes. If the original transparent solution remains standing, then gradually (more rapidly for Y than for Er) a crystalline residue of simple salt begins to precipitate.

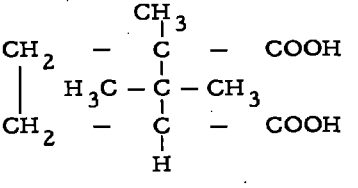
IV.5C-1(f). Glutaric Acid, $HOOC-(CH_2)_3-COOH$. During interaction of a solution of the ammonium salt of glutaric acid with a solution of $Y(NO_3)_3$, no residue is formed. From the clear solution under action of NH_4OH and $(NH_4)_2C_2O_4$, a precipitate is deposited. $K_4[Fe(CN)_6]$ does not create a precipitate. These qualitative experiments exhibit that here a complex compound is formed which is stable in solution.

IV.5C-1(g). Adipic Acid, $HOOC-(CH_2)_4-COOH$. Upon interaction of ammonium adipinate with the salts La, Ce, Pr, Nd, and Sm, crystals of residue are deposited immediately in the form of long spicules which are not soluble in an abundance of reagent. With salts of elements in the yttrium subgroup, the residue is not obtained immediately; but after the solution has stood for a time, the crystals are deposited in the form of rhombohedrons. Under the action of $K_4[Fe(CN)_6]$ on the clear solution, the mixture deposits its characteristic crystalline residue of ferrocyanide rare-earth elements after a few minutes. With NH_4OH and $(NH_4)_2C_2O_4$, the precipitate is formed immediately. It follows that the resultant complex compounds possess insignificant stability.

IV.5C-1(h). Pimelic Acid, $HOOC-(CH_2)_5-COOH$. Upon action of ammonium pimelic acid on the solution $La(NO_3)_3$, a fine, crystalline residue is deposited which is not soluble in abundant reagent. For $Y(NO_3)_3$ there is a different behavior: At first the residue is not formed, but after several minutes crystals separate whose form differs from crystals of lanthanum salt.

IV.5C-1(i). Azelaic Acid, $HOOC-(CH_2)_7-COOH$, and Sebacic Acid, $HOOC-(CH_2)_8-COOH$. Ammonium salts of the highest homologous series of dibasic acid (azelaic and sebacic), during interaction with the salts of cerium and yttrium subgroups, immediately produce an abundant finely-crystalline precipitate which is insoluble in excess reagent. This precipitate is composed of the simple azelaics and sebacics of rare-earth elements.

IV.5C-1(j). Camphoric Acid has the structural formula

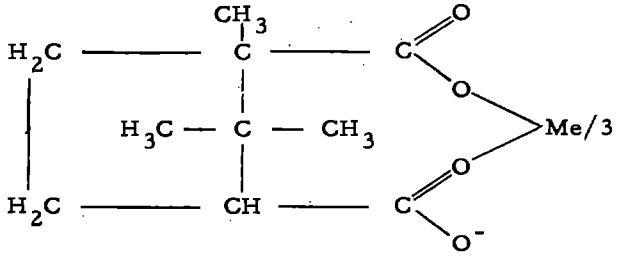


The d-Camphorates of rare-earth elements are prepared[105] by double decomposition of aqueous solutions of their chlorides and sodium camphorate.

According to the degree of increase of the latter, the voluminous amorphous deposits which have become colored are precipitated characteristically for ions of rare-earth elements. They form a powder which does not melt when heated to 300°C.

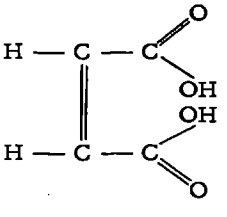
Chemical analysis data correspond to the general formula $Me_2(C_{10}H_{14}O_4)_3$, i.e., the formula for simple camphorates. At 20°C the camphorates are soluble in water; their solubility decreases in the series Nd, Pr, Ce, and La, and lessens with increase of temperature. Upon heating of an aqueous solution, hydrolysis occurs with the formation of subsalts. In organic solvents camphorates are practically insoluble.

Regrettably, the authors[477] did not examine the capability of camphoric acid in the role of a complex-forming agent. In view of the fact that camphoric acid is able to produce inherent anhydrides, we might reasonably expect that it is capable of forming complex compounds (although perhaps not very stable ones):

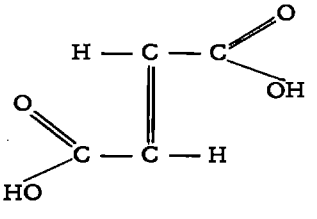


Complex compounds of rare-earth elements with dibasic organic acids possess one interesting peculiarity: they decompose in the course of time, producing a simple salt (of the appropriate acid) that is hard to dissolve in water. This process of decomposition takes place more rapidly for elements of the cerium subgroup which form less stable complex compounds, and takes place more slowly for elements of the yttrium subgroup. This rule is observed for malonic, succinic, adipic, and pimelic acids.

IV. 5C-1(k). Maleic and Fumaric Acids. The most important unsaturated dibasic acids are the β-dicarboxylic acids. The best studied are the first representatives of this series, namely maleic and fumaric, which are stereoisomers:



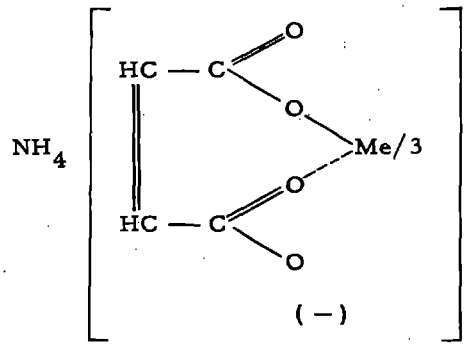
cis-form
(maleic)



trans-form
(fumaric)

Under the action of various factors (temperature, light, hydrogen ion, etc.), the less stable maleic acid converts to the more stable fumaric acid.

Upon interaction of $La(NO_3)_3$ with ammonium maleate, no external changes occur; however, the experiments indicated that, in the resultant solution, La^{3+} is not detected by the action of $K_4[Fe(CN_6)]$ and NH_4OH. This indicates that a complex compound was formed. If one runs a solution of ammonium fumaric acid into a solution of $La(NO_3)_3$, a crystalline deposit is laid down which is insoluble in excess reagent. This fact might be explained in the following manner. Maleic acid (in the same way as dibasic saturated acids) produces, with rare-earth elements, soluble complex compounds of the type



Fumaric acid possesses no capability of forming complex compounds, and in its case the hard-to-dissolve simple salts are deposited rapidly. When it stands (or is heated) in the presence of HBr, there occurs a gradual conversion of the easily soluble complex maleinates of the rare-earth elements in the hard-to-dissolve salts of the fumaric acid.

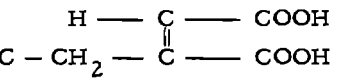
IV. 5C-1(*l*). Citraconic Acid, $CH_3 - C(COOH) = C(COOH) - H$, like maleic acid, has the cis-form. It is easily converted into the trans-form which is mesaconic acid. In regard to the salts of rare-earth elements, citraconic acid acts similarly to maleic — creating water-soluble complex compounds which do not decompose under the action of $K_4[Fe(CN_6)]$ and NH_4OH. One may assume that, under the action of known agents, the soluble complex compounds of citraconic acid will revert into hard-to-dissolve mesaconics of rare-earth elements.

Tribasic carboxylic acids create significantly more stable complex compounds than do the dibasics.

IV. 5C-1(m). Tricarballylic Acid, $CH_2(COOH) - CH(COOH) - CH_2 - COOH$, with rare-earth elements forms a precipitate which is dissolved by further addition of the acid in large quantities. It is remarkable that salts of elements of the yttrium subgroup are easier to dissolve than salts of the cerium

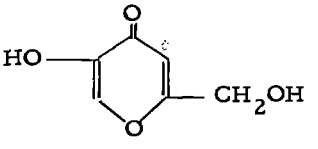
subgroup. In the transparent solutions produced, rare-earth elements do not appear under the action of $K_4[Fe(CN)_6]$ and NH_4OH, and with the addition of $(NH_4)C_2O_4$ only a slight opalescence is created. When acidifying this solution the stability of the complex decreases.

IV. 5C-1(n). Aconitic Acid.

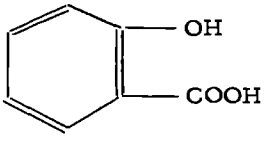


Aconitic acid is an unsaturated tribasic acid of the cis-series. Pouring a solution of its ammonia salts into a solution of rare-earth-element salts (La, Y) causes a residue to be deposited which is soluble in excess reagent. In the solution a complex compound is created which is not decomposed under the action of $K_4[Fe(CN)_6]$ and NH_4OH; ammonium oxalate causes only a slight opalescense. This example again confirms the fact that acids of the cis-form produce complex compounds soluble in water.

IV. 5C-1(o). Kojic Acid. Musante[325] reports that kojic acid (see structural formula below) precipitates La, Pr, Nd, and Sm from solution essentially completely but does not indicate any complex formation.

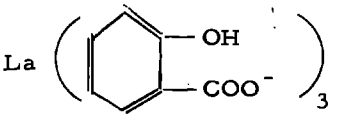


IV. 5C-1(p). Salicylic Acid (see below) has been reported[134] to form compounds of the type $La(Sal)_3$, and Sudarikov, Zaytsev and Puchkov[469] have succeeded in extracting salicylate complexes of several rare earths into iso-amyl alcohol.

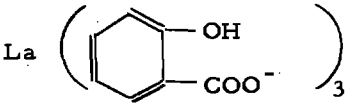


In this medium, scandium exhibits the interesting property of being essentially completely extracted in the pH range 3.5 to 6 but not extracted at all at pH's greater than 7.5. All the other rare earths are extracted completely at all pH's above 6.

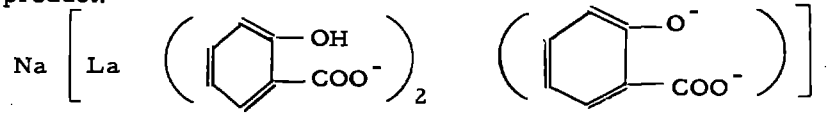
Fialkov and Ermolenko[135] have recently published a paper on the lanthanum salicylate complexes and their dissociation constants. The "normal" lanthanum salicylate salt



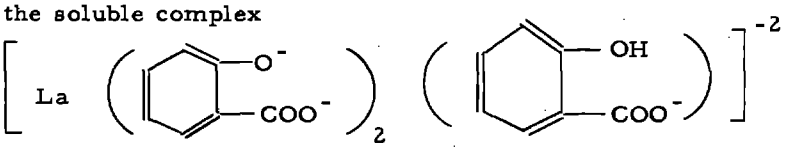
is relatively insoluble (the authors report that the La^{+3} concentration in 0.05M sodium salicylate solution is 3.7×10^{-8}M) and lanthanum salicylate does not dissolve in an excess of sodium salicylate. When the pH is raised to the point where the phenolic hydrogen is dissociated, however, three distinct complexes can be formed. Addition of one mole of NaOH to one mole of



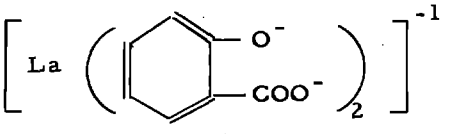
gives the product:



which is also quite insoluble (3.5×10^{-3} mole/l). Addition of a second mole of NaOH gives the soluble complex



or the somewhat less soluble



IV.5C-2. Hydroxycarboxylic Acids

The presence in carboxylic acid of the OH group, especially in the α position to the COOH group, notably strengthens its character as a complex-forming agent.

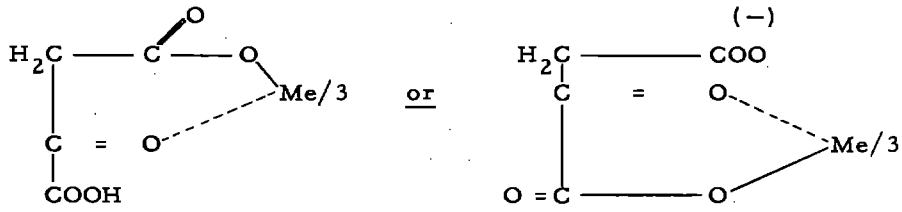
IV.5C-2(a). Glycolic Acid, $H_2C(OH) - COOH$, which differs from acetic acid only by the presence of an OH-group, combines with elements of the cerium and yttrium subgroups to form complex compounds, more stable than acetates, which do not decompose under the action of either $K_4[Fe(CN)_6]$ or NH_4OH. Sonesson[445, 446] has made a very detailed study of the glycolate rare-earth complex system, and has found that anionic rare-earth glycolate complexes exist. Complex glycolates can be utilized for separation of rare-earth elements.[458] It is noted that glycolic acid permits, in specific conditions, the same degree of separation as citric acid, and has some advantages over the latter: Its complexes are less sensitive to change of the pH of the solution,

it is more stable in aqueous solutions, and it can be well-preserved for weeks, not changing pH and not losing its eluant property.

IV. 5C-2(b). Lactic Acid, $H_2C - \underset{\underset{H}{|}}{\overset{\overset{O}{|}}{CH}} - COOH$. In 1913 Jantsch[218] described compounds with lactic acid. The complex character of these compounds has been supported by electroconductivity measurements of their aqueous solutions. During interaction of a solution of salts of rare-earth elements with ammonium lactate, in the same way as with ammonium glycolate, no visible change occurs and the solution remains transparent — although in the resultant solution, under action of $K_4[Fe(CN)_6]$ and NH_4OH, no Me^{3+} ions are detected. If the transparent solution containing a mixture of ammonium lactate and rare-earth element salt is allowed to stand, after 15 to 20 minutes a crystalline residue is deposited. In this characteristic, lactic acid is reminiscent of analogous compounds with dibasic acids — malonic, succinic, and adipic. Recently, lactates have begun to be used successfully for separating mixtures of rare-earth elements.[334, 536]

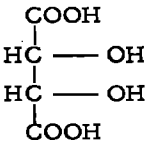
IV. 5C-2(c). Amygdalic Acid, $C_6H_4(OH)CH_2COOH$, with rare-earth elements forms simple salts of composition $Me(C_8H_7O_3)_3 \cdot nH_2O$ (where n = 2, 3), which differ from each other significantly in solubility. Solubility of these salts depends strongly on the pH of the solution and its temperature. This fact was exploited by Weaver[511] for separation of mixtures of rare-earth elements and likewise for Y-removal from heavy elements of the rare-earth group. In Weaver's work there is no mention of the fact that salts of amygdalic acid form complex compounds with rare-earth elements; however, it seems to us that such possibility is not excluded.

IV. 5C-2(d). Oxalacetic Acid. Rare-earth elements form complex oxalacetates which are somewhat stable in solution.[168, 127] The hypothesis is expressed that they can exist in two forms:



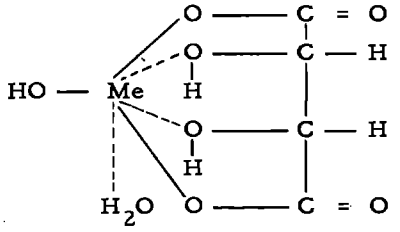
IV. 5C-2(e). Tartaric Acid (see below) and its salts are widely used in analytical chemistry for complexing ions of various heavy metals. During inter-

action of alkaline salts of tartaric acid with rare-earth elements, there is



formed a complex compound of a significant stability which does not decay under the action of $K_4[Fe(CN)_6]$, NH_4OH, and $(NH_4)_2C_2O_4$.

The process of forming tartaric-acid complex compounds takes place in two stages: 1) formation of an intermediate salt that is hard to dissolve in water, and 2) dissolving of the intermediate salt in excess alkali tartrate. For erbium, in particular, the intermediate salt is a powder of a rose color that is characteristic of all simple erbium salts. Its composition corresponds to $Er_2(C_4H_4O_6)_3 \cdot 8H_2O$. The salt is difficult to dissolve in water, but dissolves easily in excess ammonium tartrate and forms a complex compound. The latter can be deposited from the solution (after removal of NH_4Cl) by the addition of ethyl alcohol. An oily liquid is formed which, after evaporation of the alcohol, hardens into a glassy mass. Complex tartrates, with properties very close to those of complex citrates, are sometimes used in the role of an eluant when separating mixtures of rare-earth elements on ion exchangers.[164] As regards the structure of complex tartrates, one may assume that it will be analogous to the structure of the complex tartrate of indium produced by Cozzi and Vivarelli:[91]

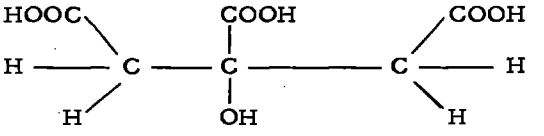


IV.5C-2(f). Mucic Acid, $HOOC-(CHOH)_4-COOH$. Upon interaction of ammonium mucic acid with salts of rare-earth elements, a simple salt is formed which, upon addition of reagent, dissolves due to formation of a complex compound. The resultant solution, as in the case of complex tartrates, does not react with known reagents. However, if ammonium oxalate is poured into the solution, in time there will be spontaneously deposited oxalate of the rare-earth element; acidification of the solution speeds decay of the complex compound and deposit of the residue.

IV.5C-2(g). Saccharic Acid. It is interesting to note that saccharic acid, which is a stereoisomer of mucic, does not form soluble complex compounds with rare-earth elements. During interaction of sodium saccharate with

lanthanum, neodymium, and yttrium salts, a copious powdery residue is formed which is not soluble in excess precipitant.

IV. 5C-2(h). Citric Acid is a tribasic oxy acid of the saturated series



In a molecule of this acid, one has the very fortunate union of three carboxyl groups and one hydroxyl group. When citric acid acts on a solution of salts of rare-earth elements, no visible change occurs;[395] but if one pours a solution of citrate salts into a solution of the salts of the cerium group, a precipitate is rapidly deposited which is difficult to dissolve in water but easy to dissolve in abundant alkali citrate. In the case of Sm and its succeeding elements, no precipitate is observed. When testing the transparent solutions produced in both mentioned cases by a series of precipitants, one fails to obtain precipitates of rare-earth elements. In alkaline solution, even under the action of NH_4F, no fluorides of rare-earth elements are deposited. Therefore, only a very stable complex compound is created in the solution. The process of complex-compound formation takes place in two stages:

1) formation of an intermediate salt difficult to dissolve in water,

$$(C_6H_5O_7)^{-3} + Nd^{+3} = NdC_6H_5O_7 ;$$

2) dissolving of the intermediate (precipitated) salt in excess sodium citrate, with formation of the complex compound

$$NdC_6H_5O_7 + (C_6H_5O_7)^{-3} = [Nd(C_6H_5O_7)_2]^{-3}.$$

The resultant HCl is driven off by evaporation in a water bath, and the residue is diluted with water. The resultant solution is carefully neutralized with a solution of KOH. This neutral solution is processed with 4 to 5 times its volume of ethyl alcohol. A heavy, oily fluid of a rosy hue separates. The upper layer is decanted, the alcohol is evaporated, and the syrupy mass of residue is dried in a desiccator. After a few hours, it is converted into a transparent, fragile product. Analytical data conform to the formula $K_3[Nd(C_6H_5O_7)_2]_2 \cdot 3H_2O$. This same salt can be produced by interaction of a determined quantity of $NdCl_3$ and citric acid salts, with further addition of ethyl alcohol.

Ammonium salt is produced by the neutralization of $H_3[Nd(C_6H_5O_7)_2]$ with a solution of ammonia gas, the residue of which is driven off by heating. Calcium salt of composition $Ca_3[Nd(C_6H_5O_7)_2]_2 \cdot 3H_2O$ is formed upon addition of a $CaCl_2$ solution to the above-described complex compounds. During processing of the reaction mixture by alcohol, calcium salt is deposited in

the form of a powdery residue. It is worthy of note that the $Ca_3[La(C_6H_5O_7)_2]_2$ compound is significantly less soluble than a compound of other elements of the cerium group. It is precipitated directly from an aqueous solution, without addition of alcohol.

In the outer sphere of complex citrate compounds one may produce all kinds of interchanges; in particular, ammonium and alkali metal ions can easily be replaced by ions of rare-earth elements: $Ce[Nd \cdot (C_6H_5O_7)_2]$. This salt is a crystalline substance of a light rose color. It is difficult to dissolve in alcohol, but markedly soluble in solutions of citric acid and its alkaline salts. In the latter case, a mixture of complex citrate compounds of cerium and neodymium is produced in solution.

The existence of a stable complex of $[Me(C_6H_5O_7)_2]^{3-}$ in the solution is demonstrated by a series of methods. Thus, when passing a fixed current through a solution of the citrate complex for a certain time, in the anode region a flocculent residue is formed as a simple citrate of a rare-earth element. This indicates that the rare earth-citrate complex is negatively charged. Under the action of an electric current it heads for the anode; here, the complex decomposes and forms a simple citrate of the rare-earth element. Polarographic investigation of the solutions of complex citrates established that the complex possesses significant stability. In the presence of the citrate ion, the half-wave characteristic for ions of rare-earth elements was not detected. When neutral solutions of complex citrates were passed through a column with a cation exchanger, the complex ion was not absorbed.

All this indicates that ions of rare-earth elements form a complex with citrate ions, carrying a negative charge and possessing significant stability in solution; under these conditions, rare-earth elements possess a coordination number equal to six. Here it is interesting to note the influence of ion radius on complex-forming properties of rare-earth elements. According to the findings of Ketelle and Boyd,[226] a specific succession in absorption capability (at a specific pH) occurs in the presence of a citrate-ion:

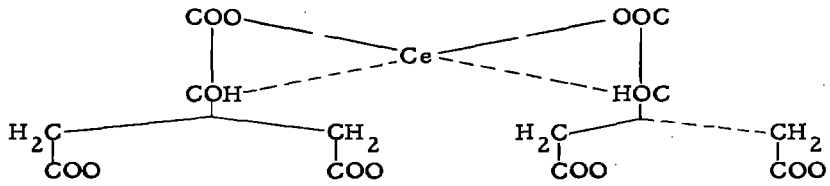
$$La > Ce > Pr > \text{------} > Dy > Y > Ho \text{------} > Lu.$$

This series exactly coincides with the decreasing order of the size of ionic radii of these elements. It therefore follows that the stability of complex citrates increases with decreasing ion radii of rare-earth elements.

In 1955 Bobtelsky and Graus[35] published a study of complex citrates of trivalent cerium. The investigations were made by the heterometric method. A solution of $Ce(NO_3)_3$ was titrated by a solution of $Na_3C_6H_5O_7$ (abbreviated Na_3Citr). The maximum optical density was found at the molar ratio $[Ce] : [Citr] = 1 : 1$. Upon attaining the ratio of $[Ce] : [Citr] = 2 : 3$, the precipitate dissolved with formation of $[Ce_2Citr_3]^{3-}$. With further addition of

Na_3Citr the complex changed into $[CeCitr_2]^{3-}$, likewise soluble in water. Upon addition of a $Ce(NO_3)_3$ solution to the complex thus created, a precipitate was deposited. The precipitated substance was either $Ce(CeCitr_2)$ or $Ce\ [Ce_2Citr_3]$; it was impossible to establish which as they both have the composition $[CeCitr]^0_n$.

Data of the heterometric method were supported by the conductometric method of titration and by measurement of the pH. The authors proposed a whole series of structural formulae for the citrate complexes discovered, in particular for $[CeCitr_2]^{3-}$:



In this structural formula the coordination number for trivalent cerium was taken to equal four.

Complex citrates have found a wide usage for separation of mixtures of rare-earth elements by ion exchange.[226, 220, 448, 450, 374, 10]

IV.5C-3. Amino Acids

When glycine, $CH_2(NH_2) - COOH$, and α-alanine, $CH_3 - CH_2(NH_2) - COOH$, act on lanthanum and erbium salts in solution, no visible change occurs.[396] However, a negative reaction on La and Er with ammonia indicates that a complex compound is formed.

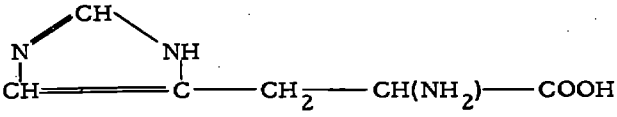
In the case of aspartic acid, $HOOC - CH_2 - CH(NH_2) - COOH$, the following phenomena are found: In the first moment after mixing the solution, its ammonium salt and the solutions of lanthanum and erbium salts form a precipitate which disappears with further addition of reagent. $K_4\ [Fe(CN)_6]$ and NH_4OH do not induce precipitation, and $(NH_4)_2C_2O_4$ creates opalescence. It seems that in this case a fairly stable complex compound is formed.

When α-glutamic acid, $HOOC - CH(NH_2) - (CH_2)_2 - COOH$, reacts with salts of lanthanum and neodymium, there is formed a flocculent precipitate soluble in an excess of precipitant. Upon interaction of the resultant transparent solutions with $K_4\ [Fe(CN)_6]$, residue is not deposited and under the action of ammonia a slight precipitate is formed.

The first of the amino acids of the aromatic series is anthranilic acid, $(o\text{-}NH_2 \cdot C_6H_4) - COOH$, which forms, with salts of rare-earth elements, an abundant curdled deposit that is very difficult to dissolve even in abundant precipitant. When these residues are washed with water they become crystals. After baking at 85-90°C the crystals take a reddish tone.

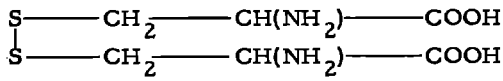
The ammonium salt of phenyl-anthranilic acid forms with the salts of lanthanum, cerium, and erbium, a voluminous residue of greenish hue which darkens when heated. The residue is not soluble in an excess of reagent.

In 1950 Vickery[498, 501] studied the process of interaction of salts of rare-earth elements with amino acids and came to the conclusion that, of all the amino acids, only histidine,



and glycine are capable of reacting with hydroxides of rare-earth elements in neutral or ammonium solutions to produce complex compounds.

With cistine,



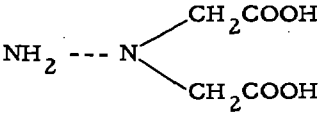
Vickery made the compound $Me_2(C_6H_{10}O_4N_2S_2)_3$, which appears as a monoclinic rosette; with glutamic acid, $Me_2(C_5H_7O_4N)_3$, which forms in plates of rhombic shape; and with aspartic acid, $Me_2(C_4H_5O_4N)_3$, which forms monoclinic prisms.

Vickery writes that he discovered two types of coordination between rare-earth elements and amino acids. If an excess quantity of hydroxide of a rare-earth element is mixed in an aqueous solution of glycine or histidine, and the excess hydroxide is filtered out, then fractionating with the help of oxalic acid causes separation in normal sequence: i.e., first, elements with the larger atomic numbers, and then, those with the smaller numbers (there are some deviations from this sequence, however, which are related to solubility of the oxalates of the rare-earth elements). If amino acids are added in corresponding excess to a fully dissolved hydroxide, then, when fractionating the precipitate in the form of oxalates, in the first series to be deposited will be lanthanum, and after it will come elements in order of increasing atomic number. Data on analysis of the precipitated compounds are introduced, and are the basis of formulae for the "complex" compounds with glycine, $Me(NH_2 \cdot CH_2COO)_3$, and histidine, $Me(C_6H_8O_2N_3)_3$. Moeller,[316] in referring to the above-noted work of Vickery, writes that the mentioned compounds with amino acids have the character of salts rather than complex compounds, with which one may fully agree. Evidently the process of interaction of these two components takes place in two stages. When dissolving the excess quantity of $Me(OH)_3$ in amino acid, a simple salt of amino acid with the rare-earth element if formed. This salt dissolves well in water. Naturally, with the introduction of $C_2O_4^{2-}$ ions into the solution, oxalates of rare-earth elements begin to precipitate in normal order; i.e., beginning with the very "heaviest." If the excess amino acids are now removed, a compound of interior-complex type is formed (also easily soluble in water); its solution

does not produce the characteristic reactions on Me^{3+} with such precipitators as $K_4[Fe(CN)_6]$ and NH_4OH. With the introduction into the solution of $C_2O_4^{2-}$ ions the reverse order of depositing oxalates of rare-earth elements is found. The depositing begins with oxalate of lanthanum – the element being the least weakly complex-forming of the rare-earth series.

IV. 5C-4. Aminopolyacetic Acids

The aminopoly acids in which more than one CH_2COOH group is attached to one nitrogen atom (i.e., the aminopolyacetic acids of the amino diacetic type $RN(CH_2COOH)_2$, nitrilotriacetic type $N(CH_2COOH)_3$, etc.) form significantly more stable complex compounds than simple amino acids.[423, 285] Fitch and Russell[143] studied complex compounds of rare-earth elements with hydrazinodiacetic, benzyl iminodiacetic and o-carboxy aniline – NN-diacetic acids. Hydrazino-NN-diacetic acid,



(abbreviated HA)

was first used by the authors[144] in the role of an eluant when separating La from adjoining elements. Vickery[503] showed that stable complex compounds are produced at the ratio Me: HA = 1: 3. He found that these compounds are unstable in acid, but stable in neutral and alkaline media. Thus, when $pH \leq 6$, solutions of these give absorption spectra characteristic for ions of Me^{3+}; and when $pH > 6$, the spectra are analogous to spectra of complex compounds with "complexons."

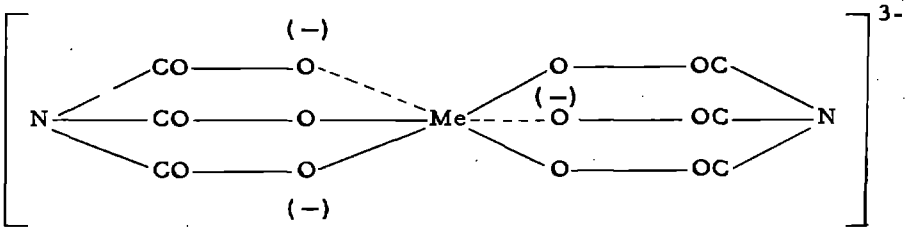
IV. 5C-4(a). Nitrilotriacetic Acid (TRILO). The first complexons were produced by Schwarzenbach[422] in 1945 and since that time they have found ever wider usage in preparative and analytical chemistry. Beck[19-21] discovered that nitrilotriacetic acid forms stable complex compounds with rare-earth elements of type $[Me\{N(CH_2COO)_3\}_2]^{3-}$. He isolated a hard-to-dissolve double compound

$$[Co(NH_3)_6]\ [La\{N(CH_2COO)_3\}_2].$$

In the presence of precipitating agents such as oxalate or fluoride, these complexes exist only in media with pH higher than certain minima. The more stable the complex, the lower the pH at which it can exist. Beck used the following values of pH in order to induce precipitation of the oxalates: La - 6.0; Pr, Nd - 5.5; Sm - 5.0; Gd - 4.5; Er - 4.0. This relationship is widely used when separating mixtures of rare-earth elements.[397, 272]

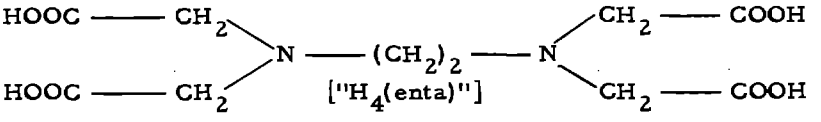
Boulanger[43] prepared a series of mixtures of $Pr_2(SO_4)_3$ with sodium nitrilotriacetate, and then added ammonium oxalate. The precipitate appeared only during the ratio Pr^{3+}: TA > 2, where TA is nitrilotriacetate. On this basis Boulanger proposed the theory that the composition of this complex com-

pound must correspond to the formula $[Pr(TA)_2]^{3-}$, i.e., the formula suggested by Beck. Evidently the structural formula of this compound can be depicted as:



As in all the above-described compounds, the rare-earth elements have a coordination number equal to six.

IV. 5C-4(b). Ethylenediaminetetraacetic Acid (EDTA)



and its ammonium salt have been widely used in the separation of mixtures of rare-earth elements. The rare earth-EDTA complexes are exceptionally stable; and Betts and Dahlinger,[28] in a thermodynamic study of these complexes, attribute this stability to a large positive increase in entropy which occurs when the complex is formed.

Brunisholz et al.[54] got complex compounds of type $Na[La(enta)]\cdot xH_2O$ by interaction of a solution of $LaCl_3$ with $Na_4(enta)$. Tri-, hexa-, octa-, and nona-hydrates were isolated. The first were crystallized at 50°C in the form of prisms, the second were in the form of spicules (conditions of their formation were not established), the third were at 35°C in the form of pyramids, and the last were at 25°C in the form of plates. The complex compounds Ce, Pr, Nd, and Sm crystallize only in the form of octahydrates. The crystals have the form of orthorhombic pyramids and possess piezoelectric characteristics. When hydrates are heated, they easily lose water. Anhydrous compounds are stable up to 350°C. Brunisholz also separated complex compounds of the type NH_4 [Me(enta)] for La, Ce, Pr, Nd, Sm, Gd, and Dy, and studied their various crystalline forms.

Complex compounds of the type H [Me(enta)]$\cdot xH_2O$ were obtained by Moeller, Moss, and Marshall[319, 289] from interaction of H_4(enta) with an aqueous suspension of Me_2O_3. The reaction takes place at room temperature when the mixture is shaken. If solutions containing H [Me(enta)] (where Me = Nd, Sm) and other rare-earth elements of the cerium group are allowed to stand at room temperature for several days, or are heated in a water bath for several hours, a finely crystalline residue is precipitated.

In the Y case no precipitation of crystals is found. This difference in the characteristics of compounds in the cerium and yttrium groups of elements can be utilized for their separation. Data of the chemical analysis of the crystals indicate the formula $Me\,[Me(enta)_3]_3 \cdot yH_2O$; the magnitude of the y coefficient was not determined. There was no success in producing anhydrous compounds. Sodium salts are easily obtained by neutralization of H [Me(enta)] with alkali, and concentration by evaporation until crystallization. Salts of type $Na\,[Me(enta)] \cdot zH_2O$ were gotten for Pr, Nd, Sm, Gd, and Y.

Brucine, strychnine, quinine, and cinchoninic salts of the acids H [Nd(enta)] and H [Y(enta)] were gotten by a direct reaction of free alkaloids with acids, taking place in equimolecular quantities in aqueous solutions with subsequent crystallization. The products of interaction of the Y salts with strychnine and brucine are crystalline; those of neodymium with strychnine, quinine, and cinchona are glasslike substances. A compound of Y with quinine and cinchona was obtained in the form of a gelatinous residue. The products were dried at 110-120°. Analysis of the compounds for brucine indicate the formula $C_{23}H_{26}N_2 \cdot H\,[Me(enta)]$.

On the basis of his investigations Moeller drew the conclusion that there are two types of complex compounds: one characterized by the relation Me: enta = 1: 1 (type I), and the other by the relation Me: enta = 4: 3 (type II). Compounds of type I can be considered as H [Me(enta)] acids, and compounds of type II as salts of rare-earth elements of the acid $Me\,[Me(enta)]_3$. One may produce compounds where Me in external and internal spheres will be different. In this case, in the internal sphere obviously there must exist the stronger complex-forming agent; and in the exterior, the weaker. For example, one may get the salt $La\,[Er(enta)]_3$, but it is impossible to get the salt $Er\,[La(enta)]_3$. This rule was utilized by Vickery[499, 500] for a unique method of separating rare-earth elements, based on the displacement of the more fundamental elements (Me_A^{3+}) by the less fundamental (Me_B^{3+})

$$[Me_A\ enta]^- + Me_B^{3+} \rightarrow Me_A^+ + [Me_B\ enta]\ .$$

Eckardt and Holleck[124] studied polarographically the capability of divalent europium to create complex compounds with ethylenediaminetetraacetic acid. As disclosed, on the mercury electrode in the acid medium, in the presence of the above-mentioned additives, there occurs simultaneously reduction of Eu^{3+} to Eu^{2+} and complex-formation.

IV. 5C-4(c). N-hydroxyethyl-ethylene diamine triacetic Acid (HEDTA), and

IV. 5C-4(d). 1, 2-diaminocyclohexanetetraacetic Acid (DCTA). Horwitz[206]

has studied the complexing behavior of the rare earths with several diaminopolyacetic acids and has obtained stability constant data for N-hydroxyethylethylene diamine triacetic acid (HEDTA) and 1, 2-diaminocyclohexanetetraacetic acid (DCTA), as well as EDTA. Stable complexes with a 1: 1 ratio of rare-earth metal to HEDTA and DCTA were prepared for Nd, Sm, Eu, Gd, and Y.

Ethylenediaminotetraacetic acid and its salts are very widely used for analysis of mixtures of rare-earth elements[18, 190] and separation of them.[1, 55, 57-60, 114, 175, 273, 287, 425, 451, 532] Recently there have appeared many reports[10, 202, 455] of new aminopolyacetic acids successfully being used in the role of complex-forming agents for rare-earth elements. It is appropriate to note the unusual similarity between rare-earth elements and calcium as complex-producers. Johnston[221] tested a series of organic acids of various classes in the role of complex-forming agents for calcium, especially H_4(enta), and discovered the very same mechanisms which have been disclosed for rare-earth elements.

IV. 5C-4(e). Diethylenetriaminepentaacetic Acid (DTPA). Harder and Chabarek[191] have made a very thorough study of the chelating behavior of the rare-earth elements with diethylenetriaminepentaacetic acid (DTPA). All of the rare earths form stable complexes containing one mole of rare earth to one mole DTPA. This reagent is quite unusual, however, in that the most stable rare earth-DTPA complex is formed by dysprosium. The curve of complex stability vs atomic number rises steadily from La to Dy and decreases slowly from Dy to Lu. The stability constant for yttrium falls between Nd and Sm, so DTPA looks most promising as an eluant for cation-exchange separation of Y-Dy mixtures.

IV. 5C-5. Compounds with Sulfo Acids

Toluenesulfonic acid does not form complex compounds with rare-earth elements. When solutions of its ammonium salts are added to the latter, no change occurs. Ions of rare-earth elements in the solution are immediately detected with the use of $K_4[Fe(CN)_6]$. Sulfanilic acid behaves similarly to toleunesulfonic acid.

Sulfo acids of the naphthalene series are divided into two groups according to their behavior toward rare-earth elements. To the first group belong the acids causing rapid deposition of hard-to-dissolve precipitates: α-naphthalenesulfo acid; 1, 3, 6-naphthalenetrisulfo acid; α-amino-β-sulfo acid; and β-anthraquinone sulfonic acid.

Members of the other group of acids, to which belong β-naphthalene sulfo acid, 1-amino-3, 5-disulfo acid, 2-oxi-3, 6-disulfo acid (R-acid), and

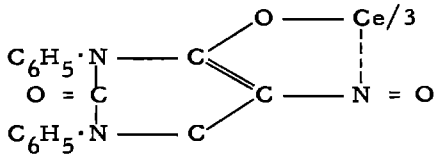
1-5-naphthalene disulfo acid, do not create precipitates, and also do not form complex compounds. Under the action of $K_4[Fe(CN)_6]$ and other known reagents, abundant residue is precipitated.

Sodium salt arsenazo (benzol-2-arsenic acid-1-azo-2-1, 8 dioxinaphthalene-3, 6-disulfo acid) dissolves in water, taking on a rose color; it develops a red-violet coloration in a neutral medium (pH 7.2) with rare-earth elements.[253] The reagent permits detection of these elements at dilutions of 1 : 3,000,000. The detectable minimum is ~0.4 μg at the noted dilution. Arsenazo acts as a group reagent on rare-earth elements.

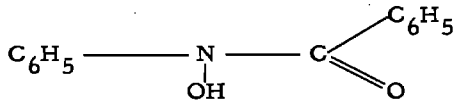
IV. 5C-6. Compounds with Diphenylvioluric Acid

During interaction of concentrated aqueous solutions of Ce^{3+} salts with a saturated solution of ammonium salt of diphenylvioluric acid, there is produced[439] a crystalline compound of yellowish-brown color. Its decomposition temperature is above 290° and absorption maximum in acetone is 450 mμ. Chemical analysis on metal content and nitrogen corresponds to the formula CeD_3 (D is diphenylvioluric). The compound belongs to the inner-complex group.

A molecule of diphenylvioluric acid exists in two isomeric forms. In nitrosoenol form it contains a free atom of H which can be exchanged for metal. On the other hand, the N atom of the nitro group can unite with a metal whose coordination link closes a 5-member cycle. Thus the structural formula of complex diphenylviolurate of cerium can be shown in the form



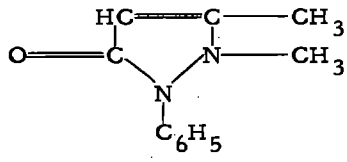
Hydroxamic acid, for example N-phenylbenzohydroxamic (see below),



is a good complex-forming agent for rare-earth elements, particularly for lanthanum.

IV. 5D. COMPOUNDS WITH ORGANIC AMINES

IV. 5D-1. Antipyrine



The first compounds with antipyrine were produced in 1913 by Kolb:[237]

$La(NO_3)_3 \cdot 3C_{11}H_{12}ON_2$; $Sm(NO_3)_3 \cdot C_{11}H_{12}ON_2$;

$Ce(NO_3)_3 \cdot C_{11}H_{12}ON_2$; $Er(NO_3)_3 \cdot 4C_{11}H_{12}ON_2$.

Later[393] it was discovered that ions of rare-earth elements ordinarily coordinate around themselves six molecules of antipyrine.

The compound $[Nd(C_{11}H_{12}ON_2)_6]I_3$ was produced by mixing concentrated solutions of $NdCl_3$, antipyrine, and KI. In this reaction, there is abundant precipitation of a light-yellow crystalline residue which is easy enough to dissolve in water and alcohol. The melting temperature of this compound is 232-238° (with decomposition).

When mixing concentrated solutions of $NdCl_3$, antipyrine, and $KClO_4$, an abundant crystalline residue of white color is formed, which is somewhat difficult to dissolve in water and has the composition $[Nd(C_{11}H_{12}ON_2)_6] \cdot (ClO_4)_3$. It was established that an interaction of salts of rare-earth elements with antipyrine generally takes place according to the equation

$$MeX_3 + 6C_{11}H_{12}ON_2 = [Me(C_{11}H_{12}ON_2)_6]X_3,$$

where Me = La, Ce, Pr, Nd; and X is the anion.

The compound $[Nd(C_{11}H_{12}ON_2)_6]Cl_3$ was produced by blending concentrated aqueous solutions of equivalent quantities of $NdCl_3$ and antipyrine, with subsequent concentration in a water bath. There remained a rose-colored oily liquid which on cooling was transformed into a hard, glassy, transparent mass.

The reaction with $Nd(NO_3)_3$ occurs similarly, except that the reaction product is in crystalline form.

It is not possible to produce analogous complex compounds with such anions as F^-, SO_4^{2-}, $H_2PO_2^-$, and $C_2O_4^{2-}$. Under the action of the enumerated anions on the complex compounds, there occur destruction of the complex and precipitation of simple salts — fluorides, sulfates, and so on — which indicate insufficient stability of these compounds. Double complex compounds of type $[Me(C_{11}H_{12}ON_2)_6]$ $[Cr(SCN)_6]$ were also obtained.

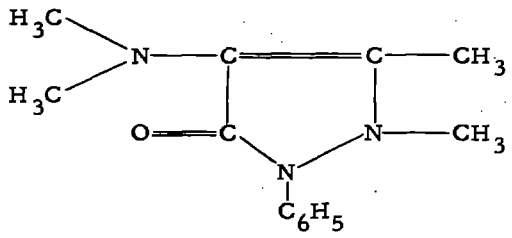
The easily soluble compounds of the type $[Nd(C_{11}H_{12}ON_2)_6]$ $(NO_3)_3$, during interaction with K_3 $[Cr(SCN)_6$, deposit a loose, powdery, lilac-rose residue. Under ordinary circumstances the reaction takes place instantly. The product possesses insignificant solubility in water and therefore it is easily separated and washed clean of admixtures. In the series of similar complex compounds for different rare-earth metals, the color of the complex is almost unchanging. It has been discovered that the elements of the yttrium

group (Y, Er) coordinate with only 3 molecules of antipyrine, not 6 as has been the case for all elements of the cerium group.

In 1953 a paper appeared by Dutt and Goswami[111] on their separation of compounds of composition $La_2(S_4O_6)_3 \cdot 6C_{11}H_{12}ON_2$ and $Pr_2(S_4O_6)_3 \cdot 6C_{11}H_{12}ON_2$ or $[La_2(C_{11}H_{12}ON_2)_6](S_4O_6)_3$. It is evident from the formulae that, in these compounds, for one atom of rare-earth element there have to be three molecules of antipyrine.

Complex compounds with antipyrine are used[286] when fractionating elements of the yttrium subgroup, frequently for concentration of lutetium.

IV. 5D-2. Pyramidone



Pyramidone differs from antipyrine by the presence of a dimethylamine group. The nitrogen of this group exhibits an intensely electronegative character and is able to exist combined with metals. As in the antipyrine case,[393] a reaction with pyramidone occurs instantly for rare-earth elements in most cases:

$$MeX_3 + 3C_{13}H_{17}ON_3 = [Me(C_{13}H_{17}ON_3)_3]X_3$$

(where Me = La, Ce, Pr, Nd, Er, and Y; and X is the univalent anion).

The coordination number is six, characteristic for elements of the rare-earth group; it is satisfied by three molecules of pyramidone, each of which has a coordination capacity of two.

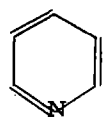
In the same way as for compounds with antipyrine, interaction of complex salt solutions with solutions of sulfuric acid and oxalic acid salts leads to destruction of the complex, and formation of simple, hard-to-dissolve sulfates and oxalates of rare-earth metals.

For complex compounds of rare-earth elements with pyramidone or with antipyrine, there is a characteristic reaction with the chromo-thiocyanate ion:

$$[Me(C_{13}H_{17}ON_3)_3]X_3 + K_3[Cr(SCN)_6] = [Me(C_{13}H_{17}ON_3)_3][Cr(SCN)_6] + 3KX.$$

As a result of the reaction, a voluminous, powdery, violet-rose precipitate is formed.

IV. 5D-3. Pyridine



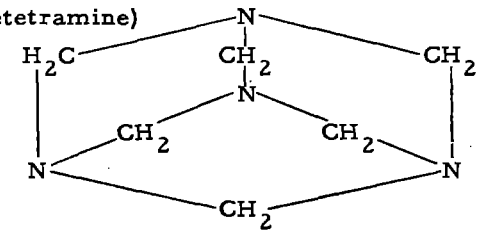
Formation of the complex anion $Nd(C_5H_5N)_n^{3+}$ in solution is easily dislosed by a reaction with $K_3[Cr(SCN)_6]$. As in the antipyrine and pyramidone cases[393] the reaction results in a double salt of composition $[Me(C_5H_5N)_n][Cr(SCN)_6]$.

The number of adjoining pyridine molecules is not as fixed as in the preceding cases. Plainly, molecules of pyridine are less stably joined with a central atom and are easily separated from it.

When mixing alcoholic solutions of $Ce(NO_3)_3$, pyridine, and $K_3[Cr(SCN)_6]$, a heavy, oily, violet liquid is separated. During concentration in a water bath the alcohol is removed and the residue forms a glassy mass which in the course of time starts to crystallize. Chemical analysis results correspond to the formula $[Ce(C_5H_5N)_4][Cr(SCN)_6]$.

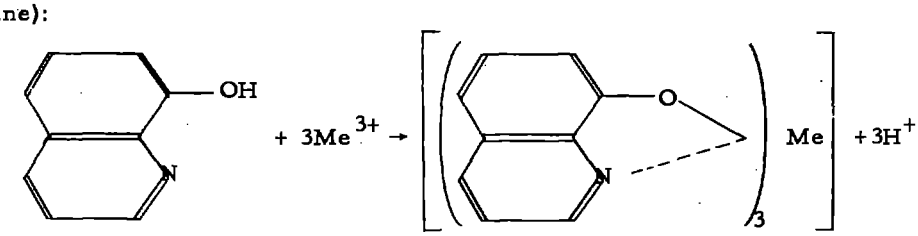
IV. 5D-4. Urotropine (Hexamethylenetetramine)

Dutt and Goswami[111] produced complex compounds with urotropine, of composition $Me_2(S_4O_6)_3 \cdot 4C_6H_{12}N_4$ (where Me = La, Ce, Pr).



IV. 5D-5. Hydroxyquinoline

Rare-earth elements form complex compounds with oxine (8-hydroxyquinoline):



There are data[115] indicating that the reaction of oxine with Me^{3+} takes place in two stages during which (in 50% dihydroxyquinone solution) one may find the compound $[MeOx]^{2+}$ (where Ox = C_9H_6ON).

The compound $[Me(oxine)_3]$ can be extracted with organic solvents such as chloroform or hexone (methylisobutyl ketone).[116, 118, 128]

A significant lowering of the pH occurs, during which the complex oxinates are withdrawn in a pH-dependent sequence. The critical pH ranges from 9.4 for Nd to 8.3 for Er. In other words, the complex oxinates of Er are more stable than the complex oxinates of Nd, and "endure" a more acid medium. Although this pH difference is not high, nevertheless it can be utilized for separating mixtures of rare-earth elements by extraction methods.

Chloroform solutions of complex oxinates are yellow and display maximum absorption at 4000 A. Some peaks of the chloroform solutions of these complexes are significantly more clearly expressed than for similar com-

pounds in aqueous solutions. In particular, the peaks at 5818 A for Nd and 5208 A for Er are used for precise spectrophotometric determinations of these elements.

Wendlandt[519] has produced the complex oxinates of Ce^{3+} and Ce^{4+}: $Ce(Ox)_3$ and $Ce(Ox)_4$.

A report on producing oxinate of tetravalent praseodymium is interesting.[248] (To date, no one has separated any Pr^{4+} compound.) A solution of 8-hydroxyquinoline sulfonic acid in ammonia is mixed with $Pr(NO_3)_3$; the resultant solution is transferred to a glass in which is placed a small cup, half full of a solution of NH_4NO_3. Around the small cup in a solution of $Pr(NO_3)_3$ is placed a cylindrical platinum leaf which acts as an anode; and in the solution of NH_4NO_3 is a platinum wire which acts as the cathode. Electrolysis is started. During the electrolysis the anode liquid is stirred energetically and kept alkaline. After the end of the process, the anode liquid is mixed with oxine and the mixture is heated in a sealed tube at 100° for two hours. Fine crystals are deposited, then filtered out, washed with hot water containing ammonia, alcohol, and ether, and dried at room temperature. Chemical analysis gives data corresponding to the formula $Pr(C_9H_6NO)_4 \cdot 2H_2O$. The substance takes on a yellowish color. It is stable in ammonium solution even in the presence of various reducers, but it is gradually decomposed by alkali. In an acid medium, Pr^{4+} is reduced to Pr^{3+}. The substance is insoluble in water and organic solvents. The oxinate of trivalent praseodymium, $Pr(C_9H_6NO)_3 \cdot H_2O$, is produced by interaction of an acidified acetic acid of a dilute solution of $Pr(NO_3)_3$ with an alcohol-oxine solution. The solution is alkalized by ammonia and heated in a water bath. A substance is deposited in the form of yellow powder. It is removed and dried in the same way as described above. It is insoluble in water and organic solvents, but decays under the action of acid and alkali. A report[330] on the stabilization of Nd^{4+} by oxine is evidently in error.[384, 423]

Ishimori[212] produced a complex oxinate of promethium. A water solution containing Pm^{147} and sodium tartrate was prepared. The pH was regulated by addition of NH_4OH. A chloroform solution of oxine was added to the water solution, containing Pm^{147}, and the mixture was stirred vigorously. The chloroform separated in a layer and was evaporated over an infrared lamp. The radioactivity of the residue was measured by a counter and compared with the original. The greatest extraction was noted at pH 9.

One can assume (considering that Pm in the solution is trivalent like its neighbors) that the complex oxinate of promethium can be depicted by the formula $Pm(Ox)_3$.

There has also been produced a complex oxinate of yttrium.[324] A water solution containing Y^{90} and tartrate of potassium-sodium was mixed with a

chloroform solution of oxine, and then the quantity of Y^{90} was determined from oxine extracted at different pH. Parallel tests were made on extractions of yttrium by pure chloroform (at the same pH values) — but yttrium was not extracted. It was found that a molecule of yttrium oxinate possesses 2 anions of Ox for each atom of yttrium: $Y(Ox)_2X$, where X is a univalent anion, differing from $(Ox)^-$.

It was proposed to utilize the reaction forming complex oxinates for quantitative determination of rare-earth elements. However, it was discovered by Dyrssen[119] that reaction products with oxine possess somewhat less oxine than predicted by the theory. This is connected, evidently, with hydrolytic decomposition of these compounds in solution. In view of this, it is doubtful whether it is expedient to use oxine for quantitative determination of rare-earth elements. For this goal it is better to use di halide-derivative oxines: for example, 5, 7-dichlor-8-hydroxyquinolinates.[315] They give a complex compound less easily dissolved in water, and they are more convenient to handle. They are likewise soluble in organic solvents and are extracted at determined pH values from the inorganic phases to the organic: for example, in chloroform.

Complex oxinates are used for exhibiting chromatograms on paper when separating mixtures of rare-earth elements.[261, 260] The chromatographs are developed by a solution of hydroxyquinoline and are irradiated by ultraviolet light. During this process, for example, a patch of La gives a green fluorescence, and Dy gives a black spot.

Freasier, Oberg, and Wendlandt[149] have prepared the 8-quinolinol-5-sulfonic acid chelates of the rare earths and report these complexes to be somewhat less stable than the corresponding 8-quinolinol and 2-methyl-8-quinolinol chelates.

IV. 5D-6. Cupferron

Cupferron, $C_6H_5N(OH)NO$, with rare-earth elements forms complex compounds which are difficultly soluble in water and organic solvents, and (at pH 3-4) can be used for group separation of these elements.[115, 162, 372]

Wendlandt[515] studied thermal decomposition of cupferronates. He established that the pyrolysis curves of the cupferronates La, Pr, Nd, and Sm have an identical character. Some intermediate plateaus could be noted at 150-180°, 280-290°, and 450-600°, which do not correspond to any sort of stoichiometric compound and seem to be a mixture of decomposition products. Similarity is evident in the pyrolysis curves for cupferronates Ce^{3+} and Y. Here, intermediate plateaus are not found. These compounds are rapidly decomposed to oxides. The least stable cupferronates are Ce^{4+} and Gd^{+3}. They begin to decay even at room temperature.

IV. 5D-7. Neocupferron

Neocupferron forms analogous compounds.[516] The thermal decay curves of the neocupferronates La, Pr, Nd, and Sm are identical. The curve for Y is identical to the Gd curve, and the Ce^{3+} and Ce^{4+} curves differ from the first two types. For all three types, decay begins at 80°. This decay corresponds to lessening of the molecular weight by 18 units, which corresponds exactly to the loss of 1 molecule of H_2O. However, it was established by analysis that the neocupferronates do not contain water of crystallization. Evidently the origin of these water molecules is connected with intermolecular rearrangements in the complex compound.

IV. 5D-8. Disalicylidal Ethylenediamine

As Dyrssen showed,[116, 118] complex compounds with rare earths are not formed.

IV. 5D-9. Methyl Amine

The salts of rare-earth elements with methyl amine form complex compounds of composition $MeCl_3 \cdot nCH_3NH_2$. A batch of anhydrous $MeCl_3$ was placed[373] in a reaction vessel. Into this vessel, which was cooled by ice, was injected dry methyl amine. It slowly merged with the chloride. The methyl amine injection was continued until establishment of equilibrium (4-12 hours). The composition of the stable material was calculated from the quantity of absorbed methyl amine. After achievement of equilibrium the produced methylammoniate was subjected to thermal decomposition. An ice bath under the reaction vessel was controlled by a thermostat to keep the temperature to an accuracy of ± 1° in the 25-300° interval. The temperature was gradually raised and after every 2-3 minutes the quantity of desorbed methyl amine was measured by buret. The transition from one compound to the other occurred in stages. Therefore it was established that $MeCl_3$ forms with methyl amine a compound of the general formula $MeCl_3 \cdot nCH_3NH_2$ (where Me = La, Ce^{3+}, Pr, Nd, Sm, and Gd; n = 1-5).

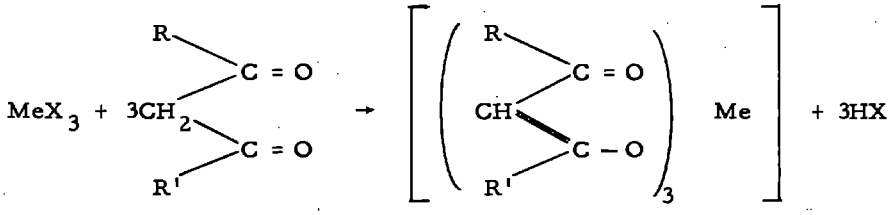
An yttrium compound of type $YCl_3 \cdot CH_3NH_2$ was studied[517] from the curves of isobaric-thermal decomposition. Four compounds were discovered, where n = 1-4. The temperatures of decay of these compounds correspondingly equal 82, 180, 232, and 360°. Compounds where n = 5, found in chlorides of other rare-earth elements, were not discovered even at 0°.

IV. 5D-10. Ethylenediamine

Ethylenediamine, $NH_2-(CH_2)_2-NH_2$, forms[440] with Ce^{4+} salts the complex compounds: $[Ce(NH_2-(CH_2)_2-NH_2)_2](SO_4)_2 \cdot 2H_2SO_4 \cdot 7H_2O$. Equimolecular quantities of $Ce(SO_4)_2$ and ethylenediamine hydrate were mixed respectively in 2N and 4N H_2SO_4. Both solutions were blended, and the mixtures were condensed by evaporation and let stand over night. Orange-colored crystals were formed. The crystals were filtered out, washed with absolute alcohol and dried at 60°. This compound is fully stable in air. Its solutions do not decay when boiled. The reagent is used in analytical chemistry in the role of a good oxidizer.

IV. 5E. COMPOUNDS WITH β-DIKETONES

Rare-earth-element salts react with β-diketones according to the system:



In 1886, Urbain[491] produced the acetylacetonates of La, Ce, Pr, Nd, and Sm. They combine with pyridine, acetonitrile and ammonia; in the latter case, the compounds obtained are of the composition $2MeAc_3 \cdot NH_3$ and $3MeAc_3 \cdot 2NH_3$ (where Ac is the acetylacetone molecule).

Erämetsä and Hämälä[126] have recently published a review of the solubility of the rare-earth acetylacetonates in various organic solvents, including acetone, chloroform, acetylacetone, carbon tetrachloride, ethyl ether, methanol, ethanol, and butanol.

Moeller, Gulyas, and Marshall,[321, 289] using an interesting technique which involved adsorbing yttrium or gadolinium acetylacetonates on columns of d-lactose hydrate or d-lactose followed by elution with benzene-petroleum ether, report partial resolution of these chelates into optically active isomers.

Acetylacetonates are a source of great interest for the researcher studying rare-earth elements[181] — especially their spectral characteristics — because they crystallize without water and are somewhat soluble in organic solvents. In 1948 a new method of producing acetylacetonates, different from Urbain's method, was worked out.[464] It consists of the following: A solution of ammonium acetylacetonate is added slowly with stirring to a chloride solution of a rare-earth element. The solution pH is maintained barely lower than that at which the hydroxides of the rare-earth elements began to precipitate. After 12 hours of mixing, formation of crystalline acetylacetonates is completed.

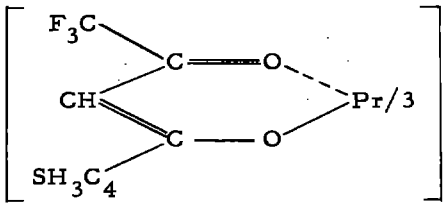
Later[402] the benzoyl acetone and dibenzoyl acetone derivatives of La, Pr, and Nd were isolated. No stable compounds of Ce^{+3} were separated; only complexes for Ce^{4+} were obtained.

Dutt and Bandyopadhyay[112] and Izatt, Fernelius, Haas, and Block[215] have measured the equilibrium constants for acetylacetone and benzoyl acetone for several of the rare-earth elements.

Derivatives of benzoyl acetone and dibenzoyl acetone exist as crystalline substances of a color close to that of the ions of the rare-earth elements. They are produced by adding an alcohol solution of benzoyl acetone to a water-alcohol solution of nitrate of a rare-earth element. Heating of the reaction mixture occurs. The mixture is diluted with water, the alcohol solution neutralizes the ammonium ion, and a precipitate is deposited which is scrubbed with alcohol and water.

The tendency of Ce^{3+} to oxidize into Ce^{4+} in the process of complex-formation is used for separating Ce from associated elements. A mixture of a nitrate alcohol solution with benzoyl acetone is neutralized by ammonia and heated, whereupon $Ce(C_{10}H_9O_2)_4$ is deposited. The derivatives La, Nd, Pr, and Sm, in contrast to the Ce compound, are easily soluble in hot alcohol. Under prolonged heating they separate and form oily drops.

In 1954, complex compounds with thenoyltrifluoracetone (TTA) were produced.[224] When a solution of $PrCl_3$ is shaken with a benzene solution of TTA, praseodymium divides between the water and benzene phases. In the aqueous layer, praseodymium exists in the form of free ions of Pr^{3+}; in the organic, in the form of the complex:



It has been found[290] that the substitution of a hydrogen ion by fluorine in the methyl group of acetylacetone lowers the melting point and increases both the solubility in organic solvents and the thermal stability of the rare-earth complex compounds.

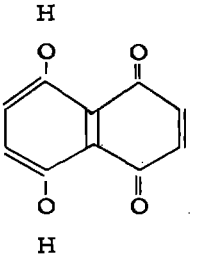
Mattern[295] has used the La-TTA equilibrium to measure dissociation constants for a number of lanthanum complexes, including Cl^-, NO_3^-, $SO_4^=$, ClO_3^-, acetate, succinate, tartrate, phthalate, lactate, citrate, oxalate, thiosulfate, and peroxide, while Bronaugh and Suttle[50] have made a very extensive study of the chelation of the rare earths as a function of pH using TTA.

IV. 5F. COMPOUNDS WITH POLYPHENOLS

Polyphenols of the type of pyrocatechin, $C_6H_4(OH)_2$(1, 2) and pyrogallol, $C_6H_3(OH)_3$(1, 2, 3), containing hydroxide groups in ortho position, form complex compounds with rare-earth elements which exist as nonelectrolytes.[132, 435] The cerium compound has a characteristic violet color which is a peculiarity utilized for qualitative detection of cerium.

A paper was published in 1954[23] on producing complex compounds of rare-earth elements with pyrocatechin, in the inner sphere of which are found molecules of ethylenediamine: $En_3[Me(C_6H_4O_2)_3]_2$, where En stands for the ethylenediamine.

Rare-earth elements, in particular La, Pr, Nd, Sm, and Gd, form colored complex compounds with naphthazarine, (5, 8-dihydroxy-1, 4 naphthoquinone)



When mixing chloride solutions of rare-earth elements with naphthazarine in ethanol solutions, complex compounds are produced. The color of the reagent during the reaction changes from red to reddish blue. The change in coloration is noted when concentrating the rare-earth element to 0.31 mg-equ/liter. In colored complex compounds the molar ratio of reagent to rare-earth element is 2: 1. Naphthazarine can act as a group reagent for rare-earth elements.

Hematoxylin, $C_{16}H_{14}O_6 \cdot 3H_2O$, (acidified) forms an intensely colored lake with lanthanum and yttrium salts, stable at pH 6.0-6.5.[407] These lakes are complex compounds in which the ratio of metal to reagent is 1: 2. The resultant complex compounds are used in colorimeters. Thus, with the help of this reagent one can determine Y and La in quantities of 0.5 and 0.2 mg/liter (computed as oxides).

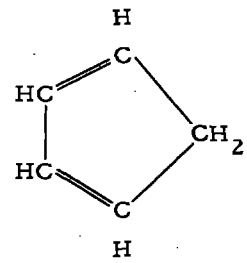
IV. 5G. COMPOUNDS WITH ALIZARIN-S

Alizarin-S forms,[387, 382] with lanthanum and yttrium salts, intensely colored lakes which appear as complex compounds. For use as a solvent, it is recommended that a 60% water solution of acetone be used (which guarantees the most intense coloration of the complex). Aqueous solutions 1×10^{-3}M of nitrates of La and Y were prepared from pure oxides, as in

the solution of alizarin-S in acetone. For spectrophotometric study, the nitrate solutions of La and Y and the reagent were mixed in different relations and water (or acetone) was added to the resultant 60% acetone solution. It was found that at the reagents' ratio of 1 : 1 the complex compound of La has maximum absorption at 520 mμ, and the compound of Y, at 510 mμ. The color reaction of La and Y with alizarin-S is very sensitive, and it is used for disclosure of micro quantities of these elements.

IV. 5H. COMPOUNDS WITH CYCLOPENTADIENAL SODIUM

Rare-earth elements, particularly La, Ce, Pr, Sm, Gd, Er, Yb, and Y, form[535, 29] compounds of type $Me(C_5H_5)_3$ with cyclopentadiene.



They are produced by shaking up anhydrous chlorides of metals with cyclopentadienal sodium in tetrahydrofuran. The solvent is recovered and the residue is heated in vacuum. The compounds $Me(C_5H_5)_3$ are obtained in the form of a sublimate with a yield of 65%. They appear as a crystalline substance, with thermal stability to 400°. At temperatures above 220° and at 10^{-4} mm Hg they sublime. The compounds of Pr, La, and Nd are colored characteristically for trivalent ions of these elements; the compounds of Gd and Y are light yellow; of Ce and Sm, orange.

In their chemical characteristics they are very much alike. They decompose in air, and $Ce(C_5H_5)_3$ darkens in the presence of traces of oxygen; under the action of water they decompose into cyclopentadienal and hydroxides of the metal which are easily soluble in tetrahydrofuran and dimethylglycol ether and dioxane. Under the action of CS_2, CCl_4, and $CHCl_3$ they decompose rapidly; they react slowly with CO_2, maleic anhydride, and ketones. When interacting with $FeCl_2$ they form ferrocen. With liquid NH_3 they form the addition compounds $Me(C_5H_5)_3 \cdot NH_3$. The absorption spectrum in tetrahydrofuran resembles spectra of rare-earth elements in aqueous solutions; this similarity is also recorded in magnetic properties. These data bear witness that the bonds in these compounds have an ionic character, although in another paper[391] it is indicated that bonds in cyclopentadienal complexes are typically covalent.

IV. 5I. METALO-ORGANIC COMPOUNDS OF RARE-EARTH ELEMENTS

A whole series of experiments designed to produce metalorganic compounds of rare-earth elements ended in failure. Alone among all the authors, Plets[366] reported having produced a thermally stable esterate of triethylyttrium $(C_2H_5)_3Y \cdot (C_2H_5)_2O$. This was produced by interaction of ethylmag-

nesium bromide with anhydrous YCl_3. It appeared as an anhydrous liquid with a unique sweetish aroma, with boiling point 222-225° (at 760 mm Hg), and d = 1.132.

Afanas'ev and Tsiganova,[5] and also other authors,[89] performed experiments reproducing Plets' work; however, they were unable to attain positive results.

Nesmayanov in 1945[335] wrote: "Alkyl groups can stably be bound with elements only at the expense of the s-, p-valent levels, whereas the presence near the atom — even if unused — of d- or f-valent electrons sharply influences the stability of the produced alkyl derivatives or even wholly eliminates their capability for existence." Evidently this behavior, in the instance of rare-earth elements, is wholly confirmed.

IV.5J. SUMMARY OF THE COMPLEX-FORMING CHARACTERISTICS OF THE RARE-EARTH ELEMENTS

From these data, several general statements concerning the complex-forming characteristics of the rare-earth elements may be made. The capability of these elements for complex-formation, as a rule, increases with decrease of their ion radii. The coordination number of rare-earth elements occurring in trivalent states, in the overwhelming majority of cases, is six. Tetravalent praseodymium and especially cerium form complex compounds, and complex compounds of bivalent europium and samarium have also been discovered. Rare-earth elements, in contrast to such active complex-producers as platinum, palladium, iron, cobalt, etc., do not create stable complex compounds with Cl^-, NH_3, CN^-, and NO.

The most stable complex compounds are formed by rare-earth elements with organic additives. For these elements the characteristic bond is through the oxygen atom of the carboxyl, carbonyl, and hydroxyl groups. Stability of the complex compounds with organic acids depends on basicity of the acid and its structure. Especially stable are complex compounds with polybasic organic acids, and likewise with aminopolyacetic acids. Dibasic unbound acids of the cis-series form water-soluble complex compounds; at the same time, acids of the trans-series form difficultly soluble salts. The phenyl, and likewise the sulfo, groups weaken the acid's properties as a complex-forming agent. The amino group has little influence on stability of complex compounds. Stability of all the noted complex compounds strongly depends on pH of the medium.

Less characteristic for rare-earth elements is the bond N . . . Me — O and completely uncharacteristic is the bond R — Me — X (where X is a halide).

In the literature there is still no light on the question of the influence of the steric factor on the properties of complex compounds of rare-earth

elements. For example, there is information on complex compounds with tartaric acid, but there is no information on complex compounds with meso-tartaric; there is information on compounds with mucic acid, but no data on compounds with saccharic acid. There is nothing on complex compounds with sugars either, although here very fine stereochemical differences can be developed.

Researches in the field of rare-earth elements to date have made only small use of organic chemistry with its unique possibilities. This is a fertile field for the future.

IV.6. EXTRACTION

IV.6A. INTRODUCTION

Solvent extraction processes are of interest to applied rare-earth chemistry in two main fields: first, the separation of uranium, thorium, and other nuclear fuels from high-cross-section impurities which include several lanthanides, on an industrial scale; and second, the large-scale separation of rare earths from each other in high purity. For research purposes, solvent extractions may be used to separate rare earths as a group from other materials (with the sometimes important advantage that added carrier is usually not necessary). Scandium and ceric cerium may readily be separated from other elements, including the trivalent lanthanides, by solvent extraction processes; the rapid separation of the individual lanthanides from the group on a laboratory scale is apparently not yet practical, although much work has been done on individual differences in extraction behavior.

IV.6B. SEPARATION OF A GROSS RARE-EARTH FRACTION FROM OTHER ELEMENTS: SOLVENT EXTRACTION OF THE RARE-EARTH GROUP

Reagents used to extract trivalent rare earths from aqueous solutions under the appropriate conditions include: tri-(n-butyl) orthophosphate [TBP]; salicylic acid; thenoyl trifluoracetone [TTA]; di(2-ethyl hexyl) orthophosphoric acid; mono- and di-(n-butyl) orthophosphoric acid; 8-hydroxy quinoline and its halogenated derivatives, and cupferron.

IV.6B-1. Tributyl Phosphate (TBP)

Warf[510] made a study of the extraction of ceric cerium (see section IV.6E below) with water-saturated TBP from nitric acid-ammonium nitrate solutions. He noted poor separation from the trivalent lanthanides but did not pursue the phenomenon. Blackmore, Bearse, and Calkins[34] studied the distribution of various rare earths and thorium between nitric acid solutions of various concentrations and TBP diluted with an inert solvent. They showed that lanthanide extractions were extremely sensitive to TBP concentration over the entire range studied (20 to 50% TBP); that a flat maximum in ex-

tractability of the lighter rare earths exists at ≈ 1.5M HNO_3; that the heavier rare earths extract increasingly well at higher nitric acid concentrations; and finally, that thorium was able to compete successfully with the trivalent lanthanides for possession of the TBP, i.e., that the presence of thorium in the organic phase reduced the extraction of the lanthanides in a manner resembling reduction of TBP concentration. On that basis they suggested that TBP extraction proceeded via actual compound formation — a suggestion strongly supported by later work. The extractions they obtained for rare earths were small — of the order of 5% of the total.

Peppard, Faris, Gray, and Mason[354] conducted an extensive study of the extractability of the lighter rare earths. Their data will be discussed in greater detail in section IV.6D below. They confirmed the strong dependence of extractability on TBP concentration. Very good extraction of all rare earths was noted from 7.2M $Al(NO_3)_3$ — 0.2M HNO_3 and from 10M NH_4NO_3 — 0.2M HNO_3, using 100% TBP. According to Knapp, Smutz, and Spedding[236] only certain cationic transition elements having two or less electrons in the d-orbitals will extract into TBP; we therefore expect extraction only of Ti, Zr, Hf, Ce(IV) and the higher valent actinides in addition to rare-earthlike elements (Sc, Y, La and lanthanides, Ac and trivalent actinides). In addition, certain anionic species show extraction — Mo(VI), Cr(VI), and of course the elemental halogens. We may therefore expect extraction of the rare earths from heavily salted, slightly acid nitrate solutions to separate well from all but the listed impurities.

Peppard, Faris, Gray, and Mason[354] also stated that the dependence of rare-earth extractability of TBP concentration was approximately third power, indicating an extracted species containing three TBP molecules per rare-earth atom. This hypothesis also has been confirmed by later work.[193]

Wendlandt and Bryant[520] listed the solubilities of many metal nitrates in 100% TBP. Solubilities are fairly large for many compounds. The solubility of $La(NO_3)_3 \cdot 6H_2O$ in TBP is about 20 g/100 g solvent.

McKay and Rees[301] reported that the rate of transfer of rare-earth nitrates between aqueous and TBP phases was fairly high, of the order of 10^{-6} g/cm^2 sec per $g/\ell \times 10^6$.

Nikolaev and Sorokina[338] have recently published a paper which indicates that the rare earths have a mutual exclusion effect with regard to their TBP extractability. For high concentrations of any rare earths in the aqueous phase, the extraction coefficients of all the rare earths are decreased.

Kirby[230] published a procedure for removing traces of thorium from cerium by extracting the impure cerium into 50% TBP in benzene from saturated $Ce(NO_3)_3$ in water, stripping the Ce from the organic layer with 8M

HNO_3, and washing the strip with 50% TBP and with benzene. He reported an 80% recovery of cerium, with a decontamination factor of about 50 from thorium. The Ce^{+3} ion acts as its own salting agent.

Bernström and Rydberg[26] reported a study of the extraction of several elements including La from $HNO_3 - Ca(NO_3)_2$ solutions using 100% TBP. They found that extraction of La was fairly good ($K \approx 10$) from heavily salted low-acid systems, but became rapidly worse as the acidity was raised. The system appears to offer no special advantage.

Hiller and Martin[197] separated a rare-earth fraction from thorium and thorium fission products by extracting the thorium with mesityl oxide from HCl saturated with $Al(NO_3)_3$; the rare earths were then precipitated as hydroxides, dissolved in 1N HNO_3 saturated with $Al(NO_3)_3$, extracted into TBP, and re-extracted into water. Further specific chemical steps were then performed to separate Ce from the other lanthanides and accompanying fission products.

Peppard, Mason, and Maier[356] have studied the extraction of hydrochloric acid and of nitric acid by TBP. Their results (presented in Figs. 34 and 35) clearly show the need for pre-equilibration of the solvent with acid of the desired concentration.

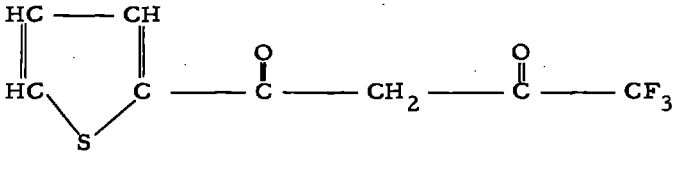
IV.6B-2. Salicylic Acid and Other Carboxylic Acids

Hök-Bernstrom[200] reported on a study of salicylic acid, cinnamic acid, and 3-5 dinitro-benzoic acid as extractants for Th^{+4}, La^{+3} and UO_2^{++} into chloroform or hexone. In general, Th^{+4} and UO_2^{+2} were much more extractable than La; thorium and uranyl ions were extracted essentially completely at pH ≈ 3, while the complete extraction of lanthanum required pH ≈ 7. No studies were made of other trivalent lanthanides.

Sudarikov, Zaytsev, and Puchkov[469] reported that a solution of 100 grams of salicylic acid per liter of solution in isoamyl alcohol was an effective extracting agent for uranium, thorium, scandium, yttrium, lanthanum, and cerium. Their data are reproduced in Fig. 36. Of particular interest is the behavior of scandium, which back-extracts completely into the aqueous phase at high pH values, and of uranium, which back-extracts partially at high pH values.

IV.6B-3. Thenoyltrifluoroacetone (TTA)

A widely used reagent for solvent extraction is the β-diketone, thenoyltrifluoroacetone (TTA). The structure of the compound is:



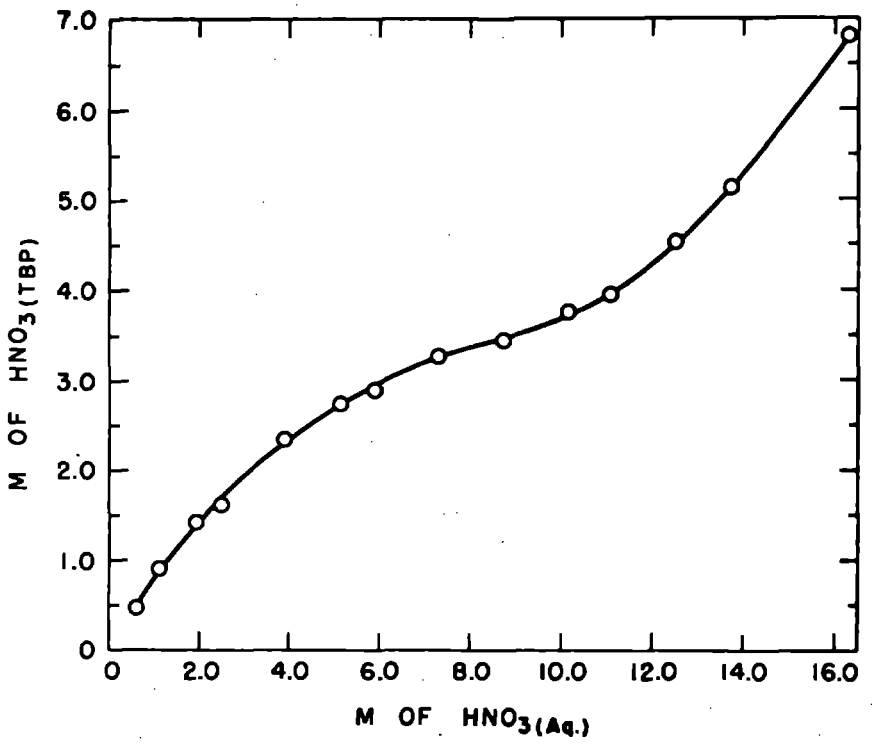


Fig. 34. Partition of HNO_3 between aqueous and 100% TBP phases at 22 ± 2°C (356)

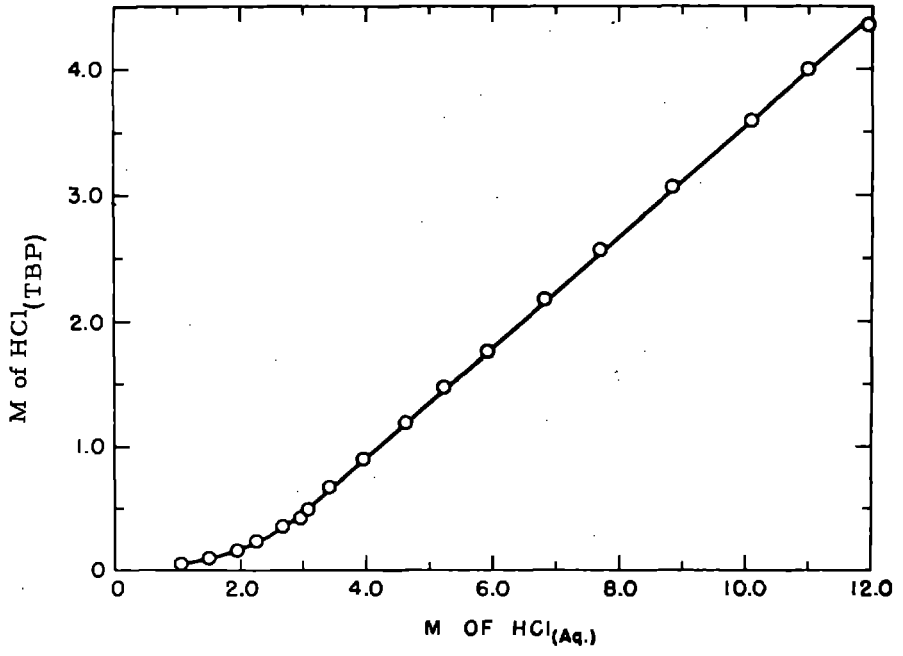


Fig. 35. Partition of HCl between aqueous and 100% TBP phases at 22 ± 2°C (356)

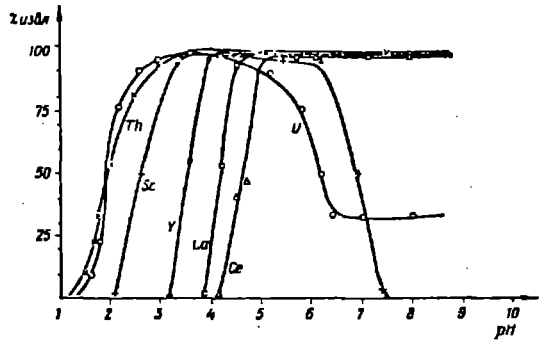


Fig. 36. Extraction of various elements into isoamyl alcohol with salicylic acid as a function of pH (469)

Reid[386] gives the acid constant of the enol form of TTA as 5×10^{-5} (25°C) and the enol/keto ratio in water as 0.016. The reagent acts as a monobasic acid, reacting with cations to make neutral chelate complexes, i.e., an n-valent cation reacts with n molecules of TTA. The chelate complexes formed are soluble to some extent in organic solvents such as chloroform, carbon tetrachloride, and benzene, and also in many polar solvents. Benzene has been most often used, though toluene or xylene are sometimes preferred because of their lower volatility.

Several compilations of extraction behavior with TTA have been published, including those by Hagemann,[183, 184] Sheperd and Meinke,[436] and Moore.[322] Their combined data are given in Fig. 37.

Broido[49] reported a purification of scandium and separation of Ca-Sc mixtures by extraction of aqueous solutions with TTA in benzene. He reports

$$K(Sc) = \frac{[ScT_3]_{org}[H^+]^3_{aq}}{[Sc^{+3}]_{aq}[HT]^3_{org}} \approx 0.9,$$

$$K(Ca) = \frac{[CaT_2]_{org}[H^+]^2_{aq}}{[Ca^{+2}]_{aq}[HT]^2_{org}} \approx 10^{-12}.$$

As a result, calcium does not extract appreciably at pH values below 6, even with 1.0 molar TTA solutions, while the extraction of scandium is appreciable even at pH 1.

He further noted that in unbuffered solutions, since H^+ is liberated as scandium extracts, the $Sc^{+3} - ScT_3$ mixture will act to buffer the final acidity close to pH 1.5, with an initial pH ranging between 3 and 11 and a scandium concentration of 1/2 mg/ml.

He noted that, as in most solvent extraction procedures, addition of carrier was not necessary.

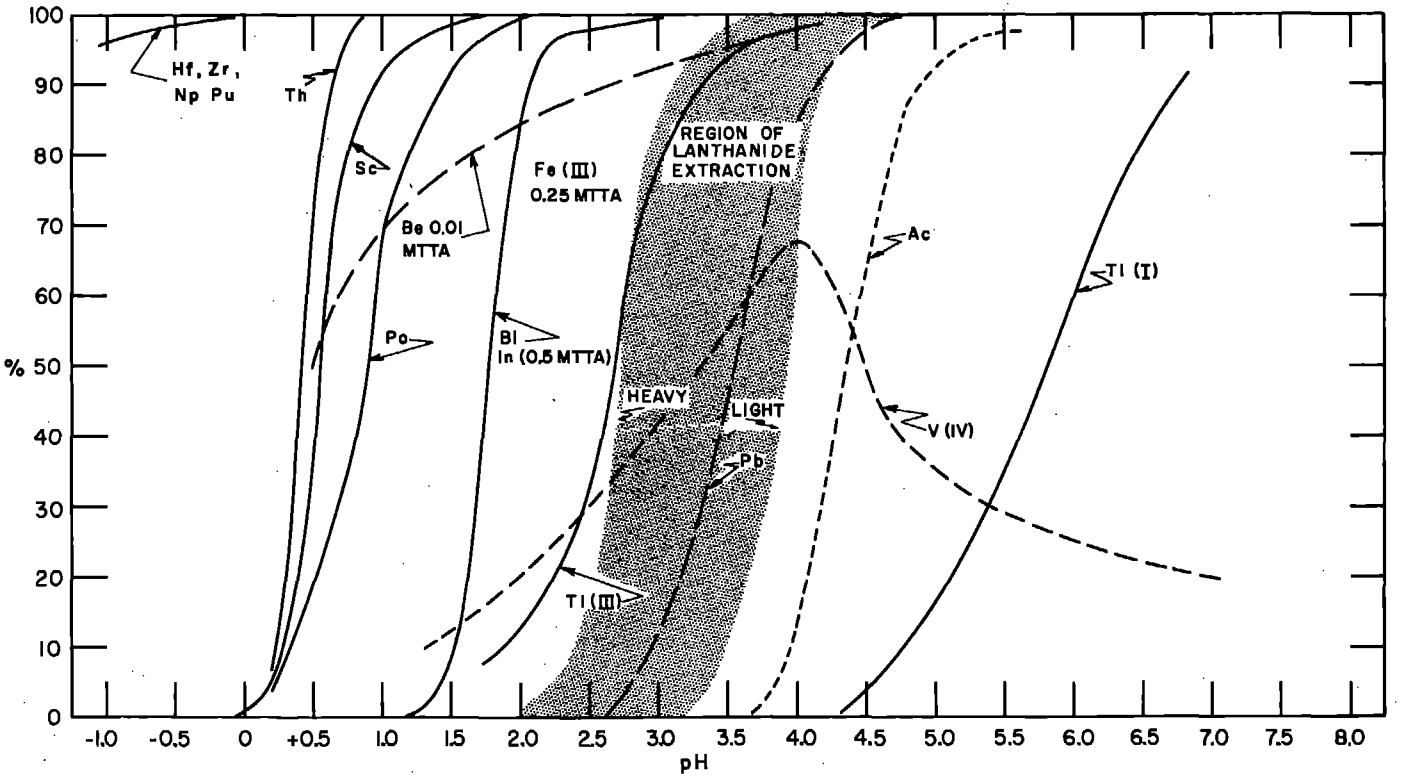


Fig. 37. Extraction of various elements with thenoyltrifluoroacetone (TTA) (436, 184, 322, 49)

Werner and Perlman[530] used TTA extraction to separate americium from large amounts of lanthanum. They report 50% extraction of americium by 0.2M TTA at pH 3.17, 50% extraction of lanthanum at pH 3.95.

Magnusson and Anderson[275] noted that 0.2M TTA would extract Eu, Yb, Ac, Am, Cm, Bk, Cf, 99, and 100 from aqueous solutions of pH 3.4.

IV.6B-4. Substituted Phosphoric Acids

In the course of an investigation into a solvent extraction separation of zirconium and niobium from fission products, Scadden and Ballou[410] remarked that mono- and di-n-butyl phosphoric acids extracted Ho, Y, La, and Ce to some extent from nitric acid solutions, with yttrium and holmium much more readily extracted than lanthanum or cerium. Since the primary purpose of their work was not rare-earth separation, their data on lanthanides are not very complete.

Dyrssen[121] remarked that dibutyl phosphoric acid extracted metal ions at lower pH than TTA and was in many instances to be preferred for that reason. He reported a procedure for milking Y^{90} from Sr^{90}, using dibutyl phosphoric acid in chloroform as a solvent. Since dibutyl phosphoric acid is highly dimerized in chloroform solution, he presumed the reaction to be

$$Y^{+3}aq + 3H_2A_2org \rightleftarrows Y(HA_2)_3\ org + 3H^+aq$$

where HA represents dibutyl phosphoric acid. He measured the extraction coefficient using 0.1M nitric acid for the aqueous phase and 0.003 to 0.10M dibutyl phosphoric acid in chloroform for the organic phase; also 0.10M dibutyl phosphoric acid and 0.10 to 10.0M nitric acid. The results were consistent with the postulated reaction, with log K = 3.24 ± 0.10. Some of his data are shown in Fig. 38. He obtained a decontamination from Sr^{90} of more than 10^4.

Peppard, Mason and Moline[357] used di(2-ethyl hexyl) phosphoric acid (HDEHP) to extract several lanthanide species. They showed that cerium(IV) could be extracted into a 0.75M or 0.30M solution of HDEHP in heptane from 10N nitric acid, with a ratio of extraction constants K(IV)/K(III) of more than 10^6. They also extracted La^{140} from Ba^{140}, Y^{90} from Sr^{90}, and successfully separated Y^{90} from La^{140}. The conditions of separation are given in Table 9.

IV.6B-5. Acetylacetone

Since TTA is such a successful reagent for extracting rare earths, it seems reasonable to assume that the lanthanides would form chelate compounds with other β-diketones. Acetylacetone, the simplest member of the class, has been examined in some detail. Urbain[492] had prepared crystalline acetylacetonates of the rare earths, generally by adding ammonium or sodium

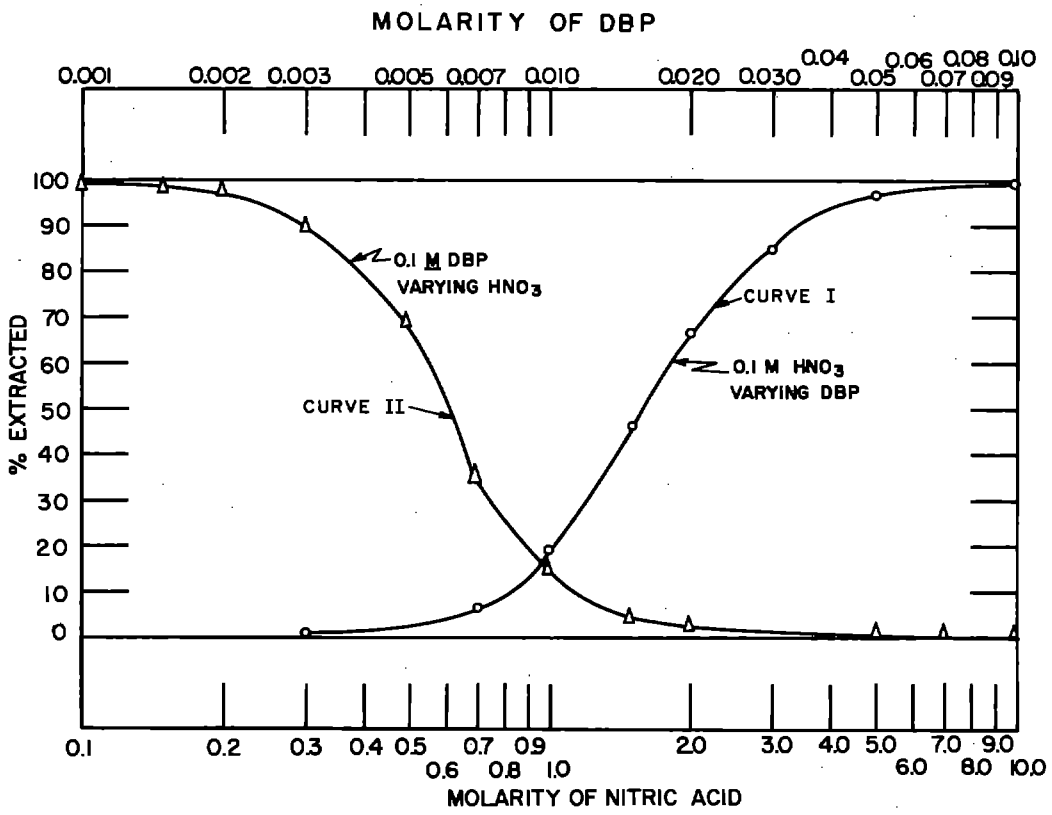


Fig. 38. Extraction of yttrium by dibutyl phosphoric acid in dibutyl ether. Curve I — from 0.1 molar nitric acid as a function of dibutyl phosphoric acid molarity. Curve II — with 0.1 molar dibutyl phosphoric acid as a function of nitric acid molarity (121)

acetylacetonate to slightly acid rare-earth-nitrate solutions. Marsh[284] proposed the formula $R[CH(COCH_3)_2]_3$ for these compounds, and his suggested formula was verified for the neodymium compound by Erämetsä and Hämälä,[126] although Seehof[429] prepared $Ce[CH(COCH_3)_2]_3 \cdot 2NH_4[CH(COCH_3)_2]$. Erämetsä and Hämälä[126] also measured the solubilities of the acetylacetonates of La, Pr, Nd, Sm, Eu, Gd, Y, and Dy in many common solvents, and found that the solubilities were very low except in methanol. Rydberg[400] reported failure in attempts to extract lanthanum and samarium into acetylacetone or acetylacetone solutions. Krishen,[247] however, reported that while lanthanum(III) and praseodymium(III) did not extract, due apparently to the very low solubility of their acetylacetonates in the organic phase (acetylacetone), cerium(III) acetylacetonate extracted very efficiently, extraction being essentially complete at pH > 4 and appreciable at pH 1. He attributes the difference to the fact that cerous acetylacetonate formed from water solution has water of coordination, while lanthanum and praseodymium acetylacetonates do not, although the composition reported by Seehof[429] seem to show that the com-

Table 9. Distribution equilibrium constants (K) for the elements Sr, Ba, Y, La, and Ce for extraction with di(2-ethyl hexyl) phosphoric acid (HDEHP) under various experimental conditions (357)

Solvent composition	Aqueous composition	Element	K
1·5 M HDEHP (toluene)	0·05 M HCl	Sr	6×10^{-3}
		Ba	3×10^{-1}
		Y	$> 10^{4}$
		La	50
1·5 M HDEHP (toluene)	0·1 M HCl	Sr	$1{\cdot}6 \times 10^{-2}$
		Ba	8×10^{-2}
		Y	$> 10^{4}$
		La	6
1·5 M HDEHP (toluene)	0·5 M HCl	Y	$1{\cdot}7 \times 10^{3}$
		La	1×10^{-1}
0·75 M HDEHP (toluene)	5·0 M HCl	Y	$<7 \times 10^{-2}$
		La	$<5 \times 10^{-4}$
0·75 M HDEHP (*n*-heptane)	10 M HNO_3	Ce(IV)	$>8 \times 10^{3}$
		Ce(III)	7×10^{-2}
		La	4×10^{-3}
		Pr	8×10^{-3}
0·30 M HDEHP (*n*-heptane)	10 M HNO_3	Ce(IV)	4×10^{3}
		Ce(III)	1×10^{-2}
		La	3×10^{-4}
		Pr	5×10^{-4}
		Pm	1×10^{-3}
		Eu	5×10^{-2}
		Tm	0·12
0·15 M HDEHP (*n*-heptane)	10 M HNO_3	Ce(IV)	$3{\cdot}3 \times 10^{3}$
		Ce(III)	$< 10^{-4}$

pound is actually a double salt without water of hydration. The unique behavior of Ce(III) indicates that the reagent should be tried on each individual rare earth.

IV. 6B-6. Oxine and Oxine Derivatives

The reagent oxine (8-hydroxyquinoline) is much used in analytical chemistry, since it forms water-insoluble compounds with many metallic ions under the appropriate conditions. By varying the conditions, considerable specificity can often be obtained. The compounds formed are in general colored and usually soluble in organic solvents; colorimetric analyses are frequently performed on chloroform extracts of metal oxinates. The halogenated derivatives of oxine have similar properties.

Moeller and Jackson[315] and Jackson[216] studied the precipitation and solvent extraction behavior of the oxinates and 5, 7-dichlorooxinates of neodymium, as a typical light rare earth, and erbium, as a typical heavy rare earth, using chloroform as the organic solvent. Their conclusion is that the halogenated oxinates are much more satisfactory compounds than the simple oxinates for solvent extraction, apparently because of the higher solubility of the chloro-compounds in chloroform. Extraction becomes appreciable at pH $\approx$ 5, and is essentially complete at pH $\approx$ 8.2 for both elements studied.

Dyrssen and Dahlberg,[115] in one article of an extensive series[116, 117, 119, 120] by Dyrssen and co-workers on the solvent-extraction properties of metal chelates, reported on a study of the extraction of the oxinates and cupferrates of La, Sm, Hf, Th, and U(VI) using both chloroform and hexone as solvents. They concluded that their data could only be explained by two assumptions: 1) that the extractable complex was partially soluble in the aqueous phase, rendering complete extraction impossible; and 2) that each of a consecutive series of addition complexes was involved in the equilibrium between metal cation and reagent, the extractable form being the uncharged complex containing n molecules of chelating reagent per n-valent cation. Their data resemble those of Moeller and Jackson[315] and Jackson[216] on neodymium and erbium; hexone seems to be superior to chloroform as a solvent. The incomplete extraction behavior of the simple oxinates is confirmed.

The work of Dyrssen's group on the lanthanides and actinides was summarized by Dyrssen[118] in a most detailed article. His results pertaining to the trivalent lanthanides may be summarized as follows:

Oxine and 5,7-dichlorooxine will extract rare earths into chloroform, the halogenated compounds being more readily and completely extracted (see Fig. 39). The range in pH for suitable extraction is from 4 to 6.5 for oxine,

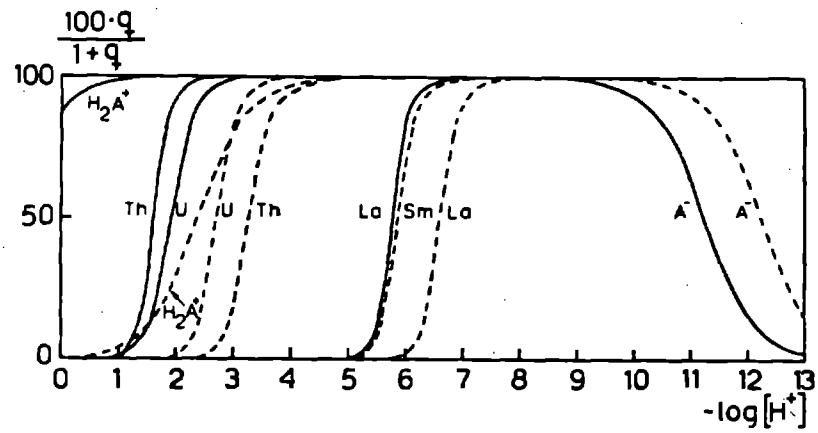


Fig. 39. Comparison of oxine (dashed curves) and 5-7-dichloro-oxine (full curves) as chelating agents for the extraction of La^{+3}, Sm^{+3}, Th^{+4} and UO_2^{+2} into chloroform. The H_2A^+ and A^- curves show the extraction of the oxines into the aqueous phase as oxinium and oxinate ions (118)

from 3 to 5.5 for dichlorooxine. This pH range is somewhat lower than that reported by other workers.[315, 216] It is also noted that n-phenyl benzohydroxamic acid will extract rare earths very efficiently into chloroform at a pH of 5 to 6 (see Fig. 40).

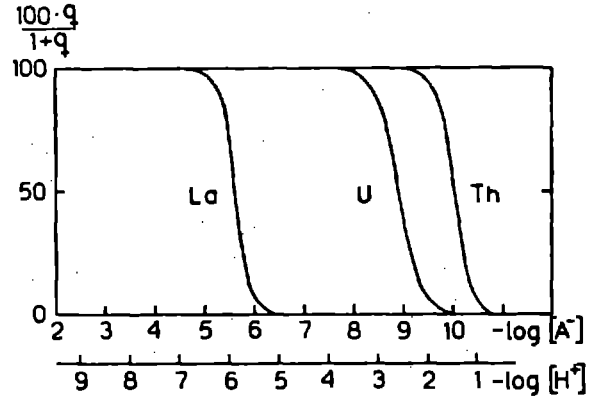


Fig. 40. The distribution of La^{+3}, Th^{+4}, and UO_2^{+2} between chloroform and 0.1M perchlorate solutions as a function of the N-phenylbenzohydroxamate ion concentration in the aqueous phase. The corresponding values of pH (-log $[H^+]$) are calculated for 0.1 molar PBHA in chloroform (118)

IV.6B-7. Other Chelating Reagents

Cupferron is in general not a very satisfactory reagent for the extraction of rare earths, since the chelates have a very low solubility in chloroform. This leads to incomplete extraction even at high pH values and limits the useful metal ion concentration to below 10^{-4}M. The chelate solubility in hexone is much higher, and better results are obtained with this solvent.

Vickery[508] reports that chloroform will extract the oxine chelate of scandium (conditions not given) but again he prefers the thiocyanate extraction. Rudenko[392] reports that extraction of carrier-free yttrium with 0.05 to 0.2 molar oxine in chloroform is complete at pH 8, and that back-extraction is complete at pH 3, but that the extraction is only useful at yttrium concentrations below about 5×10^{-4} molar.

Gruzensky and Engel[180] have reported a procedure for obtaining rare earths from euxenite ore which involves extracting the rare earths from nitric acid solution into an organic layer which consists of tri-n-butylamine in 3 methyl-2 butanone. Separation factors between the rare earths were not high but some separation was achieved. No more than 60% of the rare earths were transferred to the organic phase, even under the best of conditions.

IV.6C. REMOVAL OF CONTAMINANTS FROM RARE EARTHS BY SOLVENT EXTRACTION

Many solvent-extraction systems exist which remove unwanted materials from aqueous solutions of the rare earths without serious losses of lanthanides. Such processes may be very useful in radiochemical separations to remove large amounts of target material prior to precipitation of a rare-earth fraction, or to remove major active species to permit easier and safer handling.

Many workers[12, 37, 106, 302, 401, 475, 502] have shown that the extraction of simple salts of the rare earths (nitrates, chlorides, thiocyanates) into many classes of organic solvents such as alcohols, esters, ketones and ethers is very low, even from highly salted systems. This suggests the removal by extraction of large quantities of many elements by solvent extraction – iron from chloride solution or uranium from salted nitrate solutions, for example.

The very high sensitivity to reagent concentration of the extractability of rare earths with tributyl phosphate may be used to advantage for removal of certain species from the rare earths with diluted TBP. Blackmore, Bearse, and Calkins[34] showed that thorium could be readily removed from the trivalent lanthanides by extracting with dilute (≈ 20%) TBP from 6 molar nitric acid. A progress report from the New Brunswick Laboratory of the Atomic Energy Commission[4] describes the solvent extraction removal of thorium from yttrium and ytterbium by 22.5 volume percent TBP in inert diluent. Bernström and Rydberg[26] report the rather low extraction of lanthanum by diluted TBP even in highly salted systems, and show that uranium, plutonium, thorium, and zirconium may be effectively removed. Gal and Ruvarac[163] report that 30% TBP in dibutyl ether will extract Cd and VO_3 quite well from hydrochloric acid, Fe and Zr will extract very well at high HCl concentrations (7-8 molar), and uranium(VI) will extract quite well from ≈ 6M HCl. Extraction of cerium(III) is very low.

A systematic study of long-chain aliphatic amines has been carried out at Oak Ridge National Laboratory over the past several years.[52, 93, 94, 95] These compounds in inert solvents (hydrocarbons) act like, and are sometimes referred to as, liquid anion exchangers. Primary long-chain amines show some very slight extraction of the rare earths from low-acid sulfate solutions, but secondary and tertiary amines show practically none, while extraction of uranium and thorium are extremely high. These reagents would apparently repay study as decontaminating agents for the rare earths, since anion-exchange resins are inherently limited in their utility when high speed is necessary.

Rydberg[400] reports that 0.1 molar acetylacetone in hexone, benzene, or chloroform will extract thorium away from samarium and lanthanum in slightly acid solutions. According to Vickery,[508] scandium will extract into ethyl acetate containing acetylacetone at pH 4.5, but this behavior is probably specific for scandium among the rare-earth-like ions.

Cowan[90] has obtained a patent on a process for separating thorium from the rare earths in salicylate solution. Between pH 2 and 5 (buffered by acetate) thorium is extracted by a mixed ether-ester solvent while the rare earths remain in the aqueous layer.

IV.6D. SEPARATION OF THE INDIVIDUAL RARE-EARTH ELEMENTS FROM THE GROUP BY SOLVENT EXTRACTION

IV.6D-1. Simple Salts

Until the advent of the cation-exchange technique, the separation of individual members of the rare-earth group presented a chemical problem of the first magnitude. The methods most often used were based on fractional crystallization, but some early work was done on fractionation by solvent extraction. Fischer, Dietz, and Jübermann[136] in 1937 reported that the separation factor (ratio of extraction coefficients) for pairs of adjacent rare earths was of the order of 1.5 for the extraction of the chlorides into various alcohols, ethers, and ketones. The amount extracted was very small, however. Templeton and Peterson[475] reported some separation by extracting nitrates of La, Ce(III), and Nd into higher alcohols from nearly saturated water solutions of the salts. They reported that the degree of extraction was not large, and was very sensitive to salt concentration. They measured a separation factor of 1.4 between neodymium and lanthanum — a considerably lower value than that of Fischer, Dietz and Jübermann.[136]

Fischer and his co-workers[141] studied the possibility of separating the rare earths by extraction from lithium nitrate solutions with ether or with n-pentanone-2. Extractions were very slight (coefficients of the order of 10^{-3}) but some degree of separation was attained. Eberle and Lerner[123] studied the extraction of gadolinium, dysprosium, samarium, europium, and yttrium from slightly acid thiocyanate solutions with a large variety of solvents. They found that tributyl phosphate and isopropyl alcohol were quite effective solvents for extracting rare earths ($K \approx 1$) and that tert-butyl alcohol was somewhat effective ($K \approx 0.3$), but that many other solvents, including glycols, ketones, esters, ethers, and halogenated solvents, were very ineffective. Even other alcohols were very poor. They noted that gadolinium, samarium, dysprosium and europium all behaved similarly, while yttrium was less readily extracted. They used this phenomenon to concentrate the other lanthanides with respect to yttrium.

IV.6D-2. Tributyl Phosphate (TBP)

Considerably greater success has been attained by the use of tributyl phosphate as an extracting agent. A great deal of published work exists, much of it of very high quality, on the individual differences of extraction behavior in the rare earth-TBP system. Blackmore, Bearse, and Calkins[34] observed some differences in behavior between individual rare earths in their study on rare earth-thorium separations. Peppard, Faris, Gray, and Mason,[354] in their detailed study previously referred to, concluded that the

logarithm of the extraction coefficient K was an increasing linear function of atomic number Z for the lighter rare earths, using 100% TBP and 15.6 molar nitric acid. They assigned an artificial Z of 66.5 to yttrium in order to include that element in the scheme. The separation factor between adjacent lanthanides was reported as 1.9. Gray and Thompson[177] supplemented the data of Peppard, Faris, Gray, and Mason[354] and compared the data on lanthanides with their measurements on several trivalent actinides. They verified the logarithmic dependence of K on Z, but observed evidence for anomalous behavior in the neighborhood of Z = 67. Their data and those of Peppard et al. are shown in Figs. 41 and 42. Peppard, Gray, and Markus[355] used the comparative extraction data to demonstrate the analogy between the actinide series and the lanthanide series. Topp and Weaver[485] also studied 100% TBP – nitric acid systems, using gadolinium and samarium. Their separation factor is in rough agreement with that of Peppard et al.[354]

Scargill, Alcock, Fletcher, Hesford, and McKay[411] also studied the lighter rare earths in TBP-nitrate-nitric acid systems. Their data agree in general with those of previous workers. They extended their investigation to very low TBP concentrations and showed that the limiting dependence on TBP concentration was very close to third power. They therefore proposed a solvated extractable form containing three TBP molecules. Their data are presented as Table 10 and Figs. 43 and 44. They emphasize that free TBP alone is effective as an extracting agent; excess nitric acid tends to reduce extraction efficiency by combining with TBP. The increased extraction efficiency at low acidities and high nitrate concentration is therefore explained.

Peppard, Driscoll, Sironen, and McCarty[358] extended the study of the TBP-nitric acid system to the heavier lanthanides and americium. They verified the linear relationship between log K and Z for the lighter lanthanides, but observed an abrupt change in behavior at Z = 64. The heavier lanthanides also give a roughly linear relationship between log K and Z, but of different slope – somewhat lower slope at very concentrated (18.5 molar) nitric acid, becoming still lower as the nitric acid concentration is reduced, and actually becoming negative at low acidities (see Fig. 45). They postulate that the extracting species is $[M(TBP)A(H_2O)x\text{-}A](NO_3)_3$, where A is a function of nitric acid concentration and of Z. Hesford, Jackson, and McKay[195] also investigated the heavier lanthanides with results in good agreement with Peppard et al.,[358] but again extended their work to much lower TBP concentrations. They disagree with the interpretations of Peppard's group, ascribing the behavior of the system at high TBP concentrations to deviations from ideality. They claim the species extracted are in all cases $M(TBP)_3(NO_3)_3$. Their data are presented in Figs. 46, 47, 48, and 49 with the data of Peppard et al.[358] included for comparison.

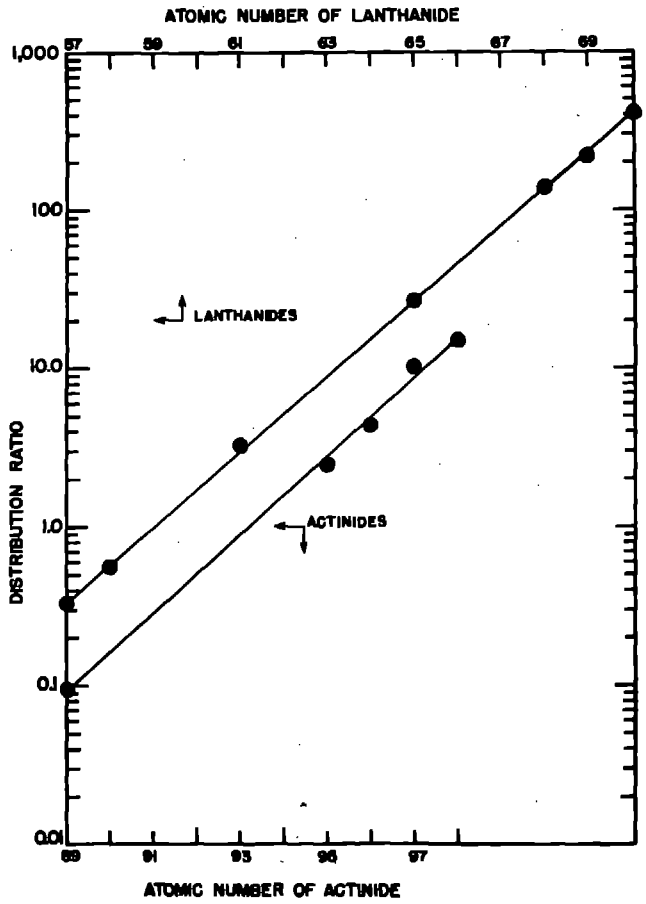


Fig. 41. Solvent extraction behavior of trivalent lanthanide and actinide elements into tributyl phosphate from 15.6N HNO_3 (177)

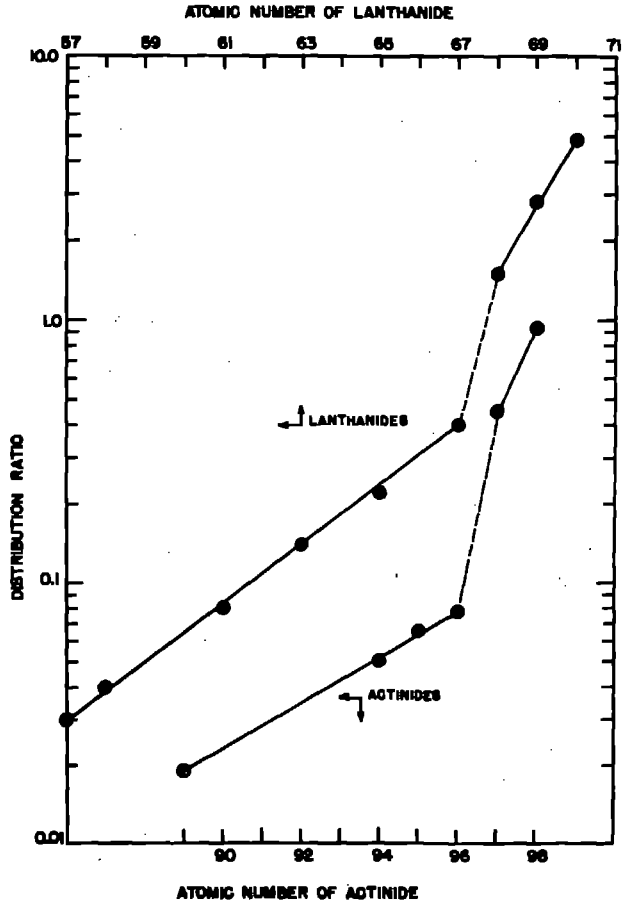


Fig. 42. Solvent extraction behavior of trivalent lanthanide and actinide elements into tributyl phosphate from 12.0N HCl (177)

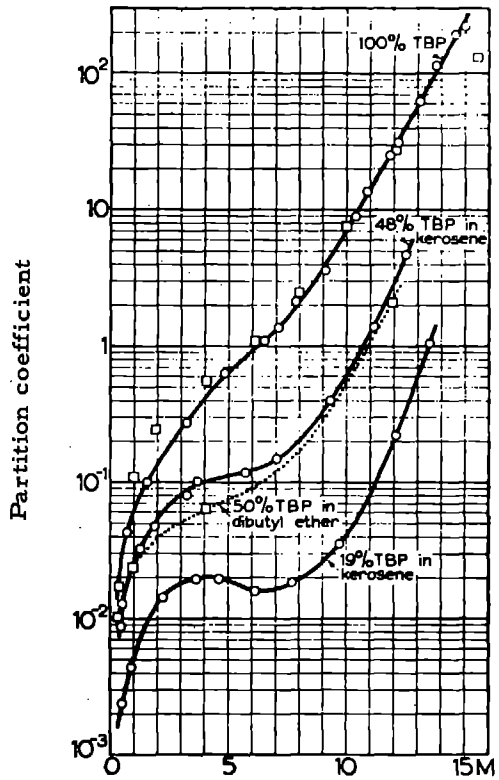


Fig. 43. The partition coefficient of yttrium between various concentrations of TBP and nitric acid.
- O Data of Scargill et al.(411)
- □ Data of Peppard, Faris, Gray and Mason (354)

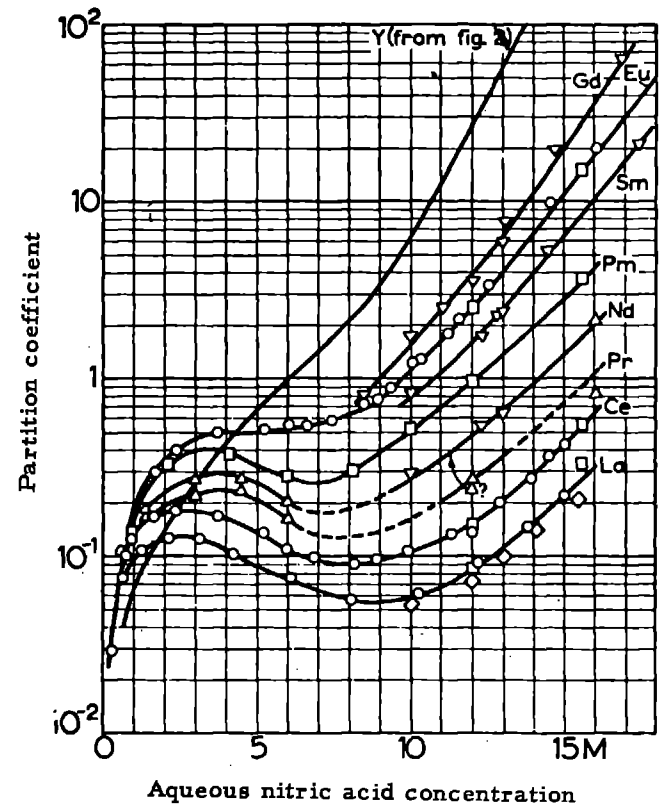


Fig. 44. The partition coefficients of the lower lanthanide nitrates: 100% TBP-nitric acid system.
- O Data of Scargill et al. (411)
- △ Data of Cuninghame et al. (98)
- □ Data of Peppard et al. (354, 355)
- ▽ Data of Topp and Weaver (485)
- ◇ Data of Suttle and Stampfer (472)

Table 10. Partition coefficients of various rare earths between organic phases containing TBP and aqueous nitric acid (411)

Rare earth	TBP conc. (kerosene diluent)	HNO_3 conc. (aq)	Partition coefficient (org/aq)
Yttrium	19% v/v	0·48 M	0·0024
		0·90	0·0044
		2·26	0·0141
		3·68	0·0196
		4·62	0·020
		6·13	0·0162
		7·72	0·0185
		9·65	0·035
		12·1	0·22
		13·5	1·05
Yttrium	48%	0·42	0·0088
		0·50	0·013
		1·29	0·033
		1·95	0·048
		3·23	0·082
		3·70	0·101
		5·78	0·120
		7·07	0·148
		9·32	0·40
		11·2	1·40
		12·5	4·7*
			4·6*
			4·8*
Yttrium	100%	0·71	0·044
		1·52	0·100
		3·23	0·27
		4·84	0·64
		6·55	1·10
		7·14	1·38
		7·83	2·2
		9·10	3·6
		10·4	9·0
		10·9	13·8
		11·9	25
		12·2	32
		13·1	62
		13·8	113
		14·6	198
		15·0	220
Lanthanum	48%	5·22	0·0189
		6·88	0·0109
		10·8	0·0085
		12·7	0·0135
Lanthanum	100%	0·63	0·074
		1·21	0·108
		2·15	0·123
		3·17	0·124
		4·27	0·102
		6·10	0·076
		8·05	0·057
		10·2	0·060
		12·1	0·088
Europium	100%	0·64 M	0·105
		1·67	0·30
		2·38	0·39
		3·76	0·49
		5·38	0·53
		6·11	0·54
		6·30	0·54
		7·27	0·59
		7·22	0·58 (?)
		8·46	0·73

Rare earth	TBP conc. (kerosene diluent)	HNO_3 conc. (aq)	Partition coefficient (org/aq)
Lanthanum	100%	13·8 M	0·142
		15·0	0·22
Cerium(III)	48%	0·40	0·0186
		1·12	0·050
		1·50	0·057
		2·70	0·056
		3·98	0·040
		5·28	0·025
		7·06	0·0155
		9·30	0·0160
		11·2	0·023
		13·0	0·039
Cerium(III)	100%	0·27	0·028
		0·72	0·099
		0·98	0·123
		1·82	0·168
		2·38	0·172
		3·64	0·169
		5·20	0·133
		6·00	0·110
		6·85	0·098
		8·15	0·090
		8·95	0·096
		9·88	0·108
		11·3	0·133
		12·0	0·137
		12·9	0·195
		13·9	0·28
		14·5	0·36
		15·0	0·42
Promethium	48%	0·47	0·027
		0·83	0·051
		1·62	0·094
		2·57	0·116
		3·53	0·108
		5·85	0·068
		6·94	0·062
		7·46	0·056
		9·51	0·077
		11·2	0·146
		12·8	0·29
Europium	48%	0·05	0·0027
		1·00	0·074
		2·00	0·136
		3·00	0·160
		4·00	0·164
		5·00	0·156
		7·00	0·118
		8·00	0·144
		9·00	0·146
		10·0	0·191
		12·0	0·47
Europium	100%	8·54 M	0·72
		8·92	0·76
		9·35	0·89
		10·1	1·24
		10·4	1·26
		11·2	1·80
		11·6	2·2
		12·5	3·4
		14·6	9·7
		16·0	19·9
		18·7	64

*Repeat experiments

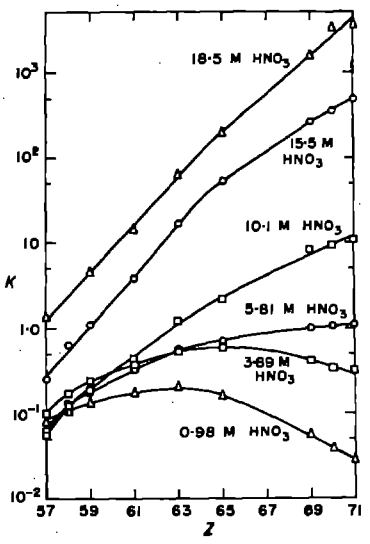


Fig. 45. Extraction of lanthanides into TBP from aqueous nitric acid phases of selected molarity as a function of Z (358)

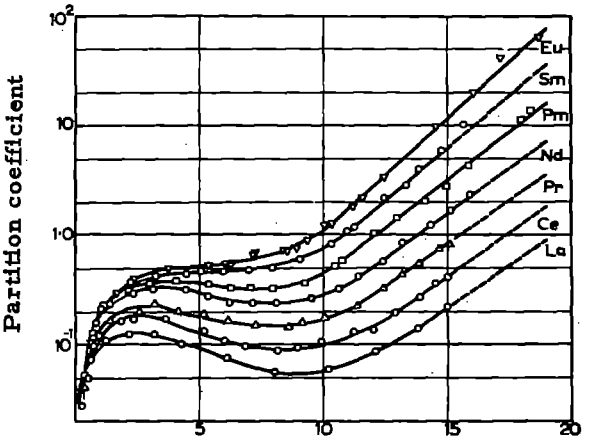


Fig. 46. Extraction of the lower lanthanides by 100% TBP (195)

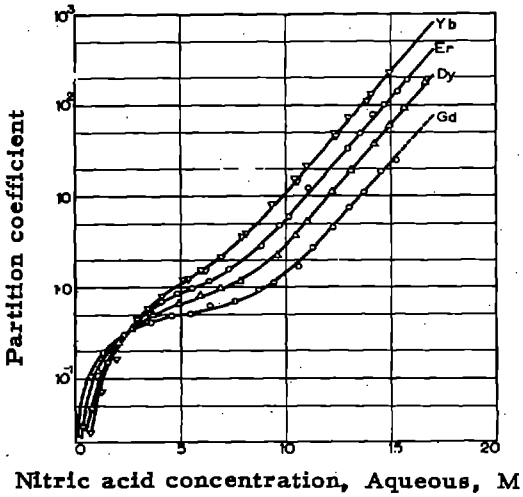


Fig. 47. Extraction of the even-Z higher lanthanides by 100% TBP (195)

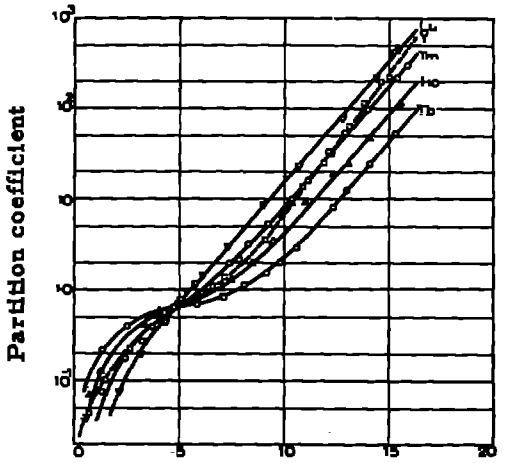


Fig. 48. Extraction of yttrium and the odd-Z higher lanthanides by 100% TBP (195)

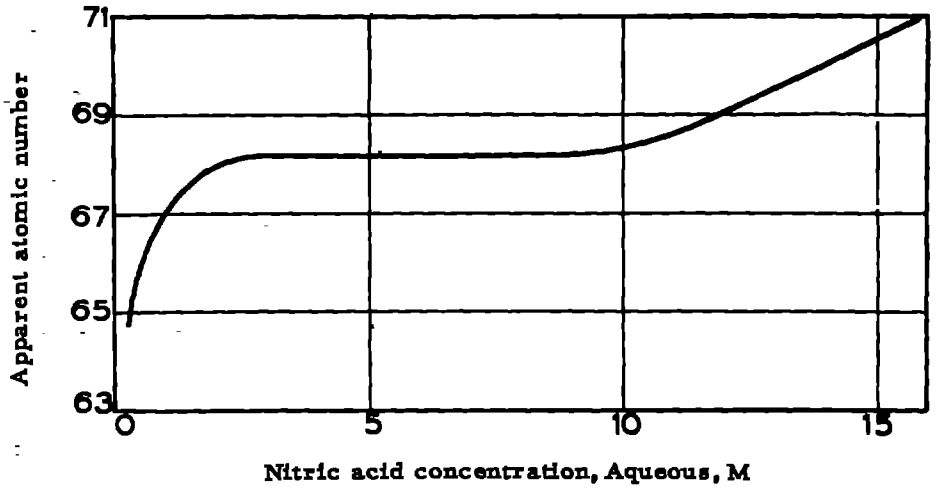


Fig. 49. Apparent atomic number of yttrium regarded as an odd-Z pseudo-lanthanide (195)

Many engineering-scale applications have been made of solvent-extraction separations of the rare earths from each other. Bochinski, Smutz, and Spedding,[36] Foos and Wilhelm,[147] Knapp, Smutz and Spedding,[236] Topp and Weaver,[485] and Brown, Coleman, Crouse, and Ryan[53] all have reported encouraging results on large-scale multistage extraction separations using TBP systems. The only reported attempt to develop a small-scale laboratory separation, by Cuninghame, Scargill, and Willis,[98] was based on extraction from nitric acid-ammonium nitrate with TBP-kerosene containing TTA. Their observed separation factors per stage were never better than 3 for the La-Pr pair. They concluded that the system was unlikely to represent any improvement over ion exchange. (See, however, page 172, this report.)

Brezhneva, Levin, Korpusov, Manko, and Bogochova[45] used a 20-stage mixer-settler solvent extraction system to separate multicurie amounts of radioactive europium and promethium from aged fission-product solutions. They used 14-15 molar nitric acid for their aqueous phase and pre-equilibrated, undiluted TBP for their organic phase. Separation of yttrium from promethium was good, but separation of europium from yttrium was poor. This defect was not serious, since yttrium was separated only from relatively young fission-product solutions in which europium was not a major activity, while separation of europium activity was done from quite old (2.5-3 years) solutions in which yttrium was no longer present to any great degree. Their data are presented in Fig. 50. The advantage claimed for solvent extraction over ion exchange in this case is, first, that of simplicity and ease of handling by remote control; and second, that for the very high levels of radiation at which they were working, there were far fewer difficulties due to radiation effects, such as bubble formation and radiation damage.

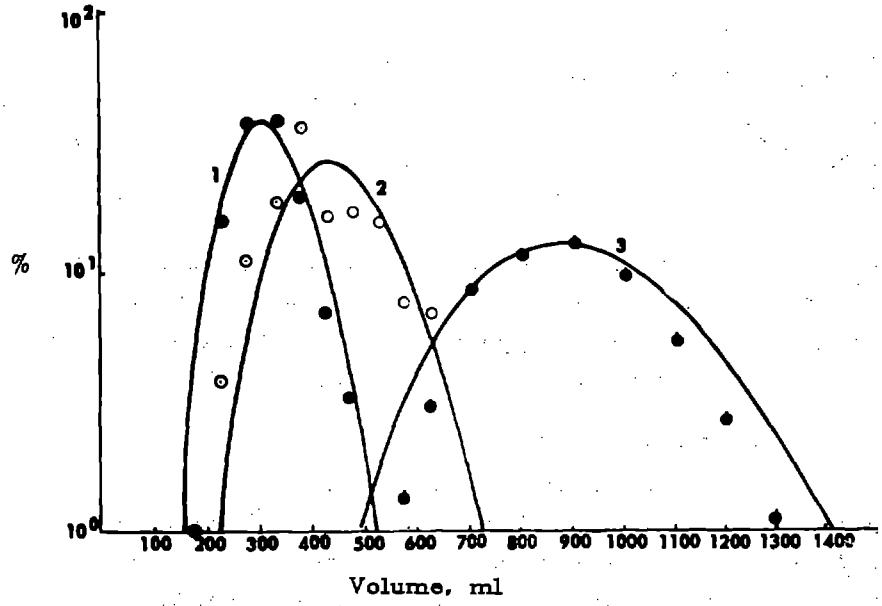


Fig. 50. Distribution of the concentrations of radioisotopes. The volume of tributyl phosphate which has passed through the apparatus is shown along the abscissa axis, and the concentrations of the radioelement as a percentage of the initial concentration along the ordinate axis. Solid lines denote theoretically computed distribution: 1 — yttrium; 2 — europium; 3 — promethium (45)

IV.6D-3. Chelating Organophosphorous Compounds

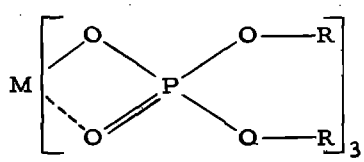
The data of Scadden and Ballou[410] indicated that dibutyl phosphoric acid or similar compounds might show differences in extracting power for different rare earths; this was confirmed by the very careful and complete

work of Peppard, Mason, Maier, and Driscoll,[359] using di-(2 ethyl hexyl) orthophosphoric acid (symbolized HDEHP) in an organic diluent as an extracting medium for the lanthanides. They found a direct third-power dependence on HDEHP concentration and an inverse third-power dependence on hydrogen ion, indicating that the reaction was

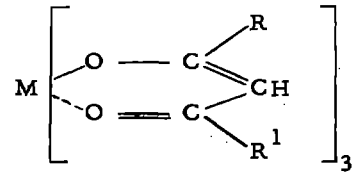
$$M^{+3} + 3HDEHP \rightleftarrows M(DEHP)_3 + 3H^+ ,$$

analogous to the dibutyl phosphoric acid reaction proposed by Dyrssen.[121]

They report a linear relationship between Z and log K over the entire rare-earth region, with a separation factor between adjacent lanthanides of approximately 2.5. The "apparent Z" of yttrium in a system 0.75M HDEHP/toluene/0.5M HCl is 67.5. Small amounts of the monoester, however, perturb the relationships seriously by increasing the extraction of the lighter rare earths markedly. Their data are presented in Fig. 51. They consider the analogy of HDEHP to TTA as valid, the extractable species being



and



respectively. HDEHP has the marked advantage that it is useful at much higher acidities than TTA, thus avoiding many difficulties with hydrolysis. Again, however, there is no obvious application to a simple laboratory-scale separation of the individual members of the rare-earth group.

IV.6D-4. Thenoyltrifluoroacetone (TTA)

Much work has been done on the individual differences in extraction behavior of the rare earths with TTA. Bronaugh and Suttle[50] published a complete series of TTA equilibrium constants for the rare earths including scandium and yttrium, reproduced in Table 11. They were unable to obtain a supply of erbium for their research, but the behavior of erbium may be assumed to be intermediate between that of holmium and that of thulium. They reported complete equilibrium was attained in less than five minutes.

Cornish[84] reported an equilibrium constant of 3.6×10^{-8} for dysprosium, which does not agree with that of Bronaugh and Suttle;[50] Keenan and Suttle[224] report $K = 3.3 \times 10^{-9}$ for praseodymium, in good agreement with Bronaugh and Suttle.[50] Again, there seems to be no simple way of applying the relatively slight differences in extraction behavior to a simple laboratory-scale separation.

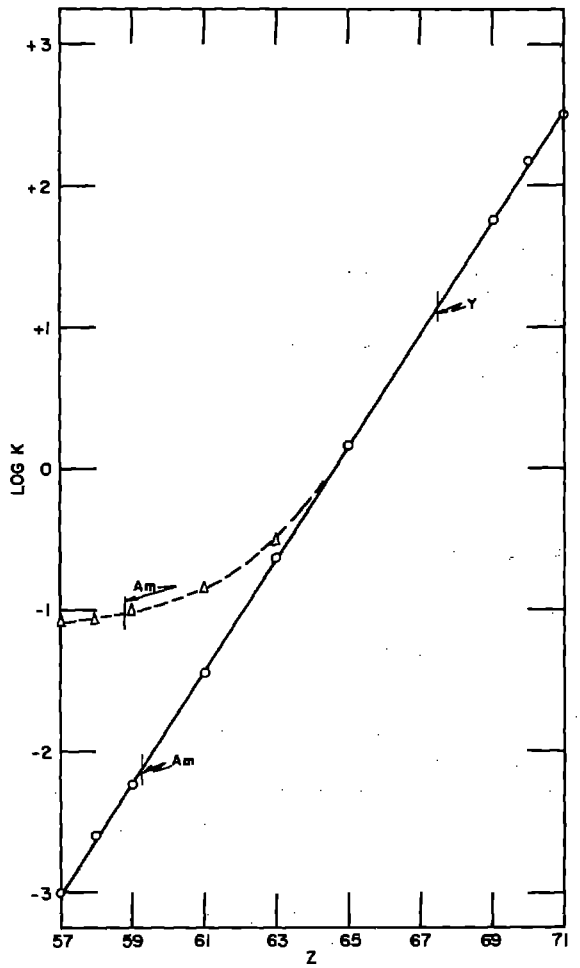


Fig. 51. Variation of the logarithm of the partition coefficient K with Z in the 0.75M HDEHP – 0.5M HCl system, yttrium and americium shown on the curve. Broken curve shows the effect of mono(2-ethyl hexyl) ortho phosphoric acid contaminant (359)

IV.6E. SOLVENT EXTRACTION SEPARATIONS OF CERIUM(IV)

IV.6E-1. Nitrates

The first reported solvent extraction separation of ceric cerium is that of Imre[210] who extracted ceric nitrate into diethyl ether. Bock and Bock[38] studied the extraction of Ce(IV) into various solvents from nitric acid. They found that cerium extracts well into diethyl ether from nitric acid more concentrated than 4.5M. Di isopropyl ether, di-n-butyl ether, methyl n-propyl ketone and nitromethane were less effective as solvents. Scandium was found to extract fairly well (K ≈ 5) from 1 molar nitric acid saturated at elevated temperature (≈ 35°C) with lithium nitrate. Lanthanum did not extract under these conditions. They also reported that thorium would extract into ether

Table 11. Average K_{eq} values for the reaction M^{+3} (aqueous) + 3 TTA (organic) $\rightleftarrows$ $M(TTA)_3$ (organic) + 3 H^+ (aqueous) (50)

Element	0.5 M TTA	0.2 M TTA	0.1 M TTA	0.05 M TTA
La	$3.06 \pm 0.25 \times 10^{-10}$	$1.27 \pm 0.17 \times 10^{-10}$	$1.66 \pm 0.36 \times 10^{-10}$	$1.45 \pm 0.14 \times 10^{-10}$
Ce	$1.98 \pm 0.26 \times 10^{-9}$	$1.53 \pm 0.22 \times 10^{-9}$	$1.09 \pm 0.28 \times 10^{-9}$	$0.897 \pm 0.207 \times 10^{-9}$
Pr	$10.2 \pm 1.34 \times 10^{-9}$	$5.91 \pm 0.75 \times 10^{-9}$		$2.45 \pm 0.30 \times 10^{-9}$
Nd	$1.76 \pm 0.17 \times 10^{-8}$	$1.10 \pm 0.17 \times 10^{-8}$		
Pm	$5.27 \pm 0.95 \times 10^{-8}$	$3.60 \pm 0.69 \times 10^{-8}$		
Sm	$12.2 \pm 1.0 \times 10^{-8}$	$8.80 \pm 1.06 \times 10^{-8}$		$2.09 \pm 0.22 \times 10^{-8}$
Eu	12.6×10^{-8}	$9.19 \pm 1.18 \times 10^{-8}$		
Gd	$1.42 \pm 0.22 \times 10^{-7}$	$1.11 \pm 0.17 \times 10^{-7}$		$0.406 \pm 0.06 \times 10^{-7}$
Tb		1.29×10^{-7}		
Y	$2.22 \pm 0.19 \times 10^{-7}$	$1.68 \pm 0.40 \times 10^{-7}$		
Ho		$2.28 \pm 0.26 \times 10^{-7}$		
Dy	$4.50 \pm 0.44 \times 10^{-7}$	$3.79 \pm 0.37 \times 10^{-7}$		
Tm		$4.58 \pm 0.40 \times 10^{-7}$		
Yb		$7.71 \pm 0.79 \times 10^{-7}$		
Lu		$6.82 \pm 0.14 \times 10^{-7}$		
Sc	0.546 ± 0.095	0.687 ± 0.045		

from 1 molar nitric acid salted with nitrates of zinc, calcium, or lithium, but hardly at all when salted with nitrates of sodium, potassium, ammonium, strontium, or barium. No explanation is given this cation effect.

They also note the necessity for removing peroxides from diethyl ether prior to use in order to avoid the possibility of explosion.

Wylie[541] confirmed the results of Bock and Bock[38] and also reported that the reduction of cerium(IV) during extraction was photocatalyzed. He examined butyl, amyl, and benzyl ethers and various ketones and reported that diethyl ether was superior to all solvents examined. He verified the results of Warf[510] on the extraction of Ce(IV) by TBP; he also reported contamination of the TBP phase by trivalent lanthanides. He reports that Ce(IV) does not extract into ether from ammonium nitrate solutions.

Liang and Yeh[269] report good extraction of Ce(IV) into butyl acetate from 7-10 molar nitric acid.

Glendenin, Flynn, Buchanan, and Steinberg[174] give the distribution coefficient for Ce(IV) between nitric acid and hexone (methyl isobutyl ketone) as a function of nitric acid molarity. Their data show maximum distribution coefficient of 3.0 between 8 and 10 molar nitric acid. This solvent is obviously inferior to diethyl ether.

Klinaev and Senyavin,[234] and Vickery[502] have both reported separations of Ce(IV) from trivalent lanthanides by diethyl ether extraction from nitric acid.

Breshneva and co-workers[45] used nitromethane as a solvent to extract fission-product cerium on a large scale away from the other lanthanides and strontium. The aqueous phase was 3-5 molar in nitric acid and 3-4 molar in calcium nitrate. They used ozone for an oxidant. Nitromethane has the advantage of being extremely resistant to ozone oxidation.

IV.6E-2. Tributyl Phosphate (TBP)

According to Knapp, Smutz, and Spedding,[236] ionic size affects the ease of extraction with TBP very markedly. One would therefore expect the ceric ion to be much more extractable than any trivalent lanthanide ion. This expectation is fulfilled, as shown by Nikolaev, Sorokina, and Maslennikova[337] and by the previously cited work of Warf[510] and Wylie.[541] The Russian group extracts cerium from 6-8 molar nitric acid containing bromate ion, using pure TBP. They report 95% extraction.

As seen from the data on the trivalent lanthanides, however, TBP extraction is probably inferior to ether extraction as a purification process for cerium. Douglass and Bauer,[550] however, have written an excellent article on the liquid-liquid extraction of cerium from bastnasite ore concentrate; a process in which they preferred TBP to ether as the extracting medium.

IV. 6E-3. Amine Extractants

Brown, Coleman, Crouse, Denis, and Moore[52] reported the extraction of ceric cerium with a distribution coefficient greater than 50, using a long-chain primary amine (Carbon and Carbide Chemical Company amine # 21F81) in 0.1 molar solution in a hydrocarbon diluent. The aqueous phase was 1.0 molar in sulfate ion, adjusted to pH between 0.3 and 1.8. Their results with secondary and tertiary amines were inconclusive. Trivalent lanthanides did not extract appreciably.

IV. 6E-4. Di(2-ethyl hexyl) Phosphoric Acid (HDEHP)

Peppard, Mason, and Moline[357] showed that ceric ion could be extracted from 10 molar nitric acid by 0.75 molar or 0.30 molar HDEHP in heptane. The ratio of distribution coefficients for Ce(IV)/Ce(III) was greater than 10^6. They used the extraction to prepare a highly purified cerium sample, essentially free of lanthanide contaminants, and to separate cerium target material from Pr^{143} and Pr^{144} daughter activities (by a factor of 10^7) in less than ten minutes. This reagent appears to be potentially very useful.

IV. 6E-5. Thenoyltrifluoroacetone (TTA)

Smith and Moore[443] reported a rapid separation from fission products based on the very high extractability of the Ce(IV) ion by TTA. They extract from 1 molar sulfuric acid containing potassium dichromate and sodium bromate, using 0.5 molar TTA in xylene, and back-extract the cerium with 10 molar nitric acid. They report severe interference from chloride ion, which effectively prevents the oxidation.

IV. 6F. SOLVENT EXTRACTION SEPARATIONS OF SCANDIUM

IV. 6F-1. Nitrate

Bock and Bock[37] remarked that "under certain conditions" scandium nitrate was extractable into diethyl ether, but conditions were not given.

IV. 6F-2. Thiocyanate

The most specific separation for scandium from trivalent lanthanides makes use of the solvent extraction of the thiocyanate into ether. Fischer and Bock,[137] in their classic article on the chemistry of scandium, recommend the following conditions: 0.5-1.0 molar hydrochloric acid, 53 g of ammonium thiocyanate per hundred ml of solution. Scandium will extract ≈ 95% into an equal volume of diethyl ether. Sulfate, and especially phosphate, interfere markedly. Beryllium, aluminum, indium, and ferric iron extract quite well; other lanthanons extract less than 0.1%. Bock[39] confirmed the results of Fischer and Bock[137] and reported data on many other

elements. He reported very slight extraction of Li, NH_4, Cd, Ni, and Pd; slight extraction (≈ 2%) of Cu(I) and Sb(III); moderate extraction of Fe(III), Al, In, UO_2^{++}; and excellent extraction of Be, Zn, Sc, Ga, Sn(IV), Mo(V), and Co. Some results confirming some of the above information have been reported by West[531] and by Vickery.[508] Vickery[502] also regards the thiocyanate extraction as the best single separation technique from the lanthanides.

IV.6F-3. Tributyl Phosphate (TBP)

Scandium is markedly more extractable into TBP than the other trivalent lanthanides. Peppard, Mason, and Maier[356] studied the extraction of scandium, thorium, and zirconium by TBP from nitric acid and from hydrochloric acid. Their data are presented in Figs. 52 and 53. It can be seen that scandium can be well separated from thorium by extraction with 100% TBP from 8.1 molar hydrochloric acid where for scandium K ≈ 100, for thorium K ≈ 0.5; or by extraction with 100% TBP from 2 molar nitric acid, where for scandium K ≈ 0.5, for thorium K ≈ 20. In the TBP-HCl system, the behavior of zirconium is nearly identical to that of scandium; in the TBP-HNO_3 system, the data are not very complete, but a separation from zirconium would seem to be difficult with 100% TBP. With 25% TBP the authors report that approximate measurements on zirconium (not shown in the figure) show zirconium to be more extractable than thorium from both 4 molar and 6 molar nitric acid. Under these conditions scandium extracts poorly; a separation is therefore possible.

Eberle and Lerner[122] also used the hydrochloric acid – TBP extraction system to separate a pure sample of scandium for analysis. They present data which is in essential agreement with that of Peppard, Mason, and Maier.[356] Their data have been included in Fig. 52 for comparison, but since they did not pre-equilibrate their solvent with acid, perfect agreement is not to be expected. They report good separation from yttrium, using equal volumes of concentrated hydrochloric acid and "as received" TBP.

According to Gal and Ruvarac,[163] 30% TBP in dibutyl ether will extract Cd, VO_3, Fe(III), Zr and UO_2^{++} ions from hydrochloric acid; these species and others may be expected to accompany scandium in a TBP-HCl extraction separation.

Peppard and Nachtman[360] have obtained a patent on a separation of scandium from the lanthanides and yttrium by solvent extraction with TBP from 6 molar hydrochloric acid.

IV.6F-4. Thenoyltrifluoroacetone (TTA)

Because of its very small ionic size, scandium is very efficiently ex-

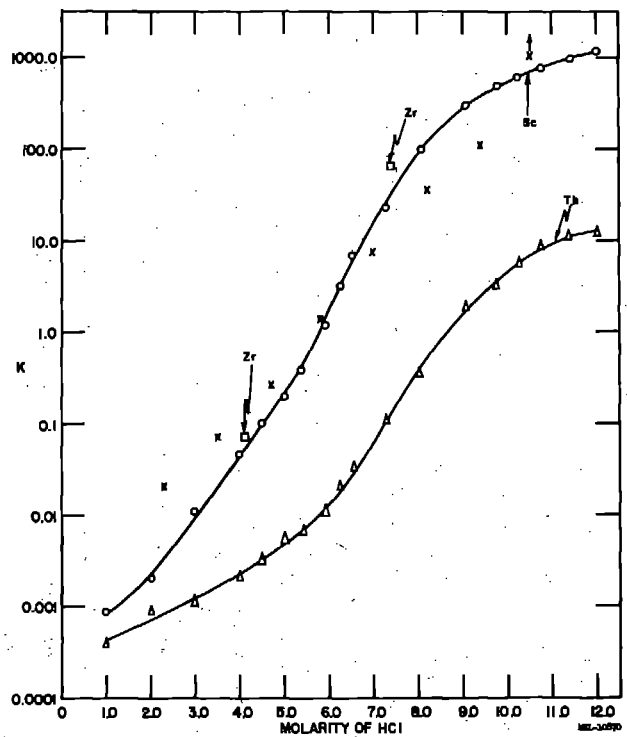


Fig. 52. Variation of the distribution ratios of Sc, Th, and Zr with aqueous HCl concentration using 100% TBP. (The approximate TBP concentration varies nearly linearly from 3.4M at 1.0M HCl to 2.8M at 11.4M HCl.)
O, □, △ Data of Peppard et al. (356)
× Data of Eberle et al. on Sc (122)
Curve drawn through data of Peppard et al.

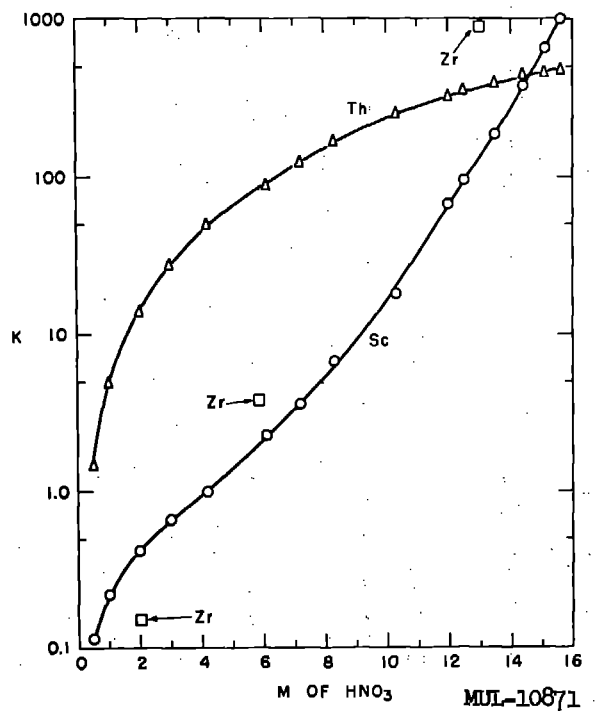


Fig. 53. Variation of distribution ratios of Sc, Th, and Zr with aqueous HNO_3 concentration using 100% TBP (the approximate TBP concentration varies nearly linearly from 3.5M at 0.5M HNO_3 to 2.7M at 16M HNO_3) (356)

tracted by TTA. Reference to the section on TTA extraction of the rare-earth group, especially to Table 11 and Fig. 37, will give conditions for separation of scandium from most elements with TTA.

IV. 6F-5. Acetylacetone

Vickery[508] reports that scandium acetylacetonate will extract into ethyl acetate from solutions of pH 4.5, but he regards the thiocyanate extraction as superior.

IV. 6F-6. Cupferron

Miller[311] and Eberle and Lerner[122] have removed impurities from scandium by extracting cupferrates into chloroform from mineral acid solutions. Scandium does not extract.

IV. 6F-7. Salicylate

The interesting behavior of scandium on extraction with salicylic acid in isoamyl alcohol has already been referred to (see section IV. 6B above).

IV. 6G. SZILARD-CHALMERS REACTION FOR THE RARE EARTHS

An application of solvent extraction to permit a Szilard-Chalmers reaction on the rare earths was reported by Herr.[194] He condensed excess phthalodinitrile with rare-earth chlorides at 320°C to make blue-green compounds, soluble in concentrated sulfuric acid and in certain organic solvents. Excess reagent was removed by subliming it off at 100°C.

The compounds so prepared could be purified by precipitating them from sulfuric acid by adding water, or from solvents such as quinoline or benzonitrile by adding diethyl ether. They were apparently completely non-exchangeable; after neutron irradiation, 80% of the activity could be removed from quinoline solution with 5% sulfuric acid containing sodium citrate. The aqueous phase contains only about 10^{-4} of the rare earth. This technique appears to offer great promise as a means of preparing high-specific-activity lanthanide tracers.

IV. 7. ION EXCHANGE

IV. 7A. INTRODUCTION

IV. 7A-1. Review

During the past fifteen years the ion exchange process has developed into the most powerful single method for separating the rare-earth elements from each other. An extraordinary number of articles have appeared in the literature describing techniques which involve a wide variety of ion exchange media and a bewildering assortment of experimental conditions. In this sec-

tion an attempt will be made to present a reasonably balanced picture of these techniques in their most modern refinements. It must be realized at the outset, however, that the ion exchange separation process has inherent in it such a tremendous flexibility that it is almost always possible to establish experimental conditions which will be distinctive to a given separation problem. These conditions will usually be chosen in such a way as to give the best possible separation in the shortest possible time with the least possible effort. With these conditions in mind, data in this section will be presented in such a way that the reader should be able to make a reasonable choice of the optimum conditions for any radiochemical separation problem.

Ion exchange materials have received such general acceptance as a useful tool in the analysis or separation of the whole periodic table of elements that it seems reasonable to assume that all practicing chemists are familiar with their history and basic properties. Those in whom this assumption is not well founded we refer to an excellent little book by Kitchener[231] or the somewhat older book by Samuelson.[405] Nachod,[327, 328] Osborn,[349] Kitchener,[232] and the Faraday Society[79] have published several books which include background material on the theory, structure, and properties of ion exchange materials. A series of papers published in the Journal of the American Chemical Society,[277] while not a book, may properly be considered as prime source material on the fundamental properties of ion exchange resins. Numerous articles have appeared in the literatures reviewing the field of ion exchange as a whole. Thomas and Frysinger,[478] Tompkins,[483] Hale,[185] and Hudgens[207] have been authors of excellent articles in this category. Also, many articles have appeared which review the use of ion exchange in the separation of the rare-earth elements. Since it is intended that this paper will supersede earlier reviews, their data, where pertinent, will be included in later sections on specific techniques.

IV. 7A-2. Effect of Variables in Ion Exchange

There are literally an infinite number of experimental conditions under which the rare earths may be separated by ion exchange methods. When a chemist approaches the problem of choosing a set of conditions which will give him a desired result he should know qualitatively how his results may be affected by major experimental variables such as kind and brand of resin, mesh size and cross linkage, eluant, flow rate, temperature, mass of the sample to be separated, etc.

Choice of an ion exchange medium is obviously an important first step in any ion exchange procedure. When ion exchange materials were first being used for rare-earth separations there were very serious fluctuations in the quality and performance of the products which were commercially available.

It was accepted as more or less standard practice that an experimenter had to purchase a single large batch of ion exchange resin, for instance, and use it exclusively if he wished to get consistent results. Variation in the performance of different batches of the same resin produced by the same manufacturer were often great enough to make one batch quite satisfactory and another completely worthless for a given separation. Happily, this situation has been corrected, at least for the synthetic ion-exchange resins, to such a point that the chemist may expect reasonably consistent performance from any given brand of resin. It is still wise, however, to check each new batch to be sure that it will perform as expected.

For separations involving elements as closely similar as the rare earths the ideal ion-exchange medium should have a large number of exchange sites per unit volume (high capacity), it should be chemically inert, thermally stable, adaptable to a wide variety of experimental conditions, reasonably inexpensive, and available.

The sulphonated styrene-divinylbenzene cation-exchange resins (Dowex-50, Nalcite HCR, Amberlite IR-120, KU-2, etc.) meet these requirements admirably and have been used most extensively in the ion exchange separation of the rare earths. The quaternary-amine styrene-divinylbenzene anion-exchange resins (Dowex-1, Dowex-2, Amberlite IRA-400, etc.) are equally satisfactory in those systems where anionic species are being separated.

Other types of exchangers such as cellulose or the inorganic zeolites have found some special applications but they have not proven to be as versatile as the exchange resins. The usual drawback is that their low capacity requires either separations on a carrier-free scale or equipment that is too bulky to be handled easily.

In the overwhelming majority of experiments which involve the ion exchange separation of radiochemical mixtures of rare earths the main goal is isolation of pure individual rare-earth elements in as short a time as possible. Important factors which affect the purity of product and the column operating time for a given separation problem are:

a. Column size. The area and length of an ion exchange column will usually be determined by the mass of the sample to be separated. Modern cation-exchange resins such as Dowex-50 have an exchange capacity of approximately 5 meq/g (dry) or 1.9 meq/ml (wet). As the weight of carrier is increased, the volume of resin needed to retain the initial loading of rare earths before elution increases proportionately. Tompkins, Harris, and Khym,[482] investigating the effect of a number of column variables, concluded

that the width of an individual rare-earth elution peak (expressed in column volumes) varies as the logarithm of the column area, while the logarithm of peak width varies inversely as the square root of the column length. Thus the column should be as long and narrow as possible, consistent with other requirements of the separation. The authors have found it a useful rule of thumb to make the column length at least fifty times its diameter and to have the initial rare-earth loading occupy no more than five percent of the column length. This will certainly not apply to all separation problems but it will indicate the general range of dimensions that are required. For carrier-free separations of radioactive species the minimum column width is limited more by resin particle size and channeling effects than anything else, and a column of 2 mm diameter is usually quite adequate.

b. Resin particle size. Ketelle and Boyd[226] have investigated the effect of resin particle size on the shape of the rare-earth elution peak. Their curve is reproduced in Fig. 54. With all other factors constant, the larger the particle size, the greater the "tailing" of the elution peak, and, for elements which elute close together, the worse the separation. Thus it is advisable to use as small a resin particle as possible, consistent with getting liquid to flow through the column.

c. Cross-linkage. One of the factors which determine the porosity of a resin particle, and thus the accessibility of its exchange sites to migrating ions, is its degree of cross-linking. The lower the cross-linking, the more porous the structure. Thus Dowex-50 with 1% divinylbenzene cross-linking is an almost colorless bead which looks very much like a gel in aqueous solution, while 16% cross-linked Dowex-50 is a very hard, almost black material. The lower cross-linked resins, however, have the undesirable property of changing volume markedly as the acidity of the solution is changed. Thus it is usually expedient to compromise between low cross-linking and low swelling by using a resin with about 8% cross-linking.

d. Flow rate. In their article on column variables, Tompkins, Harris, and Khym[482] show that for a column containing Amberlite IR-1 cation-exchange resin operating at room temperature, with 5% citrate as the eluting agent, the width of the elution curve is a discontinuous function of the flow rate. Their data are shown in Fig. 55, and indicate that the width of an elution peak is independent

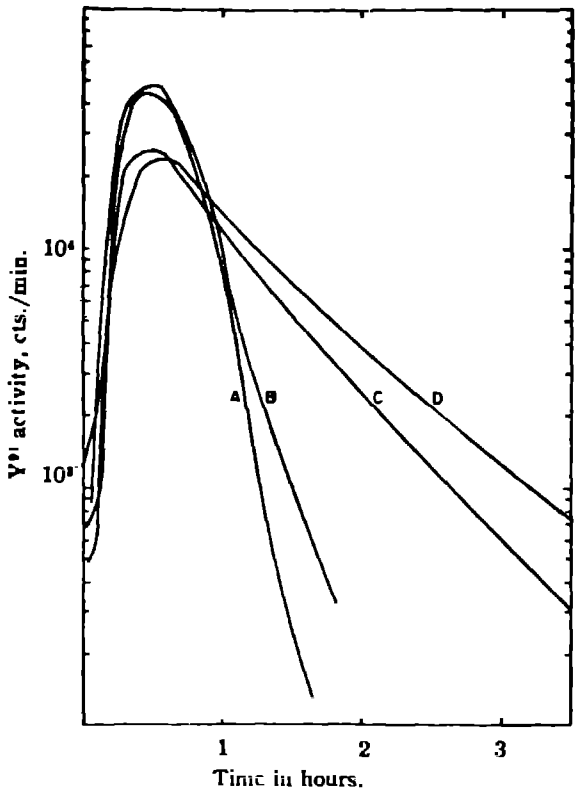


Fig. 54. Effect of mesh size of Amberlite IR-1 on desorption band width: A, 270/325 mesh; B, 170/200 mesh; C, 50/60 mesh; D, 30/40 mesh (226)

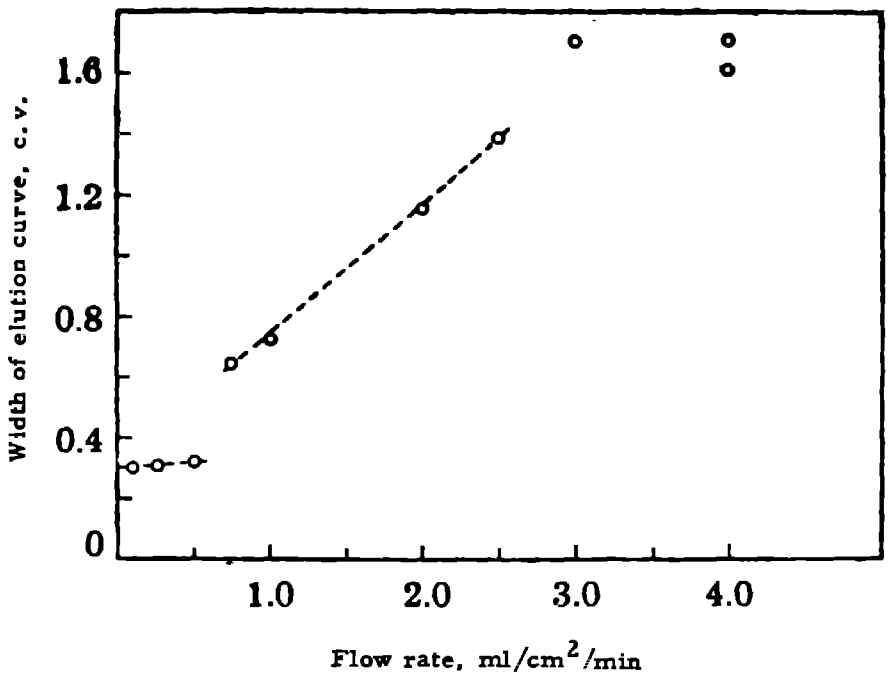


Fig. 55. The variation of the width of the elution curve with flow rate (482)

of flow rate at very low rates. Above a certain rate, however, the peak width increases as a linear function of the flow rate, while there is a second zone of independence at very high rates. For their experimental arrangement, the point at which the peak width ceased to be independent of flow rate was approximately 0.5 ml/cm^2/min. It seems reasonable to assume that this value can be increased significantly by using high column temperatures or lower cross-linked resins, both of which will increase the equilibration rate, but the qualitative conclusions drawn from the data in Fig. 55 should be applicable to any ion-exchange-resin system.

e. Temperature. Ketelle and Boyd[226] have measured the effect of elevated temperature on the degree of separation of a mixture of rare earths. Their data are reproduced in Fig. 56 and indicate that for a given elution time, columns operated at 100°C give narrower elution peaks, and better separation of rare-earth mixtures, than those at 20°C. Columns running at close to boiling temperatures are liable to prove troublesome, however, because of formation of bubbles which disrupt flow of the eluant through the resin bed. For most applications, therefore, it is expedient to operate at a lower temperature, 80-90°C usually being quite satisfactory. Kraus and Raridon[246] have studied the temperature dependence of the cation-exchange equilibria of several elements in the temperature range from 0 to 200°C. La and Eu are included in the study, and the authors show that there is an inversion in the absorption of these ions by Dowex-50 in the neighborhood of 45-50°C. At lower temperatures La is more strongly adsorbed than Eu, while at higher temperatures the reverse is true. It should be noted that these effects were observed for simple salt solutions of La and Eu in contact with the resin and did not include the effect of complexing agents on the adsorbability of these elements.

f. Mass of the sample. A great many radiochemical problems involve not only the separation of a mixture of rare-earth activities but the separation of a mixture of rare-earth carriers. The choice of experimental conditions which will give an effective separation depends on the atomic number as well as the mass of each of the elements in the mixture. Nervik[334] has published an elution curve which illustrates the effect of unequal amounts of carrier on the shape of the eluted peaks. The curve is shown in Fig. 57 and represents the elution curve that was obtained from the elution of a mixture of rare-earth activities plus 8 mg of yttrium, 10 mg of europium, 8 mg of neodymium and 2 mg of praseodymium carriers.

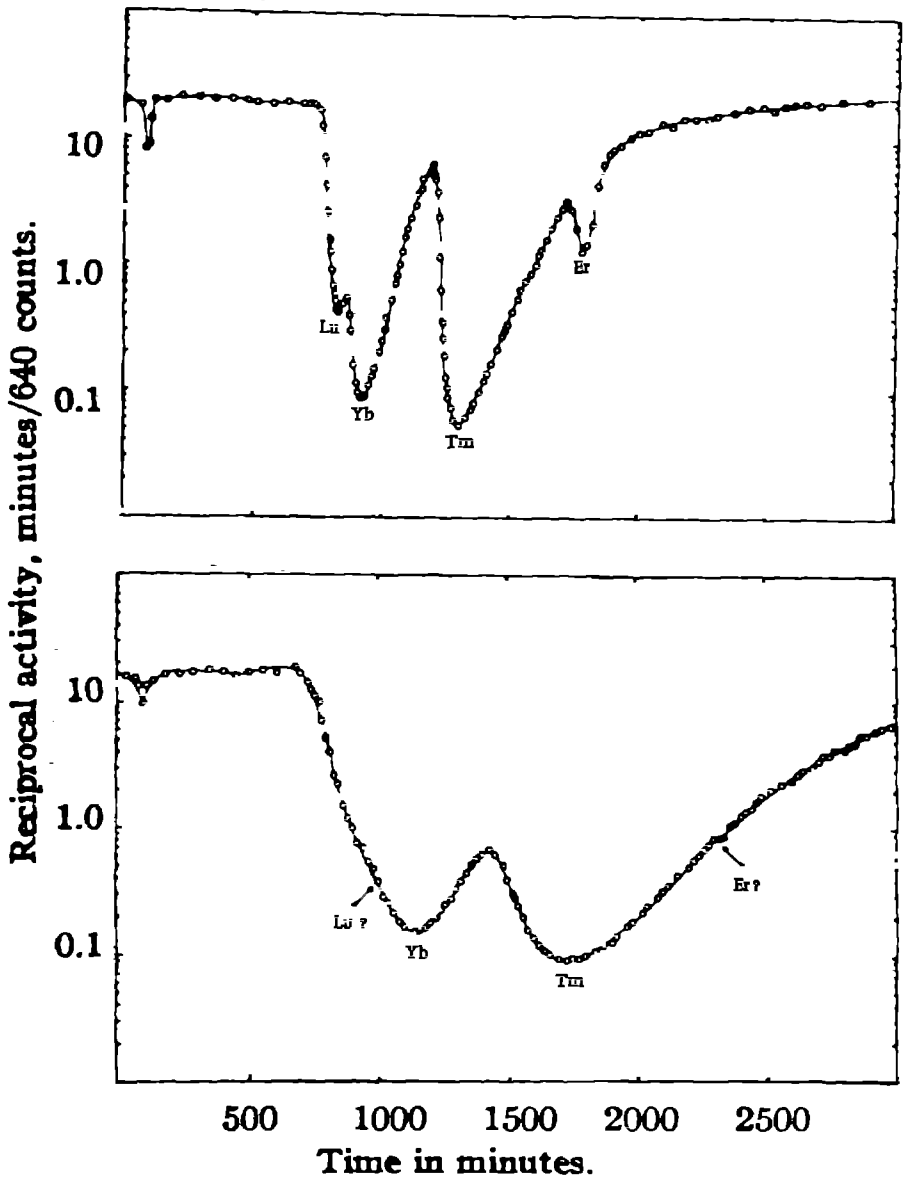


Fig. 56. Effect of temperature on the separation of the yttrium group earths with a 270/325 mesh Dowex-50 column: bed dimensions, 91 cm by 0.26 cm^2; upper curve for 100°, flow rate 0.35 - 0.45 ml/cm^2/min, and 5% citrate buffer at pH 3.2; lower curve for 20°, flow rate 0.55 ml/cm^2/min and pH 2.98 (226)

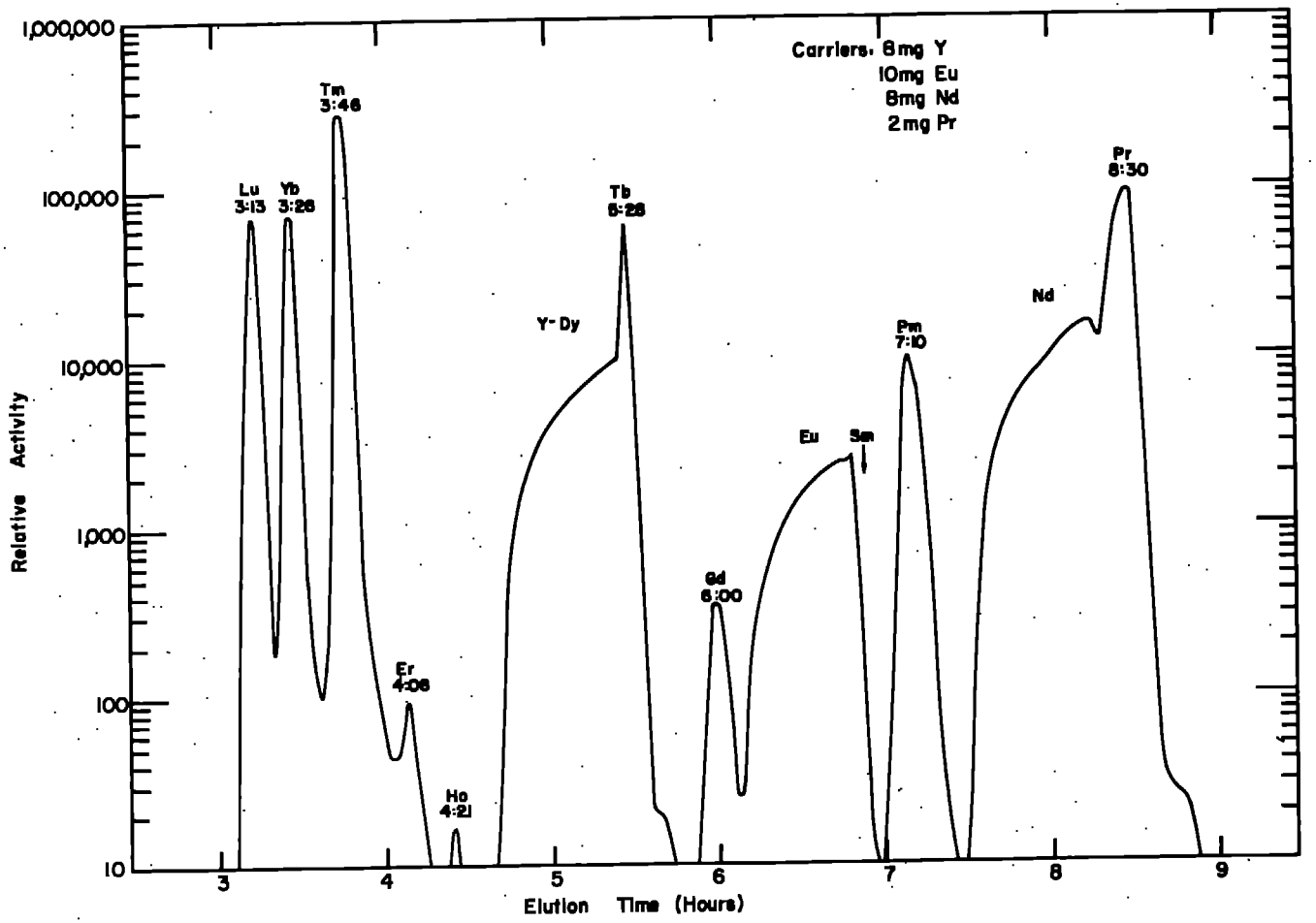


Fig. 57. Elution curve of rare-earth tracer activities plus 8 mg of yttrium, 10 mg of europium, 8 mg of neodymium, and 2 mg of praseodymium carriers; initial pH 3.19, 1M lactic acid, pH changed continuously at 0.1 pH unit/hour (334).

This particular column was operated with the "gradient elution" technique but the conclusions which may be drawn from it apply equally well to more conventional methods. In Fig. 57 the carrier-free elements Lu, Yb, and Tm, which have not been perturbed by the presence of carriers, have been eluted in fairly narrow symmetrical peaks with good separation between adjacent elements. The Y, Eu, and Nd peaks, however, contain the largest amount of carrier and are considerably wider than those for the carrier-free elements. In addition, they affect the elution of following elements to a degree which is dependent on the amount of carrier. Thus the Sm activity is hidden by the trailing edge of the Eu peak, while the Tb and Pr activities can be seen as sharp spikes on the trailing edges of the Y and Nd peaks because their activities were relatively high. If the amount of carriers had been different, i.e., if 30 mg of yttrium were present, one would expect to see more than one element (Tb, Gd, and perhaps Eu) hidden under the trailing edge of the yttrium peak and not separated at all from one another.

This type of elution curve (Fig. 57) suggests several general rules for operating an ion exchange column with any given mixture of rare-earth activities and carriers:

1. Any mixture of carrier-free rare-earth activities may be separated completely and quickly without difficulty.
2. Any essentially carrier-free rare earth may be easily separated from massive amounts of a rare earth of lower atomic number so long as there are no excessive massive amounts of a rare earth of heavier atomic number present. In Fig. 57, for example, Lu, Yb, Tm, Eu and Ho were separated from relatively large amounts of yttrium. Gadolinium was separated from europium but would not have been pure if larger amounts of yttrium carrier had been present.
3. If a small amount of one rare earth is to be separated from massive amounts of a rare earth of higher atomic number, the most effective method seems to be one in which the column is run under saturation conditions, e.g., the yttrium-terbium separation of Fig. 57. The terbium fraction was not completely free of yttrium after the first run, but the amount of yttrium carrier had been greatly reduced. A second column run on the terbium fraction should then give complete separation of the yttrium and terbium peaks without any significant loss in the total terbium activity.
4. When massive amounts of adjacent rare-earth elements are present

the chemist has two choices if well-defined peaks are desired. He may either use a wider and longer column to give an "unsaturated" rare earth carrier load per unit area of resin or he may operate a "saturated" column in such a way as to give a "square wave" type of elution curve, i.e., one element following directly behind another as in rule 3 above. This type of operation requires a second column separation if significant amounts of carrier are not to be lost.

From this brief discussion of ion-exchange-column variables it should be apparent that, while the ion exchange resins make possible separations which were out of the question twenty years ago, the separation of the rare earths with ion exchange resins still requires a certain amount of judgment, experience, and experimental skill from the chemist.

A "black art" some call it, but with the present techniques it is usually possible to separate most radiochemical mixtures of rare earths in just a few hours. The main problem is simply one of choosing the proper experimental conditions for a given separation, and in the following sections the more significant techniques will be discussed in greater detail.

IV. 7B. CATION-EXCHANGE RESINS

IV. 7B-1. Introduction

Almost all applications of cation-exchange resins to the separation of the rare-earth elements involve two major steps: a) adsorption of the rare-earth mixture by the resin from a solution, and b) selective desorption of individual elements by an appropriate eluting solution.

For the adsorption of a rare-earth ion by a cation-exchange resin the reaction may be written as

$$M^{+3} + 3NaR = MR_3 + 3Na^+ , \qquad (1)$$

where M^{+3} is the rare-earth ion and R the resin anion. Boyd, Schubert, and Adamson[44] have shown that the equilibrium constant for this reaction may be written

$$k_1 = \frac{(MR_3)\,(MR_3 + NaR)^2}{(NaR)^3} \; \frac{(Na^+)^3}{(M^{+3})} , \qquad (2)$$

where NaR and MR_3 are expressed in mole fractions for ideal solid solutions and (M^{+3}) and (Na^+) are the activities of the ions in solution. For low concentrations of rare-earth ions $(MR_3 + NaR) \cong NaR$ and Eq. (2) becomes

$$k_1 = \frac{MR_3}{NaR} \; \frac{(Na^+)^3}{(M^{+3})} . \qquad (3)$$

In adsorption processes the value of primary interest is the distribution of the rare-earth ions between the aqueous and resin phases: i.e.,

$$K_d = \frac{MR_3/\text{mass of resin}}{M_l/\text{volume of soln}} = \frac{MR_3}{M_l} \times \frac{\text{vol soln}}{\text{mass resin}} , \qquad (4)$$

in which K_d is the "distribution coefficient" and MR_3 and M_l are the amounts of the cation in the resin and liquid phases. For the rare earths, if MR_3, M_l, and the mass of the resin are expressed in moles and the volume of solution in liters, Eq. (4) may be written

$$K_d = \frac{MR_3}{NaR} \times \frac{V}{M_l} = \frac{MR_3}{NaR} \times \frac{1}{(M^{+3})} , \qquad (5)$$

where (M^{+3}) is the concentration of the rare-earth ion. Substitution of (M^{+3}) from Eq. (3) in Eq. (5) gives

$$K_d = c \frac{k_1}{(Na^+)^3} , \qquad (6)$$

where c is a proportionality constant. Since the distribution coefficient decreases as the third power of the (Na) concentration, and since all cations in the aqueous phase compete with the rare-earth ions for the resin exchange sites, transfer of the rare-earth material to the resin is best done in a solution of very low ionic strength.

In addition to varying with ionic strength, the distribution coefficient for a given rare earth can very markedly with rare-earth concentration.

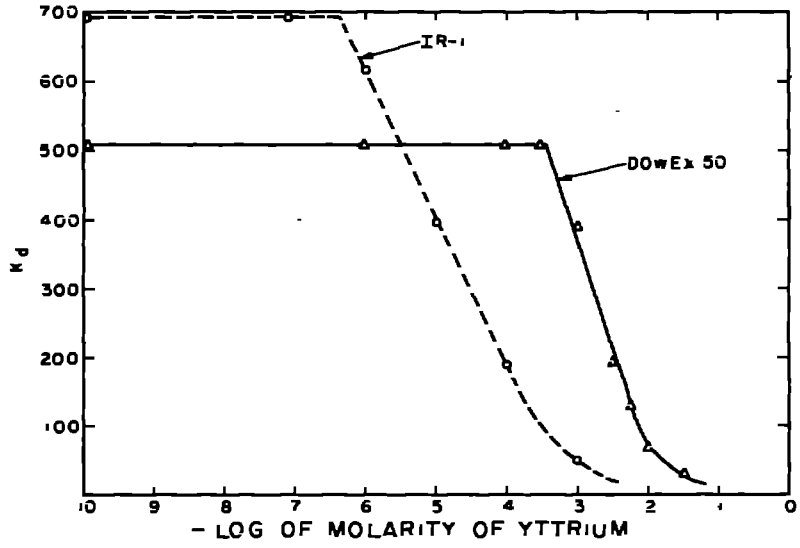


Fig. 58. Variation of the K_d with concentration of rare earth, 0.5M NH_4ClO_4 solution, Dowex-50 resin, 40-60 mesh, NH_4^+ form (481)

Tompkins and Mayer,[481] whose data are reproduced in Fig. 58, show that in 0.5M NH_4ClO_4 solutions at room temperature the K_d for yttrium on Dowex-50 remains constant until the yttrium concentration increases to approximately 3×10^{-4}M, at which point the K_d begins to decrease very rapidly. With Amberlite IR-1 resin the K_d begins to decrease at an yttrium concentration of 4×10^{-7}M. A similar type of behavior was noted for Ce^{+3} and Pr^{+3} by the same authors, and presumably occurs with all the rare earths. It is well to keep this phenomenon in mind when adsorption must be done out of solutions of high ionic strength, where a K_d that has been depressed by the salt concentration may be depressed still further by too high a rare earth concentration.

For a given resin in a solution of given composition each of the rare earths will have a distribution coefficient that differs slightly from the others.

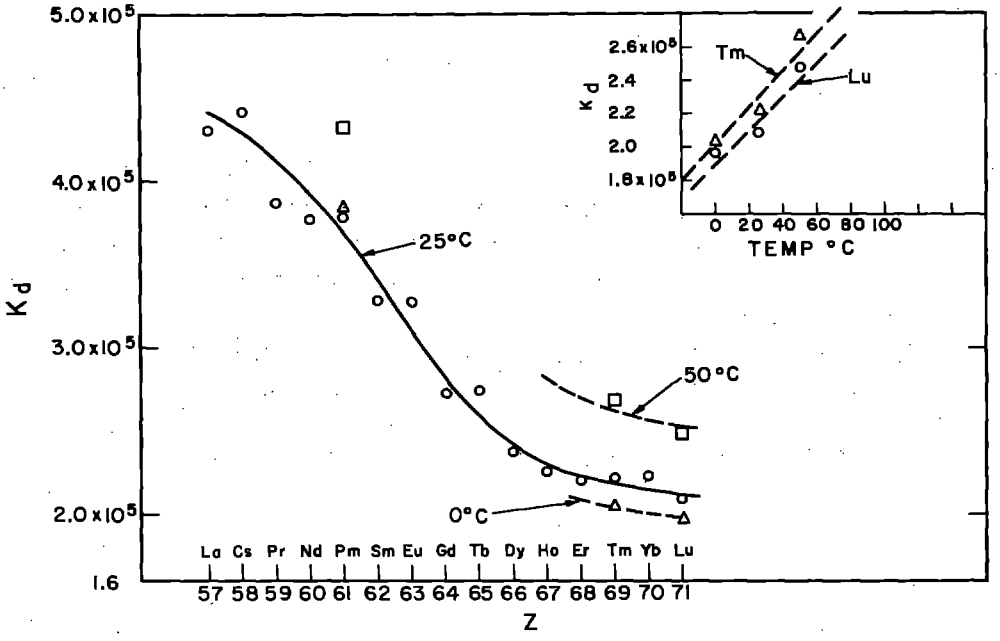


Fig. 59. Log K_d vs atomic number, Dowex-50, 0.5-1 cm/min settling rate, 4% cross-linked, in 0.1M $HClO_4$. Inset – temperature dependence of K_d (470)

Surls and Choppin[470] have measured the adsorption of various rare earths on Dowex-50 resin in 0.1M $HClO_4$ solutions. Their data have been plotted in Fig. 59 and indicate that there is approximately a factor of two difference between the distribution coefficients of the lightest and the heaviest rare earths, with the lower Z rare earths being most strongly held by the resin. The curve of K_d vs atomic number is not linear, although there is a gradual decrease in K_d from La to Dy. Between Dy and Lu, however, the distribution coefficient remains practically constant.

The distribution coefficient does not seem to vary too much with temperature, increasing approximately 10% for each 20° rise in temperature, and indications are that this behavior is reasonably uniform for all the rare earths.

In most radiochemical applications of cation-exchange resins to the separation of the rare earths the initial step involves transfer of all of the rare-earth material to the resin. Equilibration is carried out, at elevated temperatures if possible, in solutions whose ionic strength is as low as is practicable. Instead of achieving a separation in the adsorption step every attempt is made to have a small, uniform band of activity deposited at the top of the ion exchange column.

The actual separation of the rare-earth mixture is then carried out by the selective desorption of individual elements by an appropriate eluting agent. The simplest type of desorption process is one in which an appropriately high concentration of a cation such as H^+ is used to displace the rare-earth elements from the ion exchange sites and advantage is taken of the small differences in K_d shown in Fig. 59 to effect the separation.

Several authors[479, 104, 466] have published data on the use of hydrochloric acid as an eluting agent in separations of this sort. The curves of Diamond, Street, and Seaborg[104] are reproduced in Fig. 60 and indicate that separation of certain mixtures of rare earths may be achieved by this method. The small K_d differences between adjacent rare earths, however, preclude their separation by such a simple elution technique and recourse must be taken to eluting solutions which contain complexing agents.

IV.7B-2. Citric Acid

The complexing agent which received the earliest and most intensive study as an eluting agent for the separation of the rare earths was citric acid. When citric acid is added to a solution of a rare earth in equilibrium with resin the distribution of rare earth between the solution and resin is changed because of the formation of the rare earth-citrate complex. Since citric acid has three ionized forms,

$$H_3Cit = H^+ + H_2Cit^- \qquad K_8 = \frac{[H^+][H_2Cit^-]}{[H_3Cit]}, \tag{7}$$

$$H_2Cit^- = H^+ + HCit^= \qquad K_9 = \frac{[H^+][HCit^=]}{[H_2Cit^-]}, \tag{8}$$

$$HCit^= = H^+ + Cit^{\equiv} \qquad K_{10} = \frac{[H^+][Cit^{\equiv}]}{[HCit^=]}, \tag{9}$$

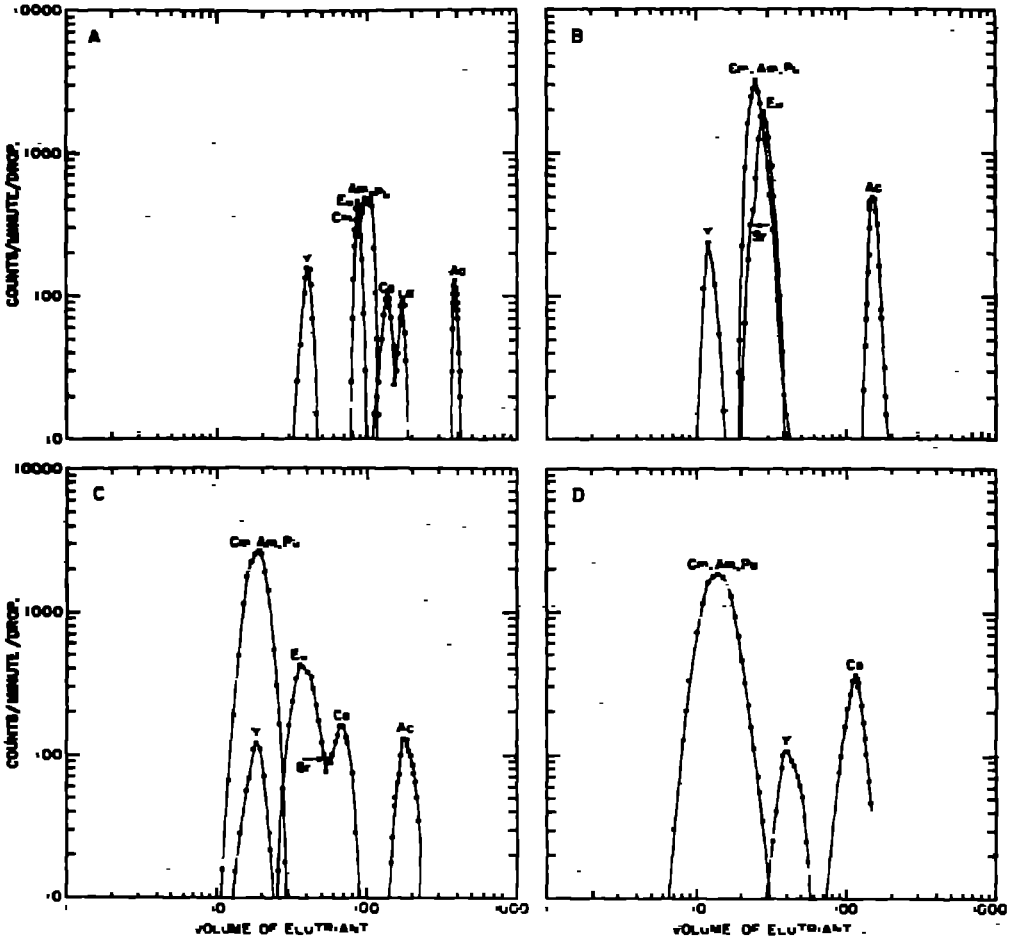


Fig. 60. Elution of lanthanides and actinides from Dowex-50 cation-exchange resin with HCl. Columns 10 cm × 1-1.5 mm; Dowex-50, H^+ form, 250-500 mesh, wet graded settling rate approximately 0.5 cm/min; room temperature; carrier-free tracer activities. Typical elution curves in: A, 3M HCl B, 6M HCl; C, 9M HCl; D, 12M HCl (104)

the exact nature of the complex is dependent on pH, but the equilibrium can be expressed by

$$M^{+3} + n(H_xCit)^{x-3} = M(H_xCit)_n^{3+n(x-3)} \qquad (10)$$

and

$$K_2 = \frac{[M^{+3}][H_x(Cit)^{x-3}]^n}{[M(H_xCit)_n^{3+n(x-3)}]} \qquad (11)$$

If the pH is such that only Eq. (7) is involved in the rare earth-citrate complex equilibrium, Eq. (11) may be written

$$K_2 = \frac{[M^{+3}][(H_2Cit)^-]^3}{[M(H_2Cit)_3]} \quad . \tag{12}$$

Combining Eqs. (5), (7), and (12) and rearranging gives

$$\frac{MR_3}{NaR} = \frac{K_d K_2}{K_8^3} \frac{[M(H_2Cit)_3][H^+]^3}{[H_3Cit]^3} \quad . \tag{13}$$

Thus the amount of rare earth in the resin phase, to a first approximation, is seen to decrease with the third power of the H^+ concentration as the pH is increased, and with the third power of the H_3Cit concentration as the total citric acid is increased. Similar strong dependence on the pH and citrate concentrations is found as the pH is increased to the point where the second and third ionization constants become important.

Tompkins and Mayer[481] (using 10 ml 0.23M citrate, 0.5M NH_4ClO_4, $Tb^{+3} < 10^{-6}$M, 0.3657 g Dowex-50 resin, 40-60 mesh) show that the formula for the rare earth-citrate complex at pH's below 3.2 is $M(H_2Cit)_3$. Spedding and Powell,[450] on the other hand, indicate that on Nalcite HCR columns eluted with 0.1% citrate in the pH range 5.4-8.2 the predominant rare-earth complex is $M(Cit)_2^=$. Whatever the pH and whatever the nature of the citrate complex, however, the primary figure of merit is the distribution coefficient of one rare earth relative to that of its immediate neighbors; this will determine how effectively a pair of adjacent rare earths may be separated under a given set of experimental conditions. Tompkins and Mayer[481] have measured the ratio $K_{d(Pm)}/K_{d(Eu)}$ as a function of pH. Their data, plotted in Fig. 61, indicates that in citrate solutions the ratio of distribution coefficients

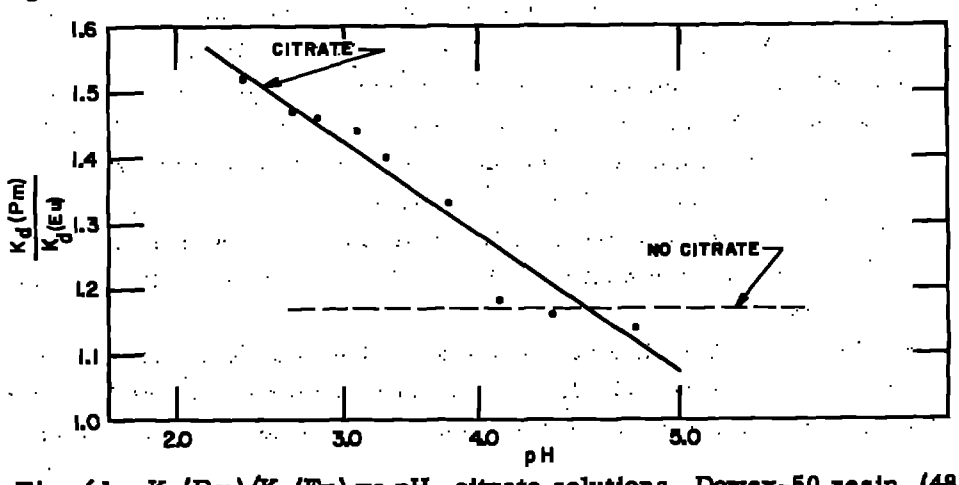


Fig. 61. $K_d(Pm)/K_d(Eu)$ vs pH, citrate solutions, Dowex-50 resin (481)

decreases markedly as the pH is increased, approaching that to be expected from the resin alone above a pH of about 4, and they conclude that with citric acid the most effective rare-earth separations are obtained at pH's below 3.2.

While it is true that the lower the pH the better the separation factor for adjacent rare earths, it is equally true that the lower the pH the longer the time required for elution of a given element. Here again, if time is a factor in the separation, a compromise must be made in choosing an adequate set of experimental conditions.

Representative of the type of radiochemical rare-earth separations which may be made with citrate as the eluting agent are those reported by Ketelle and Boyd[226, 227] (Fig. 62) in which they separated less-than-milligram amounts of each of a large number of rare earths on 97 cm × 0.26 cm^2 columns of 270/325 mesh Dowex-50 operating at 100°C. Five percent citrate buffered in the pH range 3.20-3.40 was used and, while the column running times to individual peaks varied between 6 and 110 hours, separation of adjacent rare earths was quite good, so that these early curves represented a major step forward in the chemistry of the rare-earth elements.

Wilkinson and Hicks[534] (Fig. 63) have separated 10- to 20-mg mixed samples, predominantly of the heavy rare earths, on 50 cm × 0.4 cm Dowex-50 columns by using 5% citric acid, pH 3.05, at room temperature.

Cornish[86] (Fig. 64) and Brooksbank and Leddicotte[51] have used citrate columns to separate mixtures of rare-earth activities in the neutron activation analysis method for detecting trace rare-earth impurities.

In Fig. 64 it may be noted that solutions with five different pH's were used during a single column run. One of the most distinctive characteristics of these elution curves becomes apparent when an eluant at a single pH is used to separate a mixture of all the rare earths. If the pH is such that the first elements eluted (Lu-Yb) are adequately separated, column running times between the peaks of each of the succeeding elements increase in a more or less regular manner. Thus in Fig. 64, where the time between the Lu and Tm peaks is approximately 4 hours, if a pH of 3.20 had been used continuously the time between the Pr and Ce peaks may well have been 20 hours. In order to cut down on the time required to complete the separation without affecting the purity of any of the elements Cornish[86] elected to change the eluting solution pH in discrete steps. A more complete discussion of this phenomenon, and of more effective ways of dealing with it, will be presented in the section on lactate columns.

Heretofore no mention has been made of the behavior of scandium and actinium on ion exchange resins. In most radiochemical separations involving these elements other types of separation steps are found to be more practical

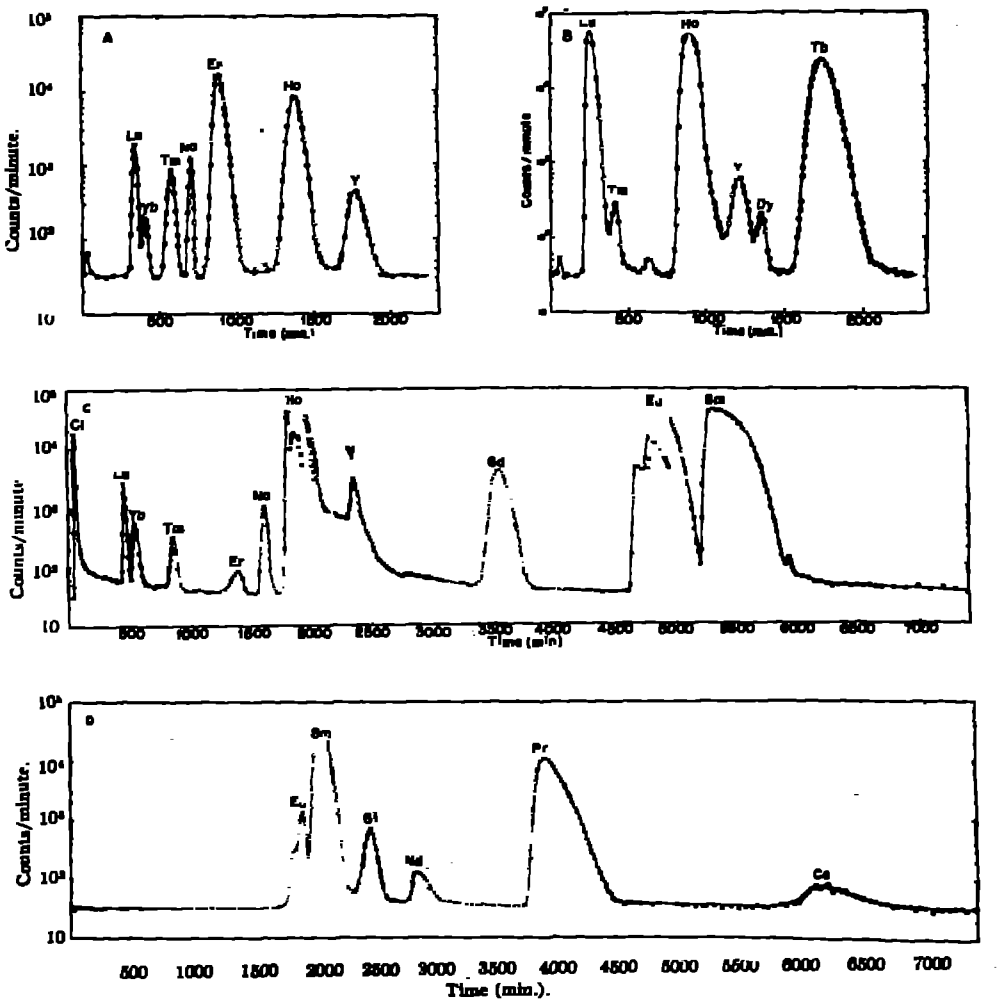


Fig. 62. Demonstrations of rare-earth separations effected with a 270/325 mesh Dowex-50 column at 100°; bed dimensions, 97 cm by 0.26 cm^2; flow rate, 1.0 ml/cm^2/min except in A where 2.0 ml/cm^2/min was used: (A) fractionation of activities produced by neutron irradiation, 0.8 mg spectrographic grade Er_2O_3 (Hilger)(pH 3.20); (B) fractionation of heavy rare-earth mixture consisting of 0.1 mg each of Lu_2O_3, Yb_2O_3, Ho_2O_3 and Tb_2O_3 [Tm, (Er), Y and Dy present as impurities] (pH 3.20); (C) fractionation of intermediate rare-earth mixture consisting of 0.1 mg Ho_2O_3 and 1.0 mg each of Dy_2O_3, Gd_2O_3, Eu_2O_3 and Sm_2O_3 (Cl, Lu, Yb, Tm, Er and Na present as impurities, pH 3.25 for 4550 minutes, then pH 3.33); (D) fractionation of light rare-earth mixture consisting of 0.1 mg each of Sm_2O_3 and Nd_2O_3 plus 0.01 mg each of Pr_2O_3, Ce_2O_3 and La_2O_3 (Eu present as impurity, 61 produced by 1.7 h $Nd^{149} \rightarrow$ 47 h 61^{149}, pH 3.33 for 1610 minutes, then pH 3.40) (226, 227)

than ion exchange. The ion exchange resins may be used, however, and several authors have published papers involving the use of citrate as an eluting agent.

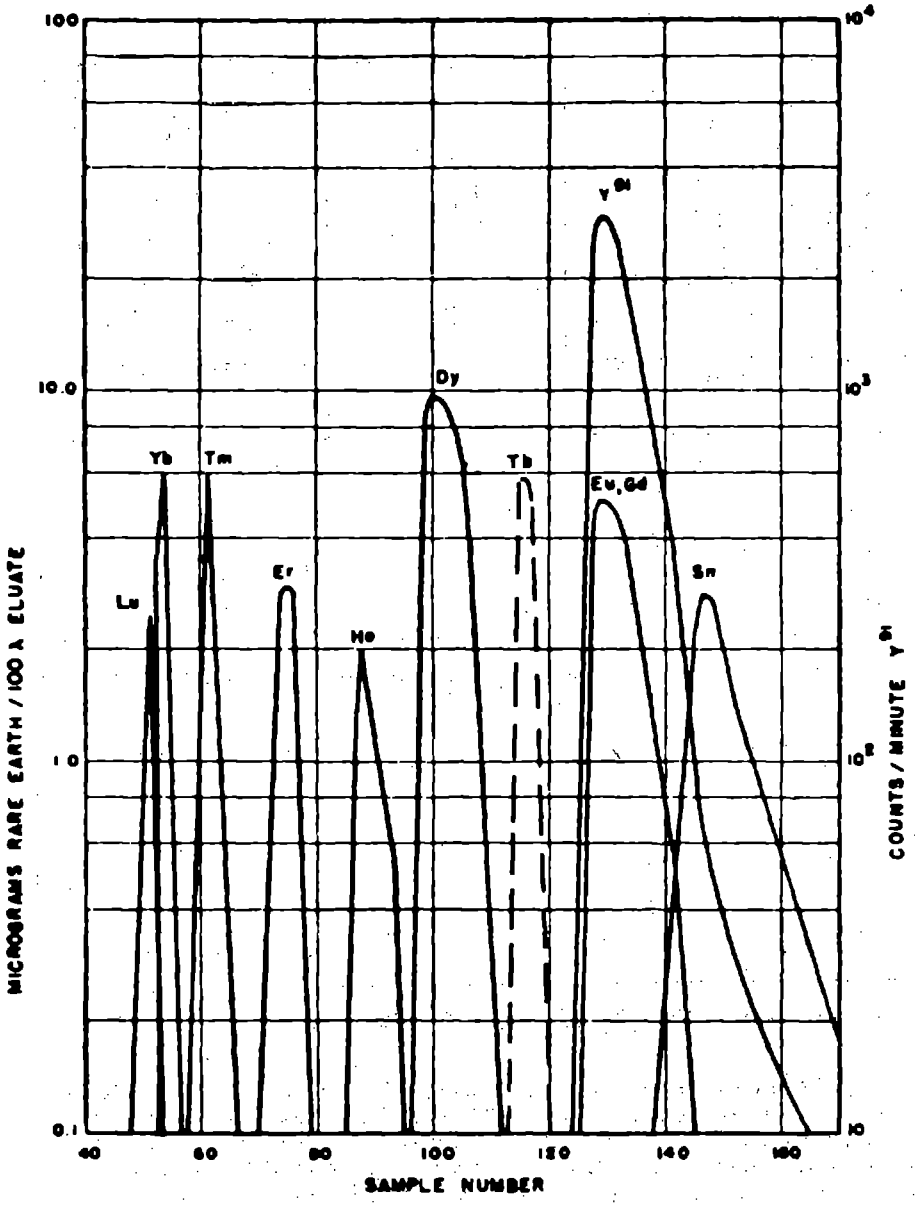


Fig. 63. Standard rare-earth elution. 50 × 0.4 cm Dowex-50 column. Flow rate 0.08 ml/cm^2/min. Sampling time 15 minutes; eluate volume in milliliters is 0.282 × sample number. Y^{91} was measured by its radioactivity, other rare earths spectroscopically. Terbium is estimated since the cyanogen bands obscure the terbium lines. Eluting agent is citric acid adjusted to pH 3.05 with ammonium hydroxide (534)

In general, scandium will elute faster than the fastest of the rare-earth elements (Lu) and actinium will elute slower than the slowest (La). Radhakrishna, [383] using 80-120 mesh Amberlite IR-100-H resin, at room temperature, in columns 36.3 cm long and 0.7 cm in diameter, has eluted

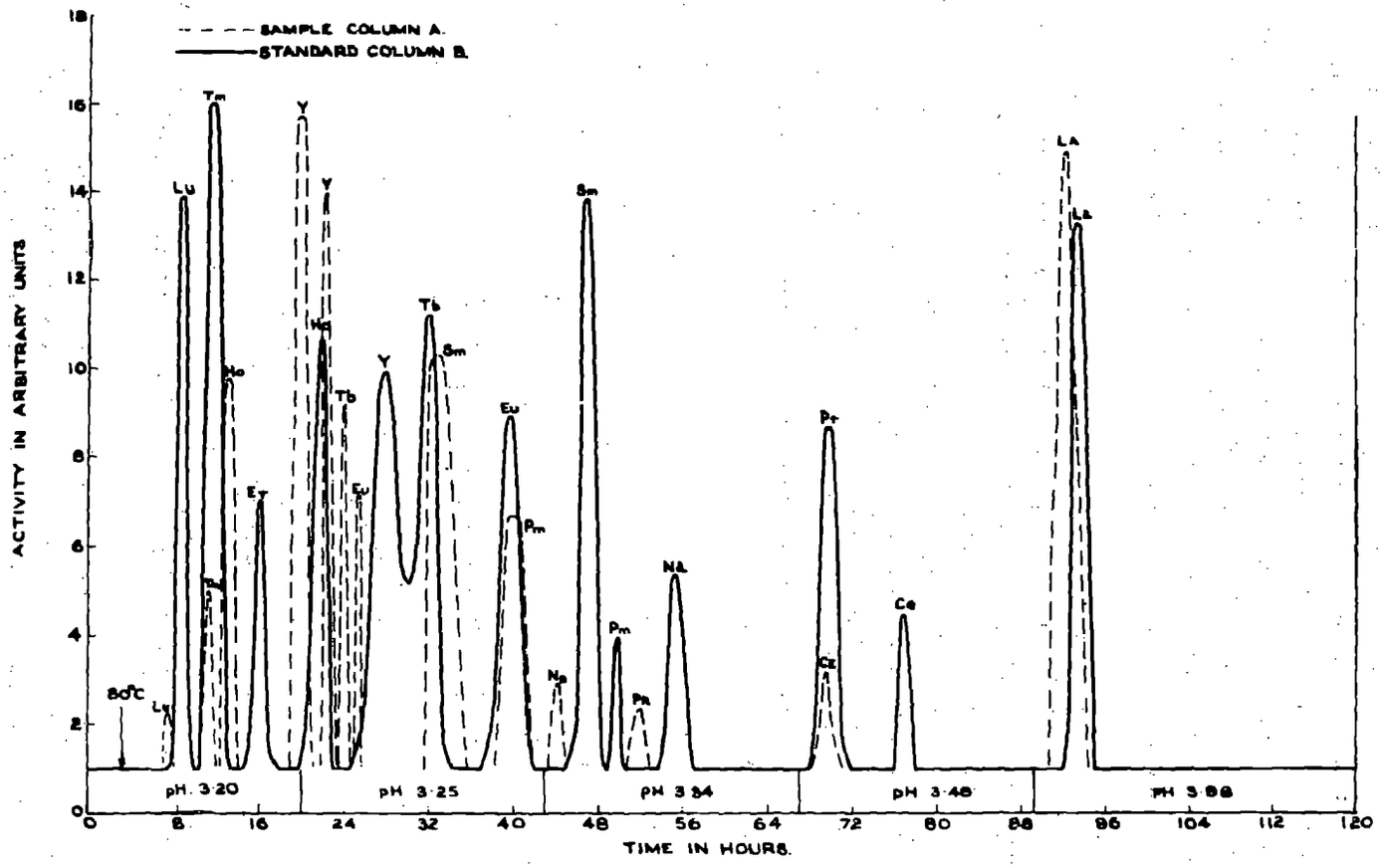


Fig. 64. Separation of rare earths using column of ZEO-KARB 225 (300-330 mesh, 115 cm × 0.20 cm^2, free col. vol. 11 ml), 5% ammonium citrate solution initially at pH 3.20, temperature 80 °C. Flow rates: column A, 0.114 ml/min; column B, 0.109 ml/min (86)

a 1.0 mg Sc-3.7 mg La mixture with 5% citrate at a pH of 2.8. When all of the Sc was eluted, he raised the pH to 3.2 for elution of the La. Iya[214] has separated fairly large samples of scandium from the rare earths by this method. Figure 65 shows the elution curve he obtained for a 6.3-g sample of scandium with 5% citrate at a pH of 3.0. While the column is much larger, and the Sc peak much wider, than would be the case in most radiochemical separations, it can be seen that most of the scandium is eluted before any of the rare earths appear.

Tsong[490] used 5% citrate at a pH of 5.5 on Amberlite IR-100 resin to separate 3.12 mc of Ac^{227} from 160 mg of La. His curve in Fig. 66 indicates that the column was run under saturated conditions but another run could have been made for a more complete separation.

In addition to being used to separate the rare earths from one another, citrate may be used to separate the rare earths from other elements. An example of this type of application is the Y^{90}-Sr^{90} separation done by Lepscky and Restelli,[268] who used 5% citric acid at a pH of 5.2 to milk carrier-free Y^{90} from its Sr^{90} parent on a Dowex-50 column, and Bonnin,[42] who used a pH of 3.2 to do the same thing.

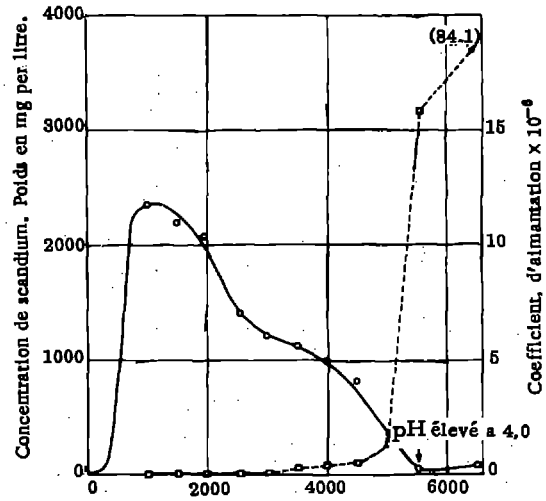


Fig. 65. Elution of a mixture of Sc and rare earths: 6.3 g Sc, 115 cm × 3 cm column, Dowex-50 (60-90 mesh), 5% citrate, pH 3.0, flow rate 300 ml/hr (214)

Concurrently with the development of the elution techniques we have been discussing here, Spedding and his co-workers at Iowa State College, shortly after World War II, developed a technique for large scale production of pure rare earths. Although they used very large amounts of rare earths and their earlier techniques have been discarded for more efficient procedures, perhaps a short discussion of their method is in order here.

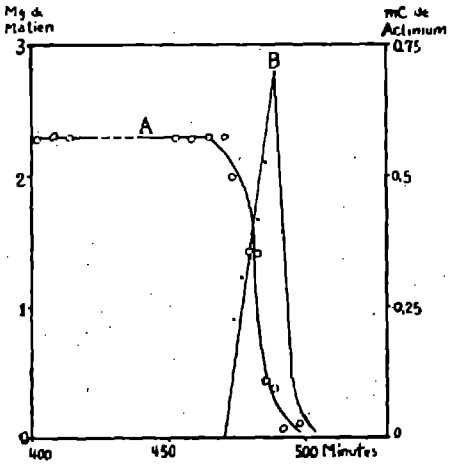


Fig. 66. Elution of 160 mg La, 3.12 mC Ac^{227} from Amberlite IR-100 resin with 5% citrate, pH 5.5. Curve A, mg La eluted, curve B, mC Ac eluted (490)

In the early work on rare-earth ion-exchange columns everyone was using 5% citrate as the eluant, Spedding et al. included. In 1947 they began publication of a series of papers[447] describing their progress in separating macro amounts of the rare-earth elements. At first they used 5% citrate at a pH of 2.5-3.0 for an eluting agent but as they gained experience and had the opportunity to investigate other conditions, their attention shifted to more dilute solutions at higher pH's, culminating in a pair of papers[450,452] describing their operations with 0.1% citrate in the pH range 5.0-8.0.

An example of the type of elution curve that they obtained under these conditions is shown in Fig. 67, when 5-g samples of impure Nd_2O_3 were separated with 0.1% citrate, pH 6.15, in columns of various lengths. The most obvious feature of these curves, of course, is that all of the rare earths are eluted in one "total rare-earth" peak; there are no widely separated peaks for individual elements. For large scale operations this is not a drawback. Indeed, it is the condition for which one strives, for if the experimental conditions are chosen properly all of the rare earths will come off the column "head to tail," with one rare earth immediately behind another, and each one pure except for a small region of overlap between adjacent elements.

One prerequisite for operating columns in this manner, however, is a large rare-earth loading per unit area of resin bed. A characteristic of elutions carried out under these conditions is that each element, whatever its mass on the column, will, if the column is long enough, develop into a band. The length of each band is dependent on the amount of each rare earth present but once a band is formed it will not increase in length or separate from its adjacent elements no matter how long the column. Theoretically,

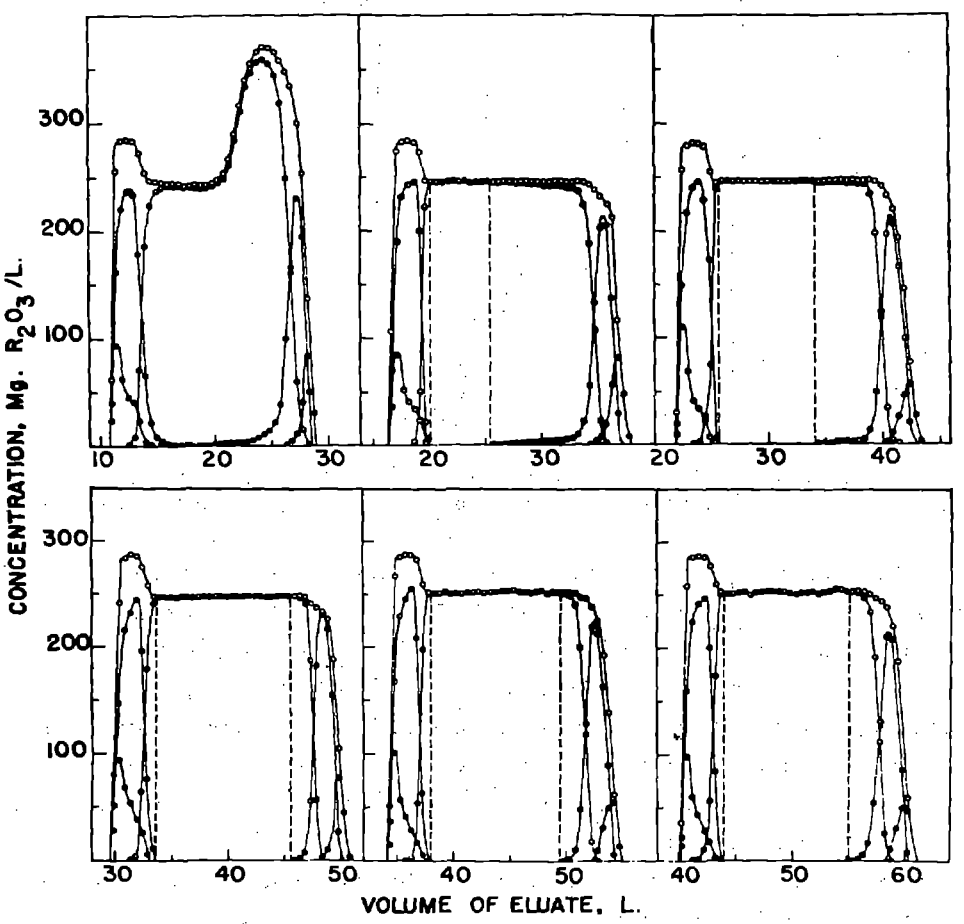


Fig. 67. The elution of 5-g samples of 76% Nd_2O_3, 11% Sm_2O_3, 9% Pr_6O_{11} and 4% other R_2O_3 from – 40 + 50 Nalcite HCR resin beds, 22 mm in diameter and 30, 40, 50, 60, 70 and 80 cm long, with 0.1% citrate solution at a pH of 6.15 and a flow rate of 0.5 cm/min: ⊖, heavy R_2O_3; ◐, Sm_2O_3; ⊖, Nd_2O_3; ◑, Pr_6O_{11}; ●, La_2O_3 and CeO_2; O, total mixed R_2O_3; vertical dashed lines indicate Nd fractions 99.9% pure (447, paper VI)

the interface between bands should be infinitely sharp, with no contamination of one element by another, but in practice there is always some tilting of the interface or channeling effect which causes mixing of adjacent elements. Thus a developed band must be much longer than it is wide if the cross-contamination of one element by its neighbors is not to be significant.

The application of this technique to radiochemical separations seems rather limited, but if the situation does arise where small amounts of one element must be separated from very large amounts of an element which elutes ahead of it on the column, this method may be the best one available. There will be an overlap of the elements, of course, but it should not be necessary to make more than two column runs to effect a complete separation of any mixture.

IV. 7B-3. Lactic Acid

Although citrate was used almost exclusively as an eluting agent in the early ion-exchange work with the rare earths, its use entailed several difficulties which did not exactly endear it to the users. The most serious of these was the length of time required to make a separation. Even with carrier-free samples, column runs took many hours, or even days, for most separations, and this was quite undesirable in cases where short-half-lived activities were being investigated. Another difficulty was the fact that the nature of the rare earth-resin-citrate complex equilibrium could not be deduced as a function of pH very easily because of the three ionizable hydrogens on the citric acid molecule. Thus many chemists were looking for complexing agents which would give better rare-earth separations in shorter times, and which would be more amenable to theoretical treatment.

Mayer and Freiling[297] published a paper in 1953 which indicated that lactic acid should be more effective than citric acid for separating the rare earths, and Freiling and Bunney followed it up with a second paper[150] describing a procedure for separating a mixture of fission-product rare-earth activities containing 20 mg each of Ce, Pr, Nd, and Sm carriers. Their apparatus consisted of a 3-mm-diameter column of Dowex-50 resin (settling rate 6 in. in 5-9 min) operated at 87°C. The best result that they obtained in a series of trials is shown in Fig. 68 and indicates that all of the activities

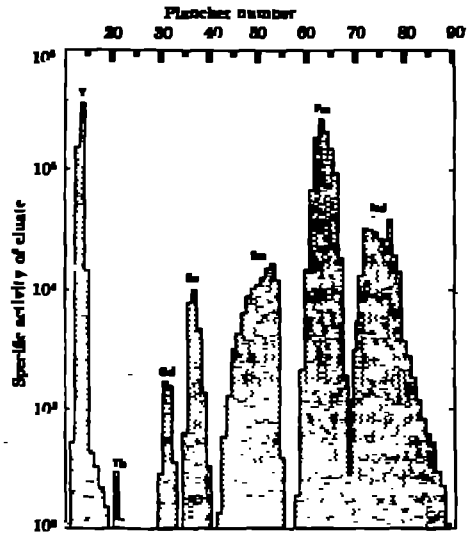


Fig. 68. Ion-exchange-column separation of fission-product rare-earth activities plus 20 mg Sm, 20 mg Nd. Dowex-50 (29-62μ), 3-mm-diam column, 87°C. Eluting agent: 10 ml 0.85M lactic acid, 10 ml 0.90M, remainder 1M lactic acid, all at pH 3. Planchets collected 1-1.5 ml eluant each half-hour (150)

were well separated in about forty hours, although four different concentrations of lactate had to be used.

Almasy[7] has recently published the results of a search for a procedure which could be used for quantitative determination of individual elements in a mixture of rare earths. He used columns of Dowex-50, 10 mm in diameter × 200 cm long, at elevated temperatures to effect the separation of samples in the range 50-200 mg total rare-earth weight. One molar lactic acid was used as the eluant and the pH was increased in discrete steps during the elution, with the number, timing, and size of each step dependent on the composition of the rare-earth mixture being separated. The author felt that this type of multiple-step elution procedure was more favorable for the purposes of quantitative determination than the "gradient elution" method (to be described later) since the relative quantities of rare-earth metals to be separated could more easily be taken into account.

Others who have reported separations of rare earths in the weight range 10 to 20 mg per element include Petrow,[364] who separated Nd and Pr on an 11 mm × 35 cm column of colloidal Dowex-50 at room temperature with 4.25% lactic acid at pH 3.30, and Troianello and Sugihara,[487] who used 1 cm × 80 cm columns of colloidal Dowex-50 at room temperature with 0.70M lactic acid at pH 3.30 to separate 8-15 mg each of Y, Sm, Eu, and Nd.

While these results are significantly better than those to be expected from a citrate column with the same rare-earth load, the column running time is still excessive for some purposes. Using only 1 mg of Y, Eu, Sm, Nd, Pr, and Ce as a carrier load, Cuninghame, Sizeland, Willis, Eakings, and Mercer[99] have shown how a mixture of all of the rare earths below europium may be separated in approximately 10 hours. Their data, reproduced in Fig. 69, were obtained with ZEO-KARB 225 resin, and indicate good separation for the Eu to La peaks, although the elements above Eu are not separated too well.

In an attempt to find conditions under which separation of rare-earth samples could be made quickly on a routine basis, one of the authors[334] made a systematic study of the "gradient elution" technique using lactic acid as the eluant. As has been mentioned previously in the citrate section, one of the most distinctive characteristics of a rare-earth elution curve obtained with a single pH of eluant is the increased spacing between peaks of successive elements as they are eluted. This is shown again in Fig. 70, where tracer activities were used and the pH was chosen to give a reasonably good separation between the Lu-Yb-Tm peaks. As can be seen in Fig. 70, the running time between peaks increases from 22 minutes for the Lu-Yb pair to 8 hours and 40 minutes for Eu-Sm. Other chemists had tried to obtain more evenly spaced peaks by changing the eluting solution in discrete steps, either by increasing the pH (Fig. 64) or by increasing the concentration (Fig. 68). Both

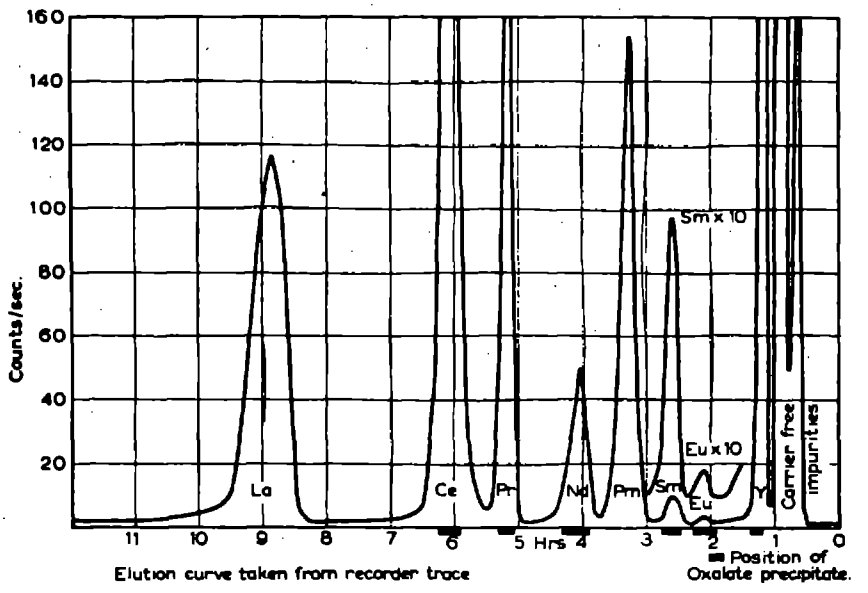


Fig. 69. Separation of rare-earth activities plus 1 mg each of Y, Eu, Sm, Nd, Pr, and Ce. Column 3-4 mm × 20-30 cm, ZEO-KARB 225, settling rate 0.5-1.0 cm/min, 87°C. Eluant 1M lactic acid, pH 3.25 ± 0.03, flow rate 10-12 ml/hr (99)

of these operations, however, require the presence of the chemist to change the eluting solution reservoirs, and, if very many columns are being operated at one time, could involve a great deal of work.

With the gradient elution technique, however, the goal of more evenly spaced peaks is reached by changing the pH of the eluting solution continuously and automatically. A schematic diagram of apparatus which is currently in use in this laboratory is shown in Fig. 71. In normal operation the "high pH solution" is allowed to drip into the "low pH solution" at a rate which will give the desired increase in pH per unit time. The "low pH solution", thoroughly mixed, is then forced through the column in the normal manner. The desired rate of change of pH will, of course, depend on the separation that is to be made, but Fig. 72 indicates the type of elution curve which may be expected when using this method. Here the initial conditions were the same as those in Fig. 70, but the pH of the 1M lactic acid eluant was increased continuously at 0.107 pH unit/hour. There is still an adequate separation between the Lu-Yb peaks but now the Eu-Sm peaks are only 19 minutes apart as compared to 8 hours and 40 minutes for the constant pH run. In addition, the column running time to the Sm peak has been cut from 38 hours 25 minutes to 4 hours 58 minutes without affecting the purity of any of the rare-earth elements at all.

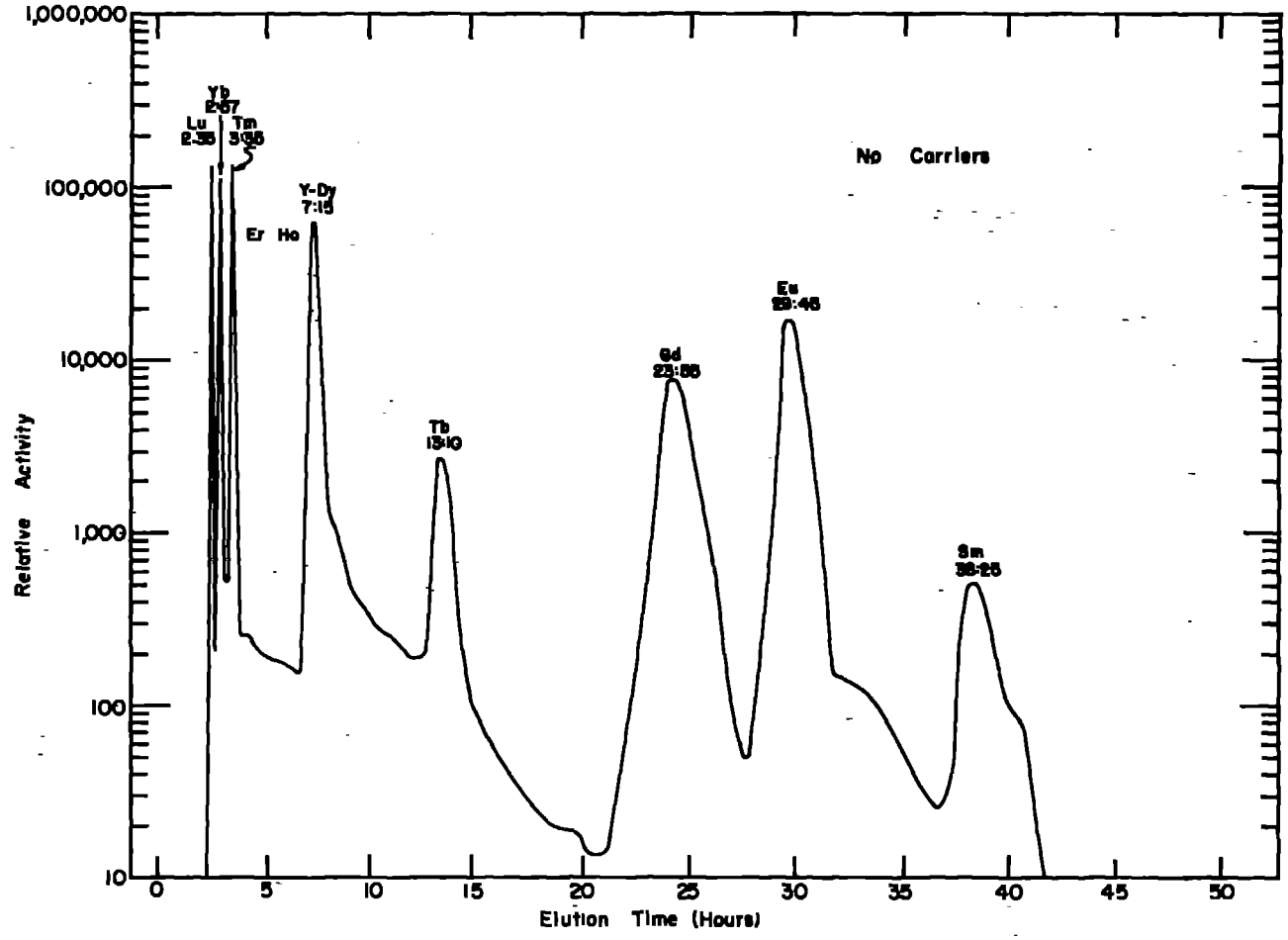


Fig. 70. Elution curve of carrier-free rare-earth tracer activities at a constant pH of 3.19. Column 7 mm × 60 cm, Dowex-50, settling rate 1.0-1.5 cm/min. Eluant 1M lactic acid (334)

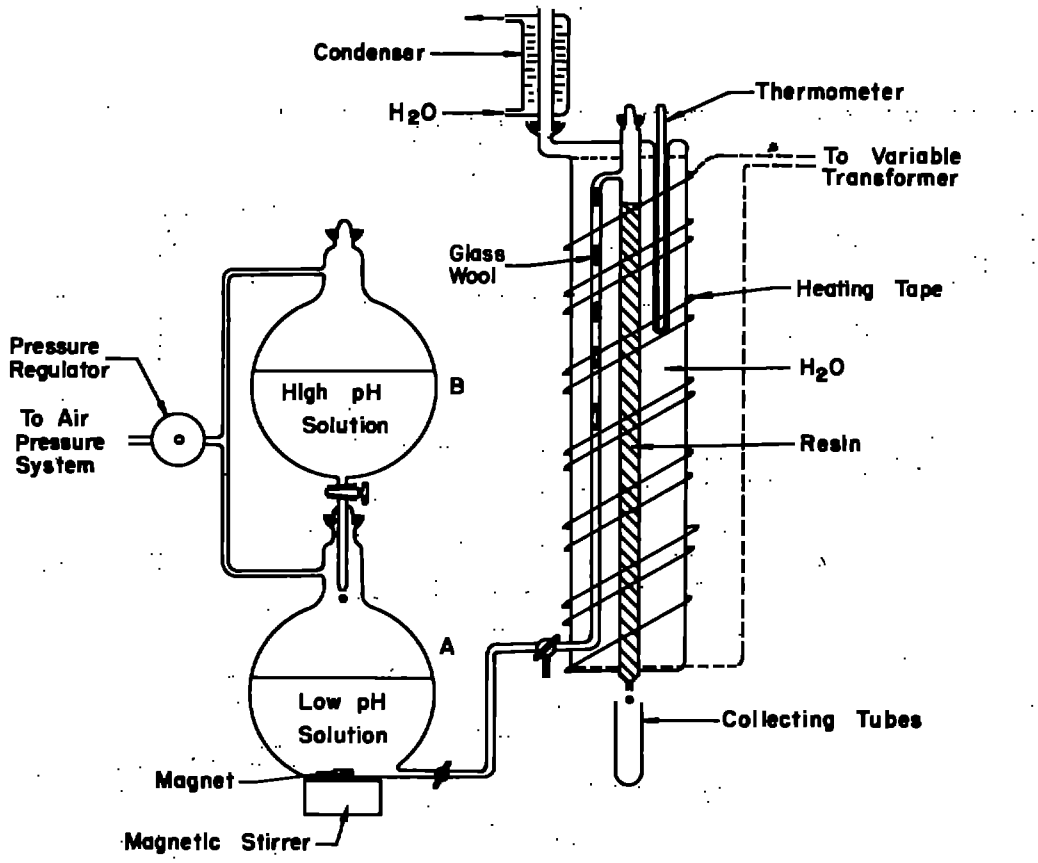


Fig. 71. A schematic diagram of an ion-exchange column apparatus in which the pH of the eluting agent may be changed continuously (334)

The gradient elution technique is obviously an improvement over previous methods for separating carrier-free mixtures of the rare-earth elements. It can be used just as effectively for rapid separation of weighable amounts of rare-earth carriers but requires careful judgment to establish the proper operating conditions. As the mass of a given rare earth is increased the column quickly becomes saturated with respect to that element and its elution peak broadens. As is shown in Fig. 57 and Fig. 73, the width of the peak is very sharply dependent on the amount of carrier. In these examples 2 mg of Pr (5.2 mg Pr/cm^2 resin bed) was enough to give a noticeable increase in the width of the Pr peak and 8 mg of Y (20.8 mg Y/cm^2) was enough to make the trailing edge of the Y peak mix with the Tb activity. It should be mentioned, however, that with 1M lactic acid these highly loaded peaks have a distinctive shape, with a slowly rising leading edge and a very abrupt trailing edge. Only a small adjustment, either in dpH/dt or column loading, would have been necessary, therefore, to give a complete separation of these mixtures. It has been the experience of the authors, based on the separation of thousands

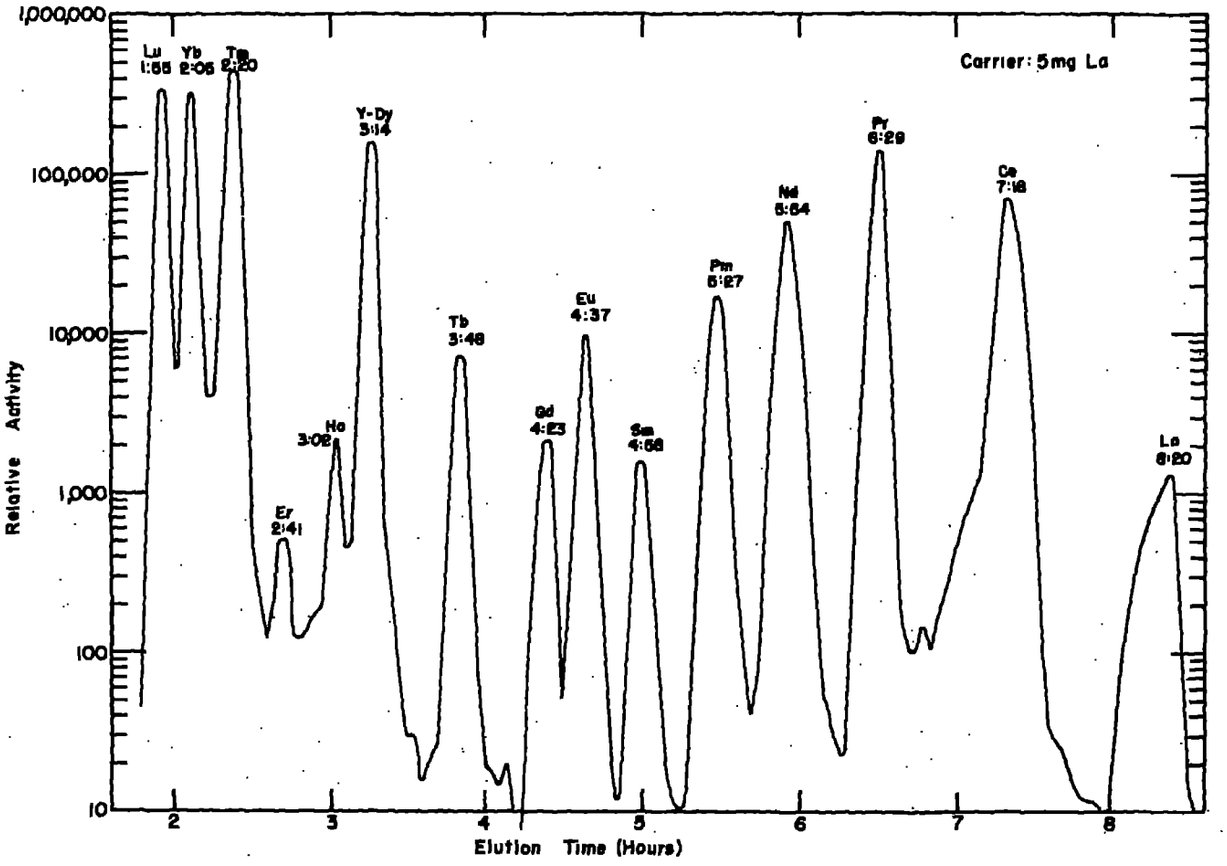


Fig. 72. Elution curve of rare-earth tracer activation plus 5 mg of lanthanum, initial pH 3.19, pH changed continuously at 0.107 pH unit/hour (334)

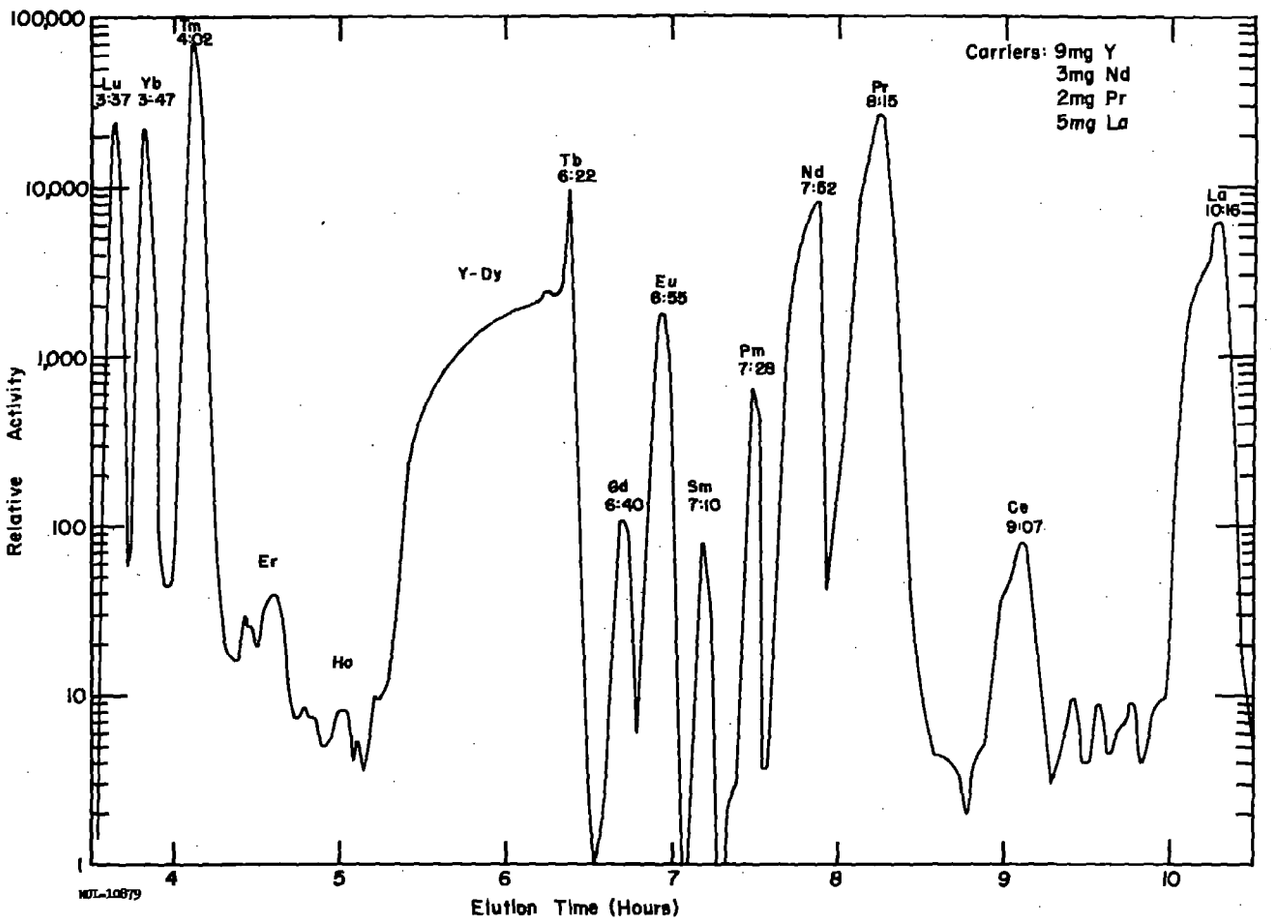


Fig. 73. Elution curve of rare-earth tracer activities plus 9 mg Y, 3 mg Nd, 2 mg Pr, and 5 mg La carriers; initial pH 3.19; pH changed continuously at 0.1 pH unit/hour, same apparatus as Fig. 70 (334)

of rare-earth samples, that any mixture of rare-earth elements in the 10-mg-per-element weight range may be separated, one or two dozen samples at a time, on a routine basis without difficulty with the gradient elution technique.

For mixtures of tracer activities, the gradient elution technique may be used with fairly small columns to give rapid separation of the rare earths. Figure 74 shows an elution curve of a mixture of rare-earth fission products which was obtained on a 1 mm × 10 cm column. The separation between adjacent elements is reasonably good and the column running time of less than an hour for most of the elements permits study of fairly short-lived activities.

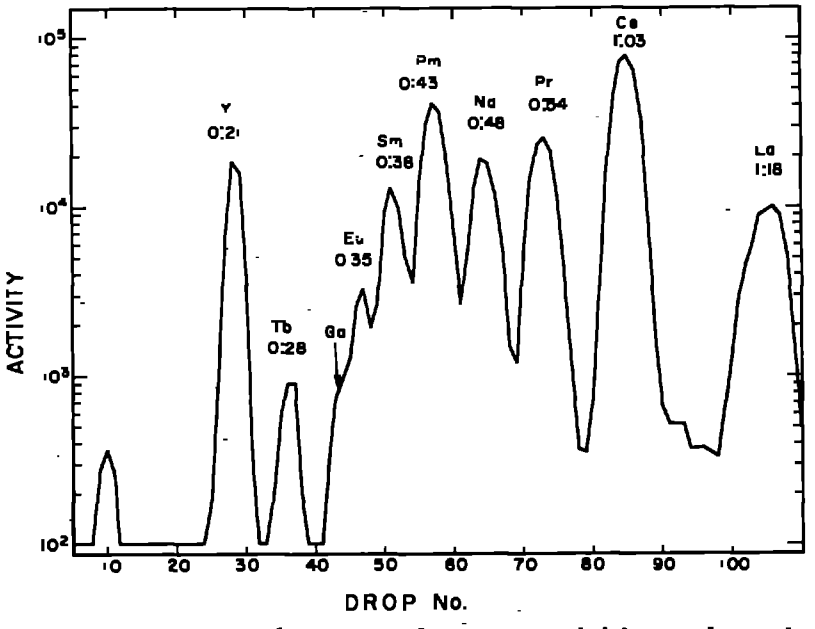


Fig. 74. Elution curve of rare-earth tracer activities; column 1 mm × 10 cm, Dowex-50, settling rate 1-1.5 cm/min, eluant 1M lactic acid, pH 3.00, dpH/dt 0.2 pH unit/hour, temperature 87°C (334)

Preobrazhensky, Kalyamin, and Lilova[378] have also used the gradient elution technique to effect very rapid separations of rare-earth tracer activities. They used 2 mm × 18 cm columns of 6% cross-linked KU-2 resin and, instead of changing the pH, used neutral solutions of ammonium lactate and gradually increased the concentration. Figure 75 shows the curve that they obtained from a mixture of rare-earth tracer activities when the ammonium lactate concentration was increased from 0.19M to 0.5M during the run. The separation between elements is very good, including the Y-Dy peak, and the column running time of about 3 hours to the Nd peak is fairly short. The authors claim, however, that the KU-2 resin reaches equilibrium at least 5 times as rapidly as Dowex-50 and that the column in Fig. 75 could have been run at a faster flow rate without affecting the separation significantly.

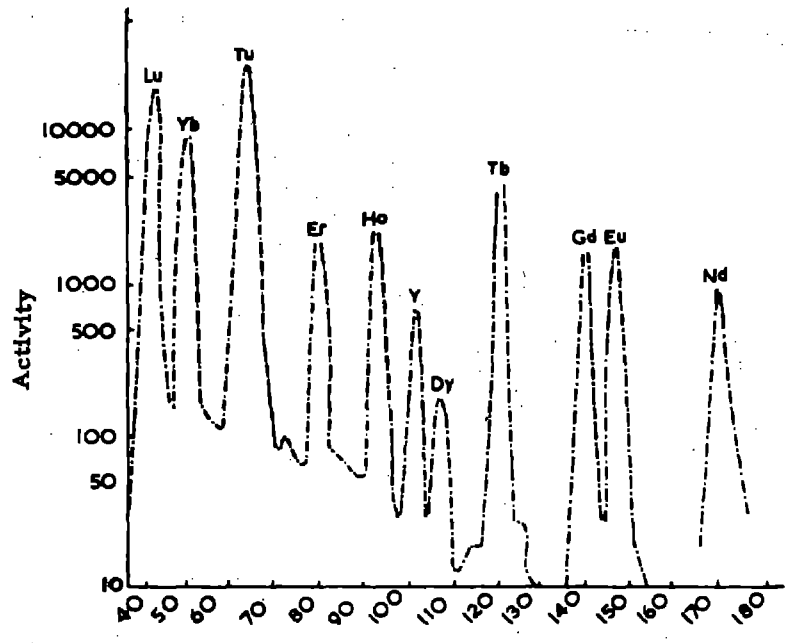


Fig. 75. The separation of radioactive rare-earth elements on KU-2 resin in a column 18 cm long × 2 mm diam; temperature 90°C, average resin particle size 15 microns, flow rate approximately 1 drop/min, eluant 0.19M ammonium lactate, gradually increased to approximately 0.5M during the run (378)

Indeed, they have used this resin to separate Lu-Yb activities in 5 minutes (Fig. 76) at 90°C, and Lu-Yb-Tm mixtures in less than 1-1/2 hours (Fig. 77) at room temperature.

Ever since the discovery of the gradient elution technique the theoretical details of chromatography by this method have received attention. Drake,[107] Freiling,[151,152] and Piez[365] have published excellent papers dealing with the theory of various aspects of gradient elution. It should be pointed out, however, that theories which predict the position, shape, and purity of eluted elements have so far been restricted to carrier-free mixtures which give essentially gaussian-shaped peaks. When weighable amounts of carrier are used and the peak shape becomes distorted, the theories break down. At the present state of the art, in any case, empirical calibrations are necessary to insure that a given separation can be performed properly.

IV. 7B-4. Glycolic Acid

Another eluant which received attention at about the same time that the lactate systems were being developed was glycolic acid. Relatively few papers concerning the glycolate systems have appeared in the literature but Stewart[460] has used it on very short columns for rapid separation of the yttrium group of rare earths and has described[461] the behavior of carrier-free rare earths on

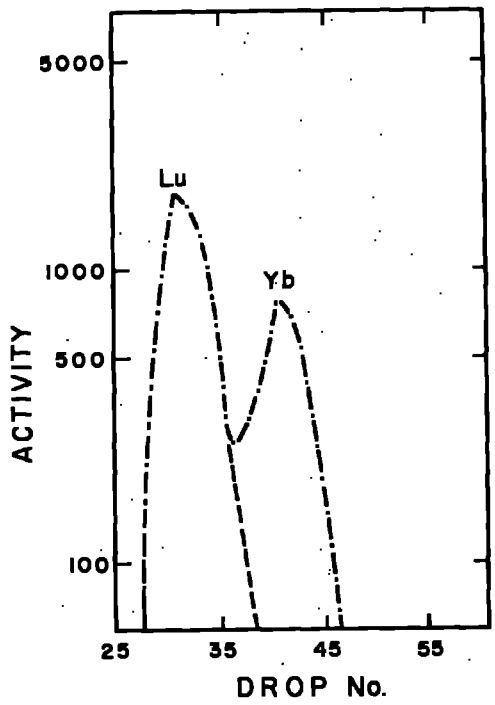


Fig. 76. Separation of Lu and Yb in 5 minutes. Column 5 cm long, temperature 90°C, eluant flow rate 1 drop every 7 seconds (50 drops/ml) (378)

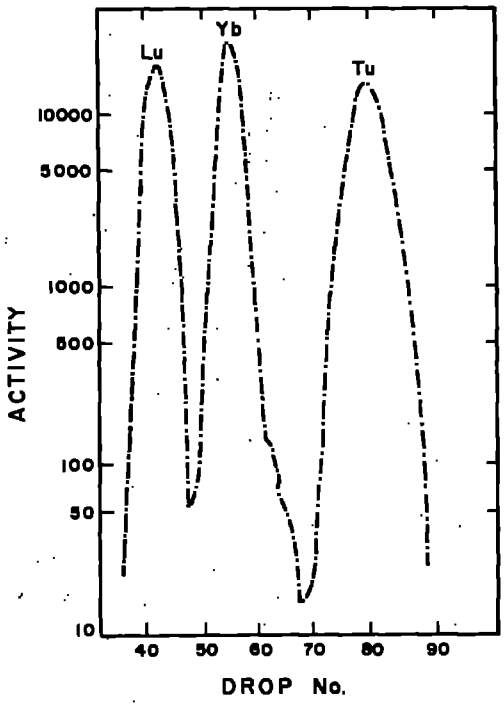


Fig. 77. Separation of Lu, Yb, and Tm without heating, in a column 10 cm long. Flow rate less than a drop per minute (378)

columns at room temperature and at 87°C. No data is available on elution of weighable amounts of rare earths with glycolate eluant but indications are that glycolate and lactate are quite comparable in their behavior.

IV. 7B-5. α-Hydroxyisobutyric Acid

An eluant which has effectively supplanted all others in the separation of the transplutonium elements, and which looks most promising for the rare earths, is α-hydroxyisobutyric acid (α-but). Choppin, Harvey, and Thompson,[77] early in 1956, showed how it could be used for the trans-Pu elements and in a subsequent paper Choppin and Silva[76] showed α-hydroxyisobutyric (α-but) to be more effective than either lactate or citrate in separating rare earths on a tracer scale. An elution curve that they obtained from a 5 cm × 2 mm column of Dowex-50 × 12 at 87°C is shown in Fig. 78. The separation of adjacent elements is excellent, but it is difficult to make a fair comparison between the various eluants just on the basis of the elution curves shown here. Additional data will be presented in a later section on comparison of eluants.

Choppin and Silva indicated that room-temperature operation of α-but columns does not decrease the separation factors by more than 10% and Smith

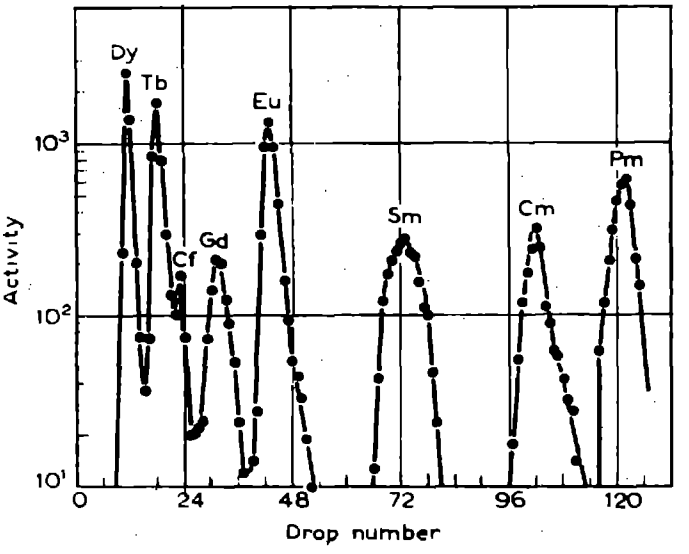


Fig. 78. Elution of tracer rare-earth-actinide activities with α-hydroxyisobutyric acid. Column 5 cm × 2 mm Dowex-50 × 12 (400 + mesh), temperature 87°C, flow rate 1.0 ml/cm^2/min, 0.2-0.4M solution, pH 4.0-4.6 (76)

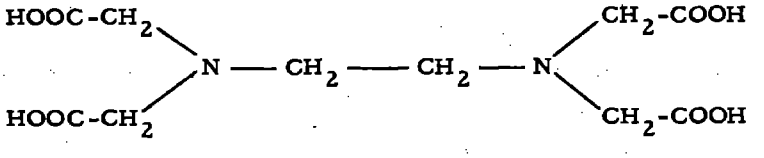
and Hoffmann[442] have shown that very effective separations can be made under these conditions.

Here again, no data are available on elution of weighable amounts of rare earths with α-hydroxyisobutyric acid but the separation factors are so much better than, and the structure is so similar to, lactic acid that the α-but system should be the most efficient one for all but macro-scale separations of the rare-earth elements.

One factor which seldom intrudes in discussions of this sort, but appears in practical applications, is cost. At the present time α-hydroxyisobutyric acid is approximately seventy times as expensive as lactic acid; and if very large volumes of eluant are needed, cost might be an important factor in the choice of the eluant to be used.

IV. 7B-6. Amino-Polyacetic Acids

It has long been known that the amino-polyacetic acid group of compounds form very tight complexes with a large number of metallic ions. The member of the group which has been investigated most thoroughly, and which has received the greatest acceptance, in the separation of the rare earth elements is ethylenediaminetetraacetic acid (EDTA):



Mayer and Freiling,[297] in a 1953 article on the comparison of eluant efficiencies, showed that the rare-earth separation factors for EDTA are much larger than those for citrate, lactate, glycolate, or malate. Duyckaerts and Fuger[114] describe a procedure for separating small amounts of a mixture of Y, Eu, Pm, and Ce activities with a 2.5×10^{-2}M EDTA solution at a pH of 3.15-3.2, but Cornish, Phillips, and Thomas,[85] investigating the distribution coefficient of rare earths between 0.005M EDTA + 0.14M acetate and ZEO-KARB 225, report that, while the separation factors between rare earths are large, the actual separation is poorer than with citric acid. This may account for the fact that so few articles have appeared in the literature concerning small-scale rare-earth separations with EDTA as the eluant.

By far the major application of EDTA has been in the large-scale production of pure rare-earth compounds. At high pH's, and under the proper conditions, EDTA is admirably suited to the elution of large amounts of rare earths with the "head-to-tail" type of elution curve described in the citrate section. The low solubility of EDTA requires that columns be used in other than the H^+ form but this is not a serious restriction on most operations. Excellent articles on the separation of rare earths on EDTA-Cu^{++} columns have been published by Spedding, Powell, and Wheelwright[453] and Powell and Spedding.[375, 376] Brunisholz[57] has used an eluant of NH_4^+-Mg^{++}-EDTA on Cu^{++}-NH_4^+ columns, and Fuger[161] has used EDTA on Co^{++}, Zn^{++}, and Ca^{++} columns for fairly large-scale separations.

In addition, Spedding, Powell, Daane, Hiller, and Adams[456] have used EDTA-Cu^{++} columns, and Iya and Loriers[213] have used EDTA-NH_4^+ acetate columns for the large-scale separation of scandium from the rare-earth elements.

An interesting application of EDTA complexing to ion exchange separations has been published by Fritz and Umbreit,[157] in which they used short columns of Dowex-50 resin to filter cationic species out of solutions containing a mixture of elements plus EDTA. The retention of cations by the resin is a fairly sharp function of pH, as shown by their data in Fig. 79, but there is sufficient difference between certain mixtures of elements to permit simple, rapid separations to be made. Thus, the authors suggest that it should be possible to separate any of the rare earths from scandium, iron (+3), bismuth, or copper; or, at pH 2, rare earths through samarium could be separated from thorium, ytterbium, or lutetium; or a complete separation of thorium from iron or bismuth could be made; or a nearly complete separation of thorium from zirconium or scandium could be made by this method.

Another interesting application, although somewhat less useful for radiochemical separations, has been reported by Bril, Bril, and Krumholz,[46] who use electrodialysis to separate cationic, anionic, and uncharged species

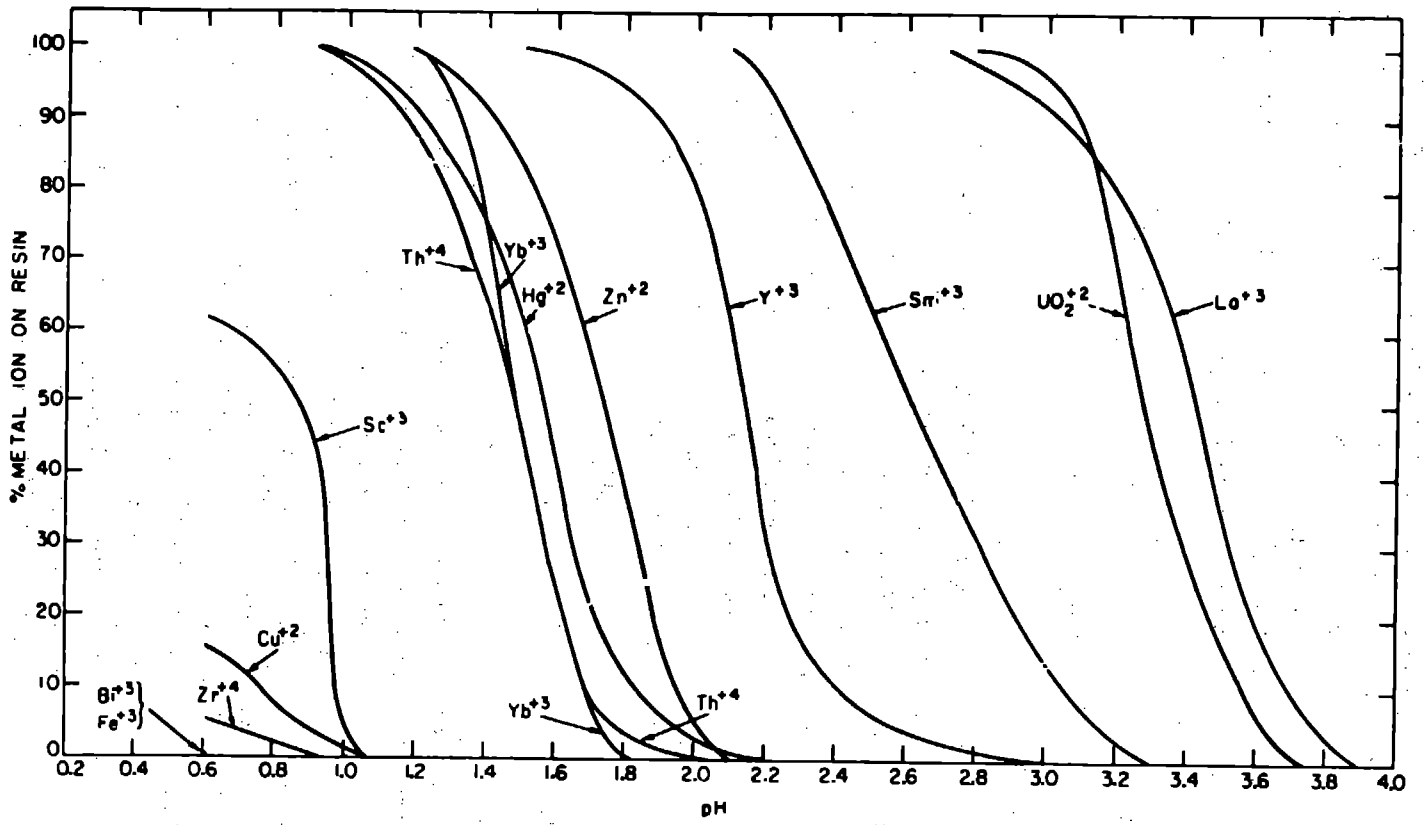
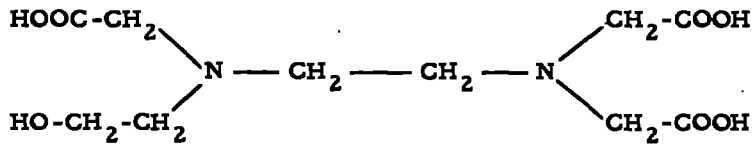


Fig. 79. Retention of different metal ions by Dowex-50 resin as a function of pH of solutions containing EDTA (157)

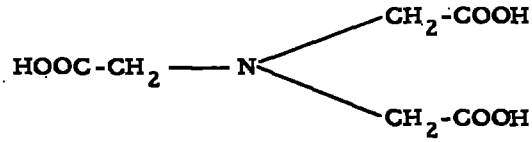
in solutions containing EDTA. The solution between electrodes is compartmented by sheets of cation- and anion-exchange membranes which act as filters for the desired ions or complexes, and the authors report significant separations of Nd-La, Nd-Pr-La, and Th-Nd mixtures, although the over-all efficiency of the system was fairly low.

A close relative of EDTA which has been used to a limited extent for separation of certain rare-earth mixtures is n-hydroxyethyl-ethylene diamine triacetic acid (HEDTA):



Spedding and his co-workers at Iowa State have published several papers[376, 533] dealing with separation of rare earths with HEDTA. The consensus, however, is that HEDTA is not as efficient in separating all of the rare earths from each other as is EDTA. Its main usefulness seems to lie in the separation of Sc-rare earth mixtures,[456] and Y-Dy mixtures,[9] (yttrium elutes between Sm and Nd with HEDTA instead of between Dy-Tb).

Fitch and Russell[143] examined various imino-diacetic acids as possible complexing agents in the ion exchange separation of the rare earths and reported excellent separations with nitrilotriacetic acid (TRILO):



TRILO has received fairly wide acceptance as an eluting agent for rare-earth separations but, as with EDTA, its use has been confined mainly to production of large amounts of rare-earth compounds. TRILO is analogous to EDTA, too, in that most large-scale production procedures use retaining ions other than NH_4^+. Thus, while Loriers and Carminati,[272] Holleck and Hartinger,[205] and Topp[486] have used NH_4^+ columns with TRILO, Massonne[293, 294, 538] has used Zn^{++}, Noddack[340, 341] has used Cu^{++}, Ni^{++} or Na^+, and Weidmann and Liebold[513] have used Cu^{++}, Ni^{++}, or Co^{++} columns for separating various mixtures of rare earths.

A fairly large number of amino-polyacetic acids, aside from those already discussed, have been mentioned in the literature in connection with the rare earths. Fitch and Russell[143] investigated O-carboxyaniline-N-N-diacetic acid, benzyl imino-diacetic acid, and hydrazinodiacetic acid as well as TRILO. They found TRILO to be the best of this group but hydrazinodi-

acetic acid was promising enough to warrant a second paper[144] describing a procedure by which La could be kept on an IR-120 column while all of the other rare earths were eluted. Wolf and Massonne[537] have reported successful large-scale separations of rare earths with β-oxyethyl-imino-diacetic acid at 70°C using columns of Wofatit KPS-200 resin.

Holleck and Hartinger[202] investigated the series of amino-tetraacetic acids: ethylenediaminetetraacetic acid, ortho-cyclohexanyl-diamino-tetraacetic acid, ββ'-diaminoethyl-ether-tetraacetic acid, and ethylene glycol-bis-β-aminoethyl-ether-tetraacetic acid. They report that, at a given pH, the separation factor increases in the sequence given, with the best separation shown by ethylene-glycol-bis-β-amino-ethyl-ether-tetraacetic acid at pH 6.75.

The Iowa State group[9] has reported successful Nd-Pr separations using salts of diamino-diethyl-ether-tetraacetic acid and diamino-cyclohexane-tetraacetic acid, and state that the performance of diamino-diethyl-ether-tetraacetate on hydrogen beds is excellent, but they do not give any elution curves for these complexing agents.

Although there are relatively few articles in the literature concerning radiochemical separations using amino-polyacetic acids, it is not to be concluded that these complexing agents have no value in this type of operation. Perhaps they have not received the attention which is their due; or they may have been used and the procedures not published. As an example of this, Bunney, Hutchin,[64] and the authors have used diethylenetriamine-pentaacetic acid to separate 5-mg-per-element mixtures of Y-Dy (Hutchin's curve is shown in Fig. 80) but nothing about this technique has appeared in the literature. Whatever the reason for the paucity of data in the past, however, the use of this group of complexing agents in the radiochemical separation of rare-earth elements warrants further study.

IV.7B-7. Other Eluants

In addition to the systems that have already been discussed, a number of very interesting cation-exchange procedures dealing with rare-earth separations have appeared in the literature.

Yoshimura, Takashima, and Waki[543] have obtained effective separation of weighable amounts of Sc from Er on Dowex-50 resin with a solution 0.5*M* in NH_4 acetate and 0.5*M* in acetic acid. Scandium passes through the column and erbium sticks.

Subbaraman, Rajan, and Gupta[467] have reported preliminary experiments which indicate that reasonably good rare-earth separations may be made on Dowex-50 resin with 0.3-0.5% solutions of sodium tripolyphosphate (pH 3.6) as the eluant.

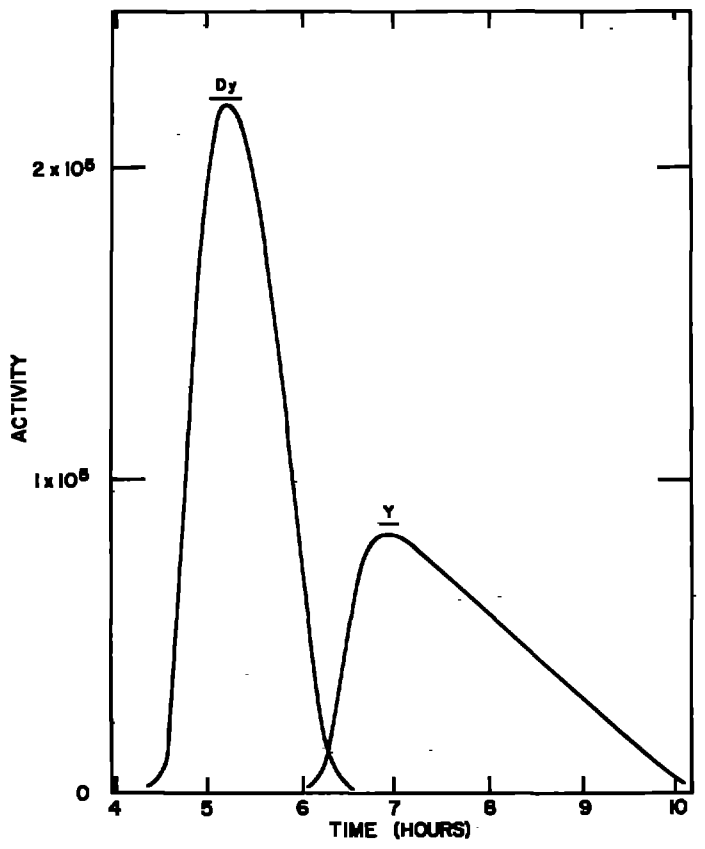


Fig. 80. Separation of 5 mg Dy-5 mg Y on 7 mm × 60 cm Dowex-50 columns, temperature 90°C, eluant 0.008M diethylenetriamine-pentaacetic acid, pH 4.25, flow rate approximately 0.3 ml/min.

Surls and Choppin[471] have investigated the Dowex-50-NH_4CNS system and report that the lanthanides elute in the usual sequence of decreasing atomic number with ammonium thiocyanate as the eluant, but the separation between adjacent elements does not seem to be great enough to permit easy purification of complex mixtures.

James and Bryan[217] have reported effective separation of small amounts of Y-Eu mixtures on Dowex-50 columns using solutions of thenoyltrifluoroacetone-dioxane-water (5 g TTA-45 ml dioxane-50 ml water, or 2 g TTA-38 ml dioxane- 60 ml water) as an eluant. Excellent separations were obtained in the pH region 5.8-6.0, with Y eluting behind the Eu, but no data are available for other rare earths.

Ionescu, Constantinescu, Topor, and Gard[211] have used acetone-water-HCl mixtures as eluants to separate Ce and La on columns of KU-2 resin. An elution curve that they obtained with an eluant containing 65% acetone, 20% HCl (d = 1.16), and 15% water is shown in Fig. 81. The most remarkable feature of this curve is the fact that La elutes before Ce. If this behavior is

systematic with all of the other rare earths this elution method could have important applications in certain types of separations.

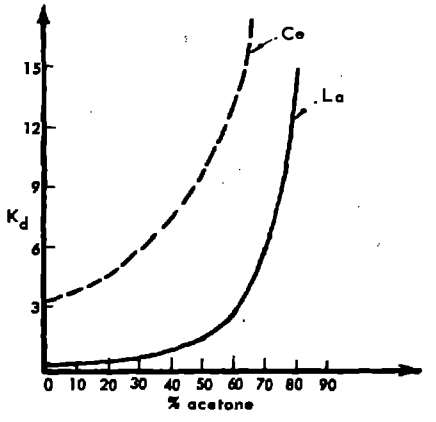


Fig. 81(a). Distribution coefficient variation for the La-Ce system (KU-2 resin with HCl-acetone eluant) (211)

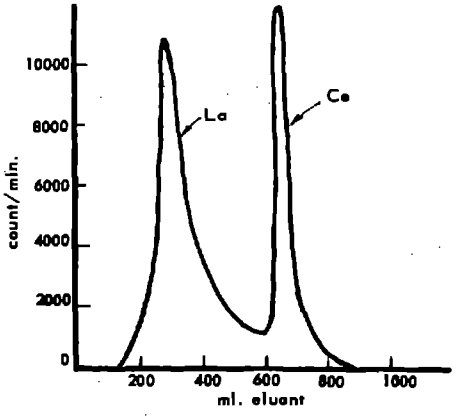


Fig. 81(b). Elution of Ce-La tracers from KU-2 resin with the eluant: 65% acetone, 20% HCl (d = 1.16), 15% water (211)

IV. 7B-8. Comparison of Eluants

It is extremely difficult to make a quantitative comparison of eluants based on data which have appeared in the literature since so few experiments have been reported in which the eluant was the only variable. It is useful, nevertheless, to plot such data as are available for whatever qualitative conclusions may be drawn from them.

Powell and Spedding,[376] in their review article on separation of the rare earths with aminopolyacetic acids, have published curves of stability constant vs atomic number for various complexing agents in this group. Their curves are reproduced in Fig. 82 and have several very interesting features. To a first approximation the stability constants determine the degree of separation of rare earths with these eluants. Thus, in Fig. 82, the best separations should be obtained with that material whose curve has the highest slope. Nitrilotriacetic acid (TRILO) has a continuous upward slope and, as we have seen, may be used to separate all of the rare earths. Ethylenediaminetetraacetic acid (EDTA) and diaminocyclohexane-tetraacetic acid (DCTA) have considerably larger slopes and commensurately larger separation factors. The curve for hydroxyethyl-ethylenediamine-triacetic acid (HEDTA), however, has an inflection in the Sm-Er region, so that separation of this group of elements is poor. And with diethylene-triamine-pentaacetic acid (DTPA) the curve has a maximum at dysprosium, which makes the Pm-Lu group of elements difficult to separate.

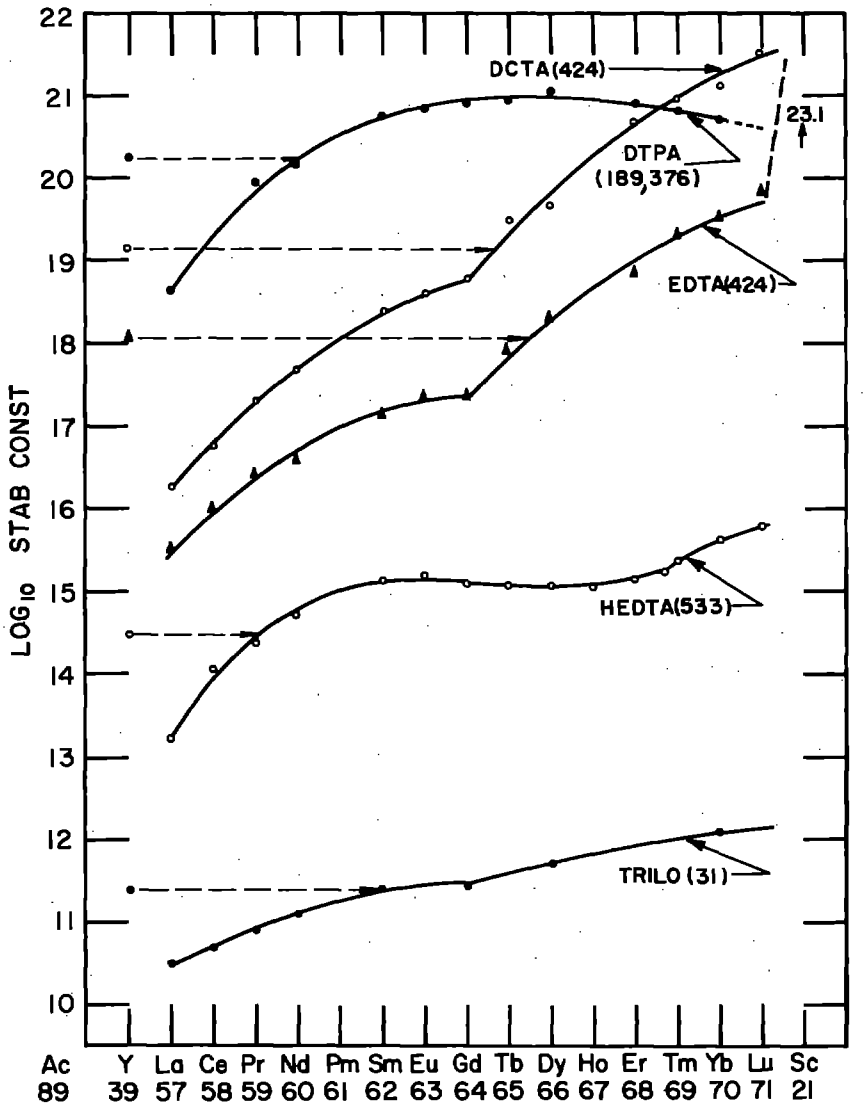


Fig. 82. Stability constants of various rare-earth chelates. The numbers in parentheses are keys to the references from which the data was obtained (376)

The behavior of yttrium varies widely with these eluants. With EDTA it elutes between Dy-Tb, with DCTA between Tb-Gd, with TRILO between Sm-Eu, with DTPA near Nd, and with HEDTA near Pr. Thus it should be relatively easy to separate yttrium from a binary mixture with any rare earth by proper choice of an eluant.

Hiller[198] has measured the stability constants for scandium complexes with EDTA, HEDTA, DCTA, and DETPA, but his data had not been received at the time this monograph was completed.

While the curves of Fig. 82 do not represent all of the aminopolyacetic acids that have been investigated they just about exhaust the available stability-constant data. As more information of this type becomes available additional curves may be drawn.

Data for a number of other eluants have been plotted in Fig. 83. Here the information has been obtained entirely from elution curves, and the logarithm of the peak elution position is plotted vs atomic number. All peak elution positions are normalized to a value of 1.00 for europium and the curves have been adjusted vertically for clarity of presentation. Most of the data have been obtained from Stewart's[461] review of ion exchange methods, although some additional information has been obtained from articles which have already been quoted in the sections on the various eluants. Preobrazhenskii[545] has published a review of the ion exchange separation of the rare earths and actinides in which he tabulates the separation factors for these elements in lactate, hydroxyisobutyrate, and glycolate eluants. He obtained his data from essentially the same sources as were used for Fig. 83 and, since he includes separation factors for the actinide elements, his tabulation is reproduced in Table 12. Note that the peak elution positions are normalized to Gd = 1.00. For each eluant, Column A is the separation factor $K_{d(Z)}/K_{d(Z+1)}$, while column B is the peak elution position relative to Gd.

In Fig. 83, the best eluant, so far as separation factors are concerned, is the one whose curve has the highest slope. In Fig. 83, α-hydroxyisobutyrate (α-but) (87°C) has the steepest slope, followed by lactate (87°C), glycolate (87°C), and citrate (87°-100°C) in that order. The room-temperature citrate and glycolate columns seem to be definitely inferior for separation of the middle rare earths, and, to a lesser extent, the heavy rare earths, although they seem to be quite satisfactory for the light rare earths.

In the high-temperature columns yttrium elutes near dysprosium, while in the room-temperature citrate and glycolate columns it elutes near Eu. Smith and Hoffmann[442] report that with room-temperature α-but columns yttrium continues to elute near Dy.

Very few data are available for either Sc or Ac but if a generalization may be made from the curves of Fig. 83, the Ac peak has a separation factor

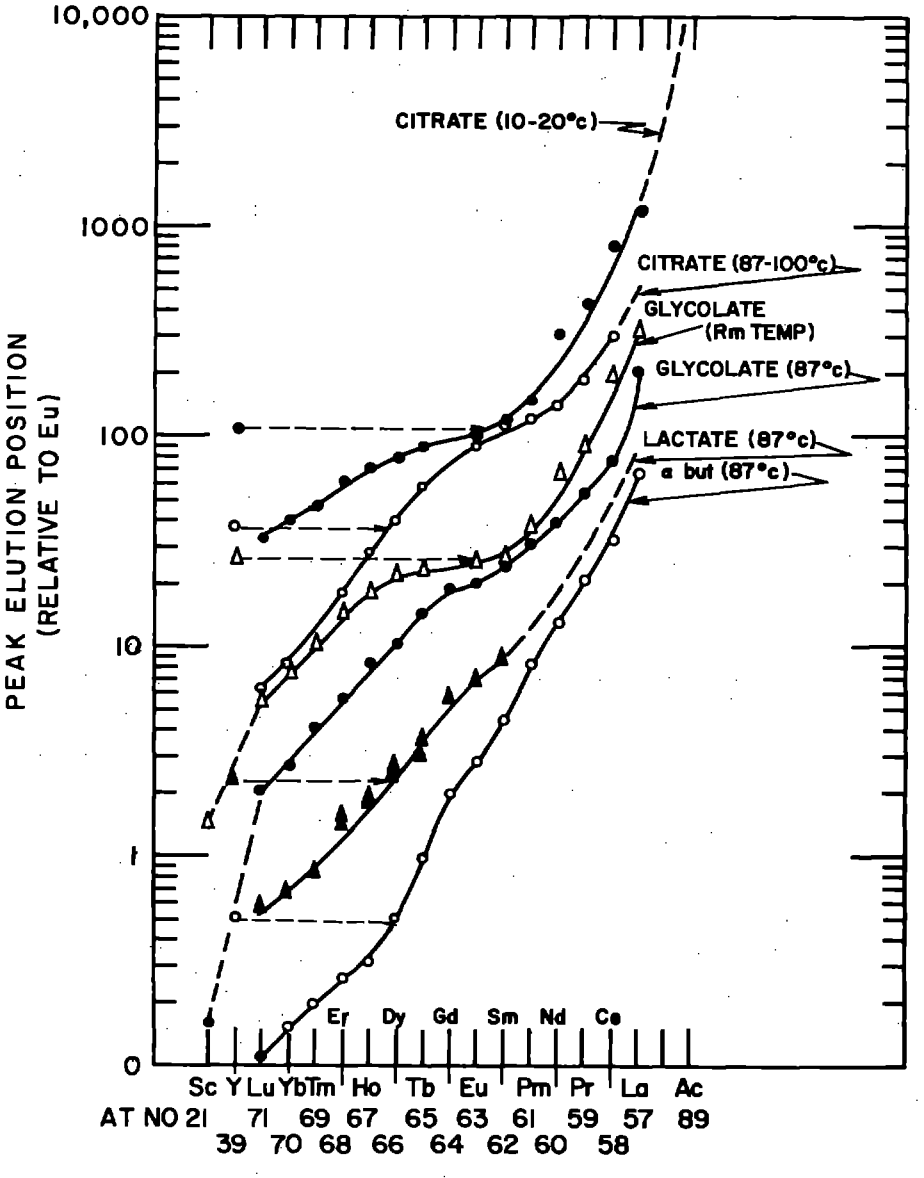


Fig. 83. Logarithm of peak elution position vs atomic number for various eluants. Peak elution positions are normalized to 1.00 for Eu and curves are adjusted vertically for clarity of presentation.

Table 12. Elution characteristics of rare-earth and actinide elements on Dowex-50 cation-exchange resin with several eluants. Column A, separation factor between pairs of elements; column B, elution position of each element relative to gadolinium (545)

	Eluant											
	Lactate				α-Hydroxyisobutyrate				Glycolate			
	90°C		20°C		87°C		20°C		87°C		20°C	
Element	A	B	A	B	A	B	A	B	A	B	A	B
Lu		0.063		0.053		0.055		0.050		0.107		0.222
	1.31		1.4		1.36		1.45		1.32		1.33	
Yb		0.083		0.073		0.075		0.073		0.14		0.295
	1.43		1.54		1.33		1.37		1.5		1.37	
Tm		0.119		0.112		0.10		0.10		0.21		0.405
	1.47		1.54		1.3		--		1.4		1.4	
Er		0.175		0.173		0.13		--		0.3		0.566
	1.52		1.60		1.23		--		1.5		1.28	
Ho		0.266		0.28		0.16		0.177		0.45		0.725
	1.21		1.34		1.56		1.77		--		--	
Y		0.321		0.37		0.25		0.314		--		1.04
	1.14		1.08		1.04		1.1		--		1.3	
Dy		0.366		0.40		0.26		0.346		0.55		0.89
	1.56		1.65		1.88		1.84		1.39		1.04	
Tb		0.572		0.67		0.49		0.64		0.77		0.93
	1.73		1.50		2.2		1.57		1.3		1.08	
Gd		1.00		1.00		1.00		1.00		1.00		1.00
	1.22		1.04		1.4		1.54		1.06		1.00	
Eu		1.22		1.04		1.40		1.54		1.06		1.00
	1.28		1.20		1.6		2.06		1.22		1.08	
Sm		1.56		1.25		2.25		3.18		1.29		1.08
	1.32		1.32		1.82		1.57		1.29		1.33	
Pm		2.06		1.65		4.10		5.0		1.67		1.44
	1.33		1.35		1.61		2.09		1.26		1.83	
Nd		2.74		2.22		6.60		10.45		2.1		2.63
	1.36		1.38		1.57		--		1.4		1.37	
Pr		3.74		3.07		10.45		--		2.94		3.60
	1.73		2.04		1.6		--		1.5		2.2	
Ce		6.47		6.27		16.70		15.5		4.42		7.93
	1.83		2.1		2.2		--		2.6		1.64	
La		11.8		13.2		34.10		--		12		15.45
Mv						0.189						
					1.4							
Fm		0.43				0.264						
	1.43				1.86							
E		0.62				0.49		0.59				0.457
	1.24				1.54		1.46				1.20	
Cf		0.77				0.76		0.86				0.543
	1.58				2.25		2.0		1.17			
Bk		1.21				1.63		1.68				
	1.54						2.7		1.43			
Cm		1.87		1.47		3.45		4.55				1.16
	1.21		1.23				1.4		1.14		1.25	
Am		2.27				5.0		6.3				1.45

of about 10 behind La, and the Sc peak has a separation factor of between 5 and 10 ahead of Lu.

In summary, then, the consensus of the literature articles seems to be that α-hydroxyisobutyric acid is the best eluant for most small-scale cation-exchange-resin separations of the rare-earth elements, followed by lactic acid, glycolic acid, and citric acid in that order. For large-scale production of pure rare earths EDTA is used most extensively, followed by nitrilotriacetic acid.

IV. 7C. ANION-EXCHANGE RESINS

IV. 7C-1. Introduction

The use of synthetic anion-exchange resins in the purification of the rare-earth elements has become a widely accepted part of many rare-earth radiochemical procedures. Under most conditions, however, the rare-earth elements do not form species which will stick to the resin, so the anion-exchange resin columns are used as filters to remove undesired impurities from the rare earths as a group in one step of their purification. In this type of operation, therefore, it is desirable to know the anion-exchange-resin behavior of the whole periodic table of elements so that a single most efficient separation may be carried out. Unfortunately, information of this broad a scope is not easily come by and we must make do with what is available.

Kraus, Moore, Nelson, and co-workers at Oak Ridge have been studying the anion-exchange-resin behavior of a large number of elements for many years and have written a superb series of articles on the subject. An excellent review article on metal separations by anion exchange has been published in 1958 by Kraus and Nelson[244] which discusses HCl, Cl^-, HCl-HF, NO_3^-, $SO_4^=$, and other anion systems, while subsequent papers[331, 245] deal with more recent developments in the field.

IV. 7C-2. Chloride

The HCl-Dowex-1 system has been studied more completely than any other. Kraus and Nelson's[244] curves are reproduced in Fig. 84 and indicate that a rare-earth solution which is greater than 6M in HCl will, when it is passed through a short Dowex-1 column, leave a large number of elements on the resin and pass the rare earths. This is the procedure used by the authors in routine rare-earth purification and has been found to be quite satisfactory.

A similar application, although one with more sophisticated overtones, is the anion-exchange separation of the lanthanides from the actinide group of elements. In most chemical steps, including cation-exchange column elution, the actinide elements will behave essentially the same as the rare earths and

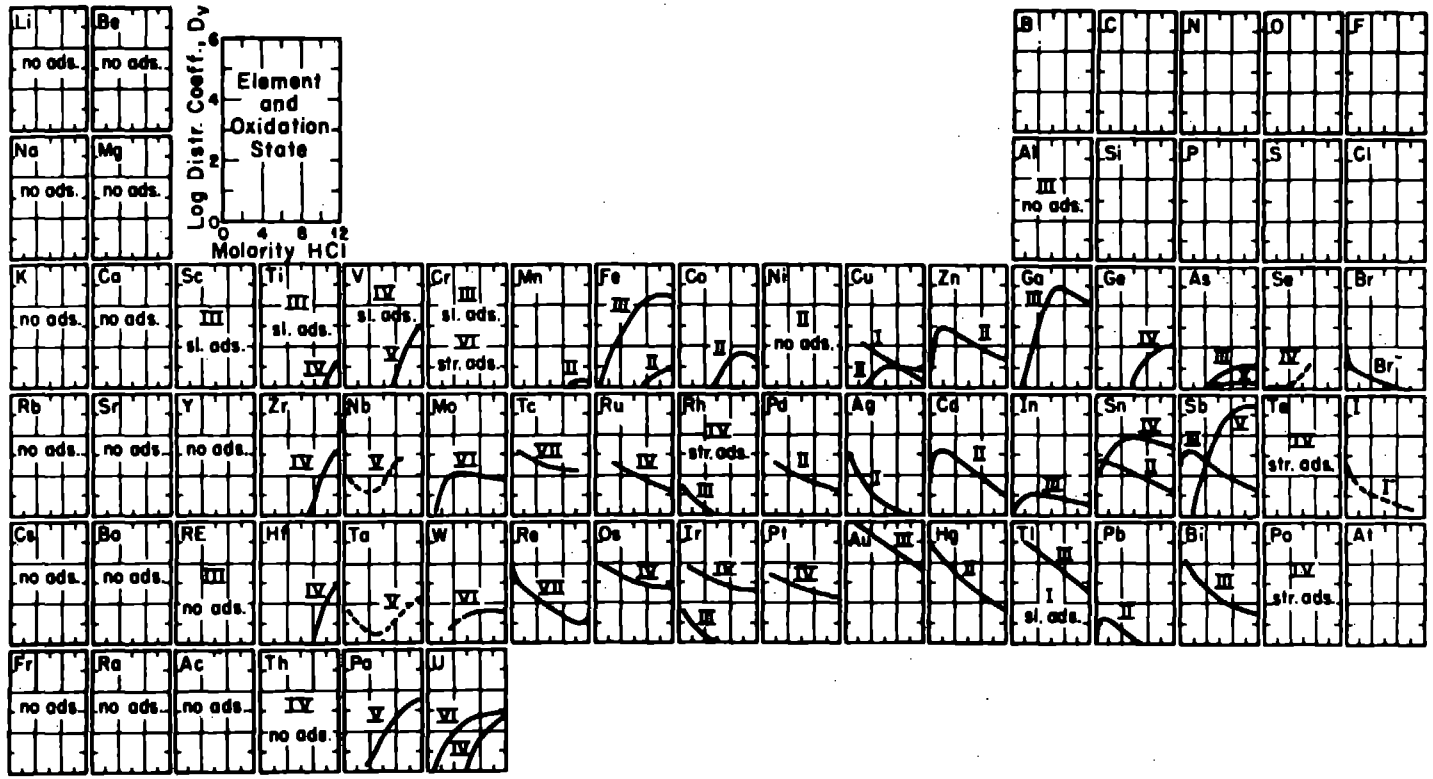


Fig. 84. Adsorption of the elements from hydrochloric acid on Dowex-1 × 8 anion-exchange resin. Legend: no ads. = no adsorption for $0.1 < \underline{M}$ HCl < 12; sl. ads. = slight adsorption in 12$\underline{M}$ HCl ($0.3 \leq D_v \leq 1$); str. ads. = strong adsorption ($D_v \gg 1$) (244)

will not separate from them. Several years ago, however, Street, Diamond, and Seaborg[104, 466] noted that on Dowex-50 with strong HCl as eluant the actinides eluted ahead of their "normal" position with respect to their lanthanide homologues (see Fig. 60) and, conversely, Thompson, Harvey, Choppin, and Seaborg[479] reported that on anion-exchange resins the lanthanides elute before the actinides with concentrated HCl. This effect has subsequently been found to be more pronounced in concentrated LiCl solutions, and Hulet, Gutmacher, and Coops[209] have recently completed a systematic study of this system. They found that excellent lanthanide-actinide separations as well as separations of the transplutonium elements (either individual elements or two-member groups) were achieved at 87°C with Dowex-1-8% DVB (8-15 mm/min settling rate in water) using 10M LiCl acidified to 0.1M HCl at flow rates of 0.3-0.6 ml/cm^2 min. An elution curve which they obtained with a mixture of 14 rare earths plus selected actinides is shown in Fig. 85.

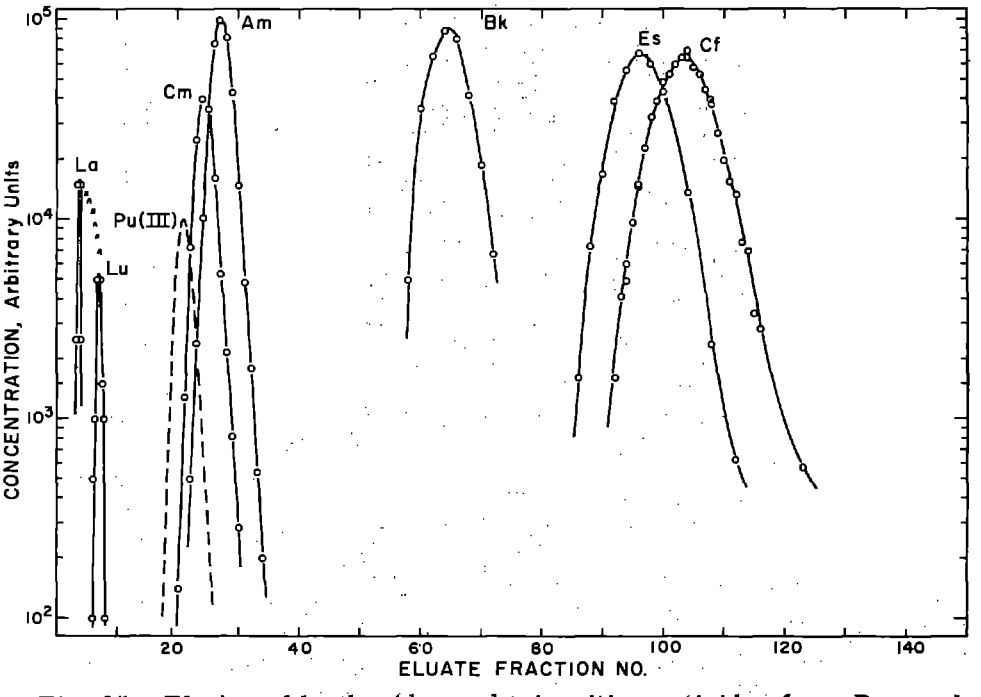


Fig. 85. Elution of lanthanides and tripositive actinides from Dowex-1, 8% DVB at 87°C using 9.92M LiCl-0.106M HCl at a flow rate of 0.27 ml/cm^2 min. Resin bed = 1 cm diam × 12 cm (209)

Under these conditions the lanthanides elute very quickly, and essentially as a group, while the actinides are retained by the resin.

Yashimura, Takashima, and Waki[543] have reported that scandium may be separated from erbium (and presumably from the other rare earths) by adsorbing it on a column of Dowex-1 × 8 anion-exchange resin from 13M HCl

solution. The scandium is then eluted with dilute HCl. This separation must be done carefully, however, since Gardner[165] reports a carrier-free scandium chemistry which is based on the fact that Sc will not stick to Dowex-2 resin in 11M HCl, and Dowex-1 and Dowex-2 behave very much alike. G. M. Iddings of LRL has been unable to duplicate the results in 13M HCl solution.

IV. 7C-3. Nitrate

A number of very interesting papers have appeared in the literature recently dealing with the anion-exchange resin-nitrate system. Buchanan, Faris, Orlandini, and Hughes[61] have reported the behavior of a large number of elements in the Dowex-1-HNO_3 system, and their data are reproduced in Fig. 86. According to this figure, none of the rare earths, with the exception of approximately 25% of the Ce in the 4-8M HNO_3 concentration range, are adsorbed by Dowex-1 in nitric acid solution. This behavior is very useful, therefore, in separating the rare earths as a group from those elements which do stick to the resin under these conditions, and the authors have found this method very satisfactory for separating the rare earths from thorium. It should be pointed out, however, that the data of Buchanan, et al., in Fig. 86 do not agree in all respects with data of other authors who have investigated the same system. Bunney, Ballou, Pascual, and Foti,[63] for instance, have published curves of K_d vs HNO_3 concentration for a number of elements with Dowex-2 resin (Fig. 87) and their results for Ru, Mo, and Zr are significantly different from the Buchanan data. It would perhaps be wise, therefore, to use the HNO_3 curves of Fig. 86 with caution until this apparent discrepancy is resolved.

While the rare earths do not adsorb to any great extent on anion-exchange resins from nitric acid solutions, their behavior varies widely in nitrate salt solutions. Thus Danon[101] reports that the adsorption of praseodymium on Dowex-1 increases with the nature of the cation of the supporting nitrate solution in the order $H < NH_4 < Li < Ca < Cu < Fe < Al$, and describes a procedure for separating Ac-La mixtures using a 4.4M $LiNO_3$ solution as eluant (Fig. 88).

Marcus and Nelson[278] have also investigated the Dowex-1-$LiNO_3$ systems and have obtained excellent separation of complex mixtures of rare-earth tracers using anion-exchange resins. Their data are reproduced in Figs. 89 and 90 and indicate that there are very significant differences between the adsorption coefficients of various rare earths in strong $LiNO_3$ solution. Above 3-4M $LiNO_3$ these differences become large enough to permit separation of individual elements and, as shown in Fig. 90, separations may be carried out very nicely with the gradient elution technique. It should be emphasized, however, that the distribution coefficients can be influenced very strongly by the presence of H^+ ion. Marcus and Nelson state that the K_d for La in 4M $LiNO_3$

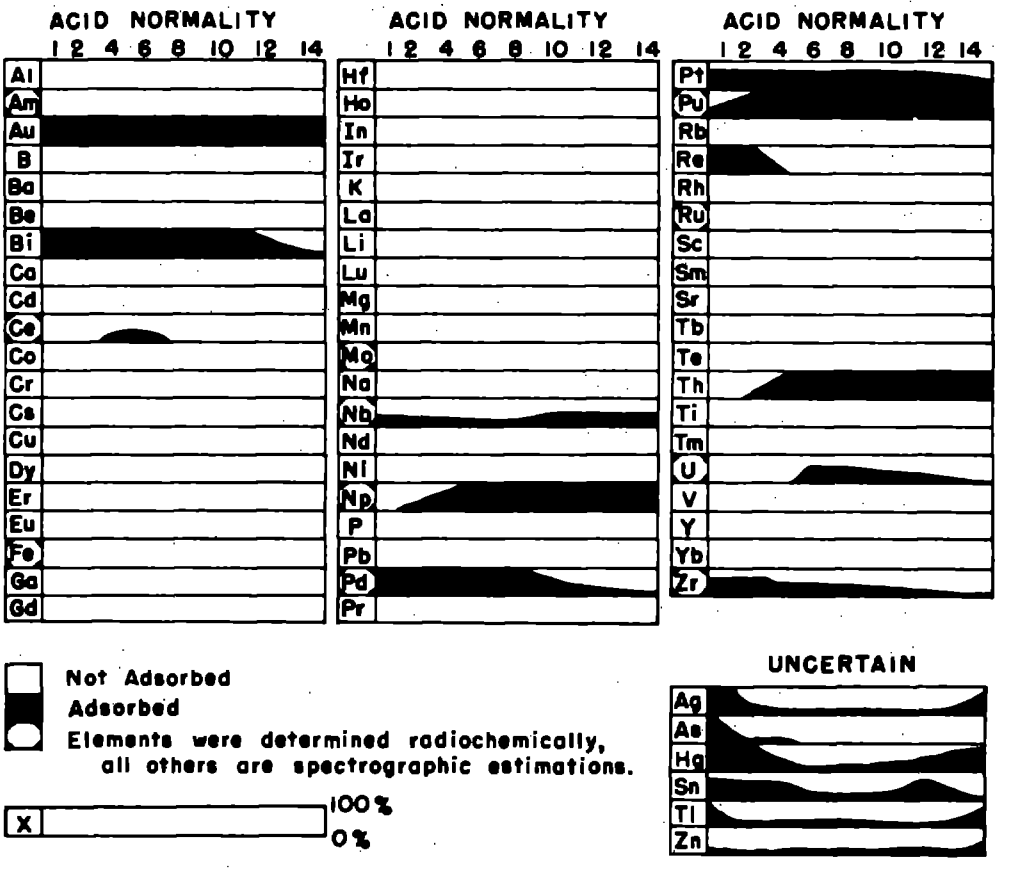


Fig. 86. Elution through Dowex-1 resin column with nitric acid (61)

remains constant between 10^{-2} and 10^{-4}M HNO_3, but decreases rapidly at H^+ concentrations greater than 10^{-2}M.

The elution curve of Fig. 90 is of interest, too, in that it shows the rare earths to be eluted in order of decreasing atomic number, which is the same sequence shown on cation-exchange column elutions and directly opposite to the LiCl anion-exchange elution order (Fig. 85).

Marcus and Nelson also report that the parent-daughter nuclides Ba^{140}-La^{140} are easily separated in a few minutes with 3-4M $LiNO_3$ and a 1-cm-long column. Lanthanum is adsorbed while Ba passes through.

IV. 7C-4. Thiocyanate

Surls and Choppin[471] have studied the ion-exchange behavior of the lanthanide and actinide elements in thiocyanate solution. On Dowex-1 at room temperatures the distribution coefficients are sufficiently high in 2M NH_4SCN to permit transfer of the rare-earth activities to the resin and column elution steps to be carried out. The K_d differences between individual rare

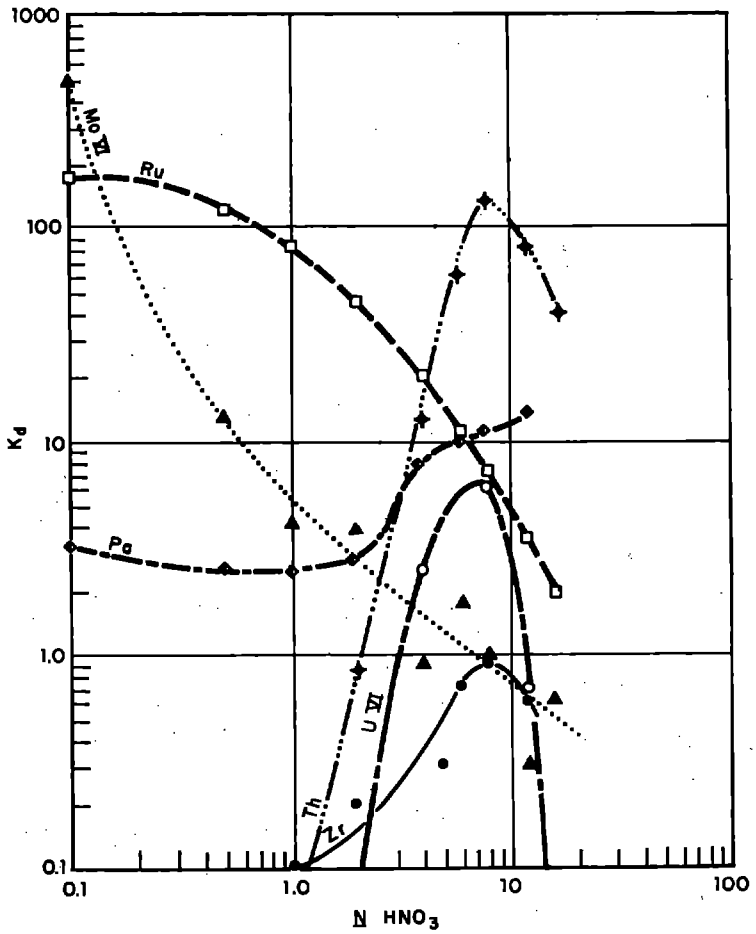


Fig. 87. Equilibrium adsorption on Dowex-2 anion-exchange resin in HNO_3 (63)

earths, however, are not great enough to effect a separation of individual elements under these conditions; but there is a large enough difference in behavior between the lanthanides and actinides to allow relatively easy group separations to be carried out on ammonium thiocyanate columns. Coleman, Penneman, Keenan, LaMar, Armstrong, and Asprey[83] have taken advantage of this fact to separate gram amounts of americium from large quantities of light rare earths in a simple one-step process using Dowex-1 × 8 resin and 5M NH_4SCN eluant.

IV. 7C-5. Sulphate

Very little work has been done with the rare earths in the anion-exchange resin-sulphate system. Bunney, Ballou, Pascual, and Foti[63] report that Y, Ce, and Am do not show any significant adsorption by Dowex-2 resin at any H_2SO_4 acid concentration, and presumably none of the rare earths are adsorbed in this medium. Other elements do stick, however, and relatively

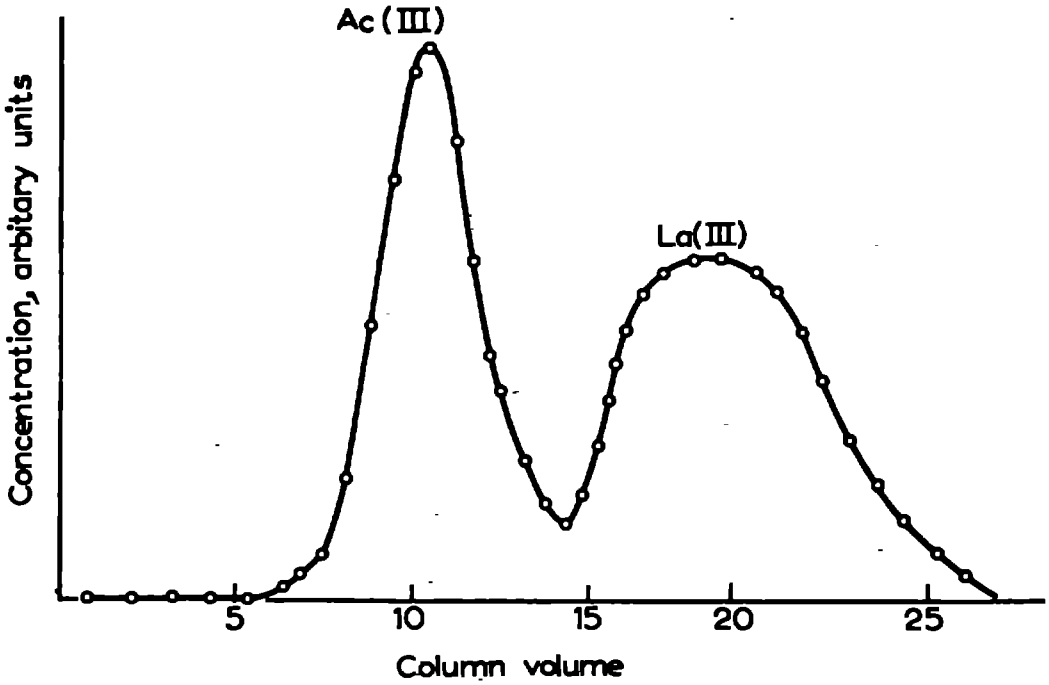


Fig. 88. Elution of tracer Ac and 30 mg of $La(NO_3)_3$ from Dowex-1 with 4.4M $LiNO_3$. Column 30 cm × 0.24 cm^2, Dowex-1 × 8% DVB, 50-100 mesh, flow rate 0.4 cm/min (101)

simple purification of the rare-earth group may be carried out on sulfate columns. Fig. 91 reproduces the data of Bunney et al., and indicate that the rare earths may be separated very easily from Ru, Th, Pa, Zr, U^{+6}, Nb, and Mo^{+6} in 0.1N H_2SO_4. Indeed, Nagle and Murthy[329] have used Amberlite IRA-400 and pH 2.0-2.5 sulphate solution to separate Ce and Th in monazite sand analysis with very good results, and Sekine and Saito[431] have used the Dowex-1-dilute H_2SO_4 system to separate La-Th mixtures.

IV.7C-6. Fluoride

The use of anion-exchange resin-fluoride systems would seem to have very little application in rare-earth radiochemistry because of the low solubility of the rare-earth fluorides. Scandium, however, forms a well-known fluoride complex which may be useful in anion-exchange separations.

Faris[130] has recently published an article in which the elution characteristics of some 50 elements in a hydrofluoric acid medium were studied on Dowex-1 resin (Fig. 92). In dilute HF solutions Sc apparently can be adsorbed on the resin without difficulty, although the K_d decreases at higher HF concentrations.

Schindewolf and Irvine[412] also report this type of behavior for scandium and have used it to separate carrier-free scandium activity from titanium

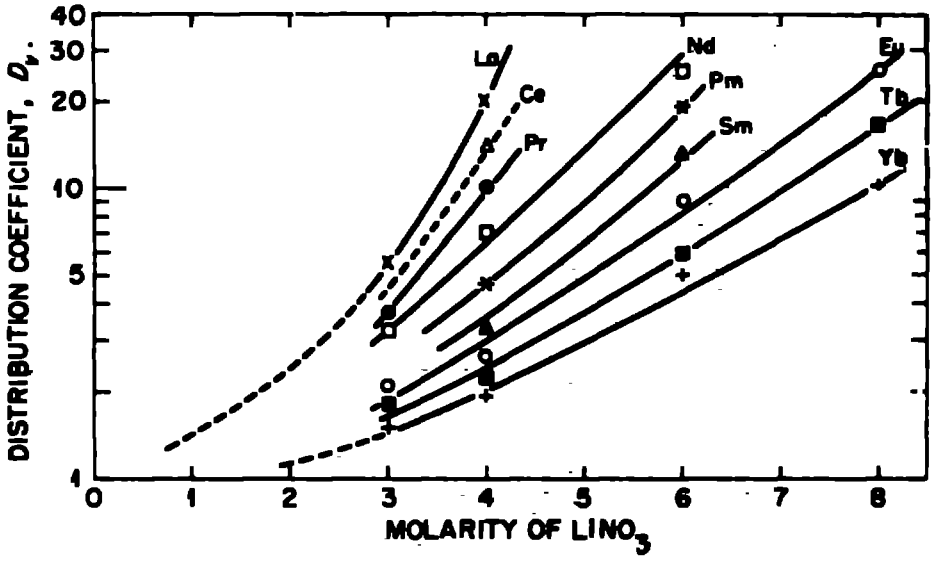


Fig. 89. Adsorption of rare earths on Dowex-1 anion-exchange resin from lithium nitrate solutions (2×10^{-3} M HNO_3, 78°C (278)

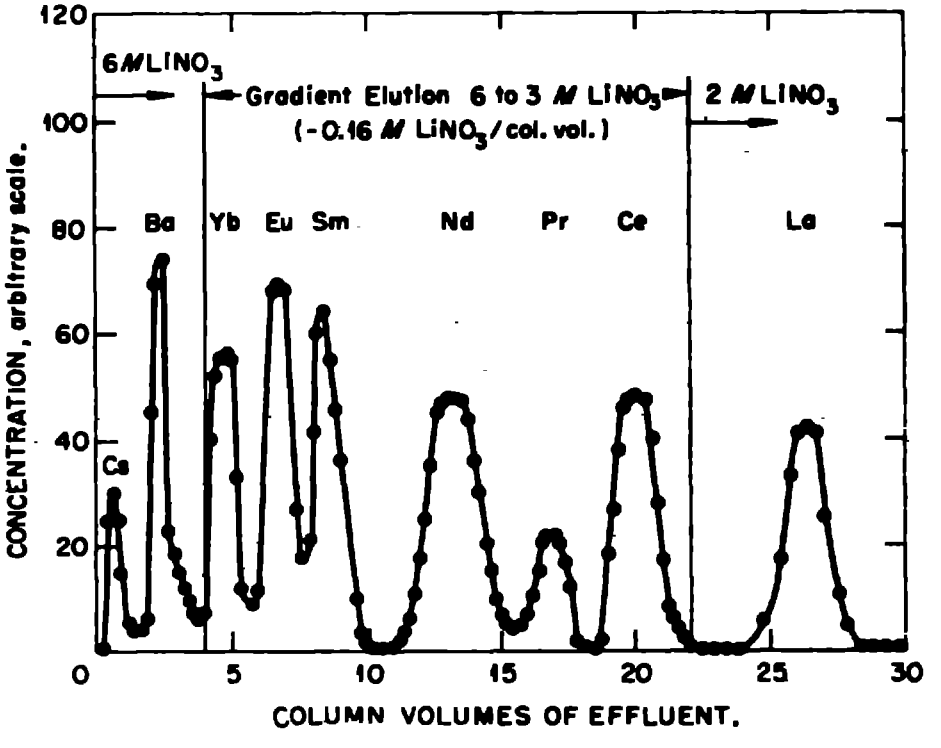


Fig. 90. Separation of Cs, Ba, and several rare earths in $LiNO_3$ solutions (78°C, 0.25 $cm^2 \times 10.5$ cm Dowex-1-10% DVB columns) (278)

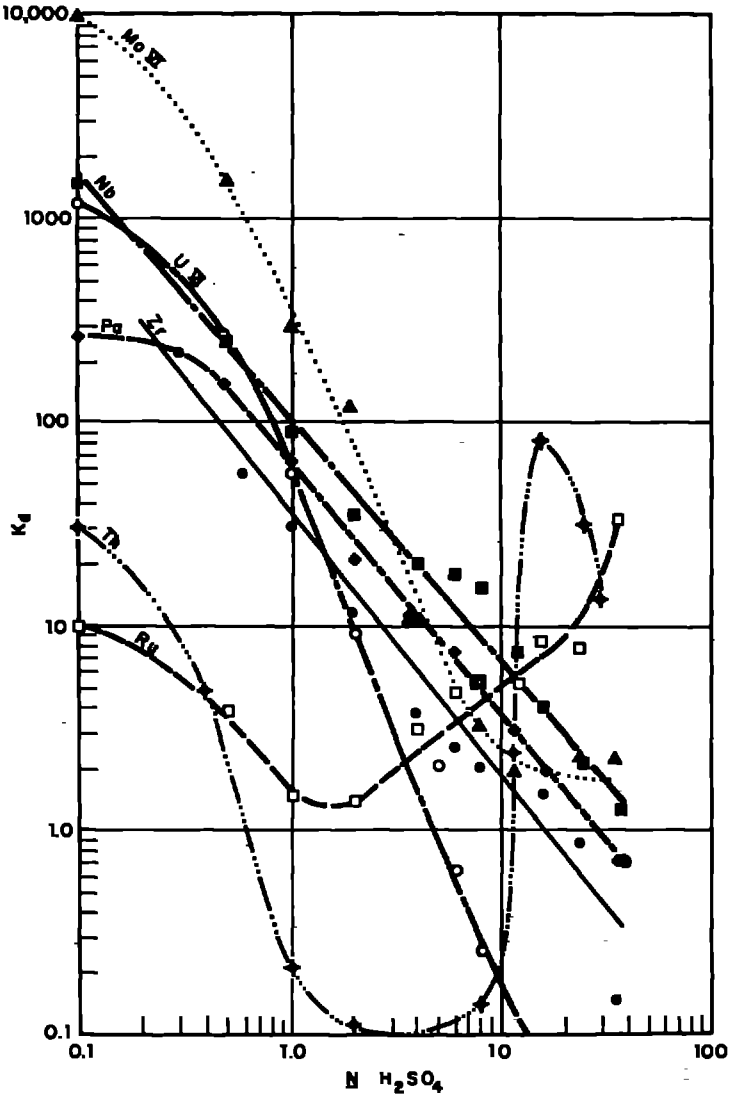


Fig. 91. Equilibrium adsorption in H_2SO_4 on Dowex-2 anion-exchange resin at room temperature (63)

targets. Scandium is adsorbed on a Dowex-1 column from 0.5M-2.5M HF solution and eluted with 15M HF.

Nelson, Rush, and Kraus[331] have recently published an article on the anion-exchange behavior of 19 elements with mixed HCl-HF eluants.

IV. 7C-7. Oxalate

Here again the low solubility of the rare-earth oxalates precludes their very widespread use with anion-exchange resin systems, but scandium forms a soluble complex with oxalate which may be used to advantage. Walter[509] has investigated the behavior of scandium in dilute sodium salts of oxalate

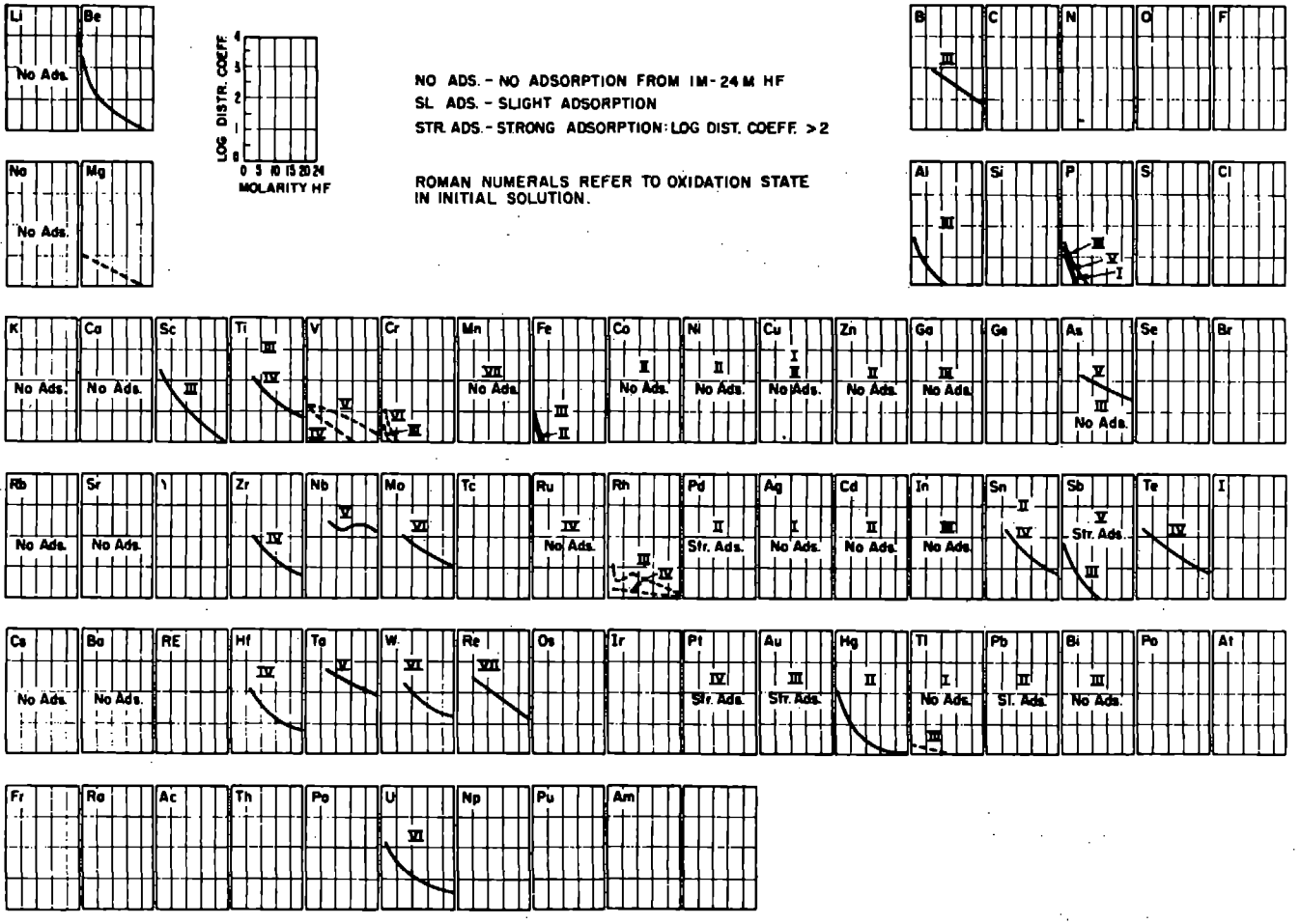


Fig. 92. Distribution coefficients in HF on Dowex-1 at room temperature (130)

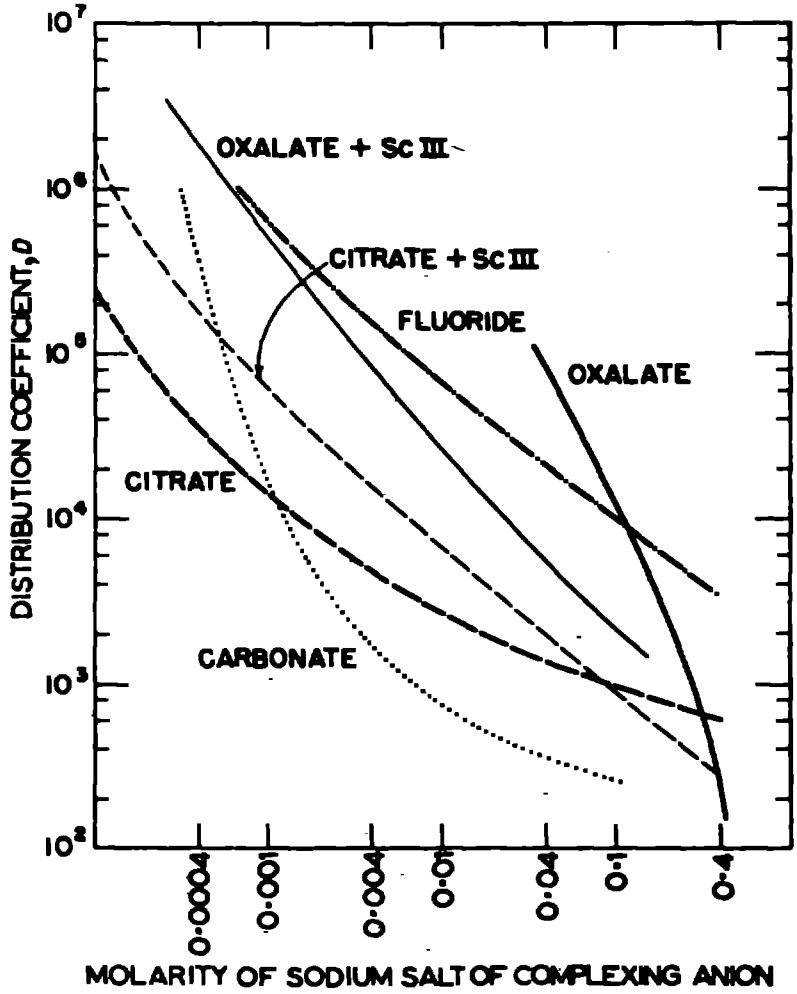


Fig. 93. Distribution coefficients of scandium(III) and vanadium(IV) on Dowex-1 anion-exchange resin as a function of chelating reagent concentration for several reagents. Light lines—scandium; heavy lines—vanadium (509)

and citrate (Fig. 93) and shows that at low oxalate concentrations scandium is very strongly adsorbed. He used a Dowex-1-dilute oxalic acid medium to separate carrier-free scandium and vanadium from 5 mg of titanium but found that better Sc-V separations were obtained with an eluate which consisted of 0.1M $H_2C_2O_4$ + 0.1M HCl.

IV. 7C-8. Phosphate

Freiling, Pascual, and Delucchi[153] have investigated the behavior of a number of elements in the Dowex-2-H_3PO_4 system (Fig. 94). If we may infer the behavior of all of the lanthanides from the data on Ce^{+3} in Fig. 94, the rare earths are adsorbed by the resin at low H_3PO_4 concentrations but are eluted by 6-7N acid. This is significantly different from the behavior of

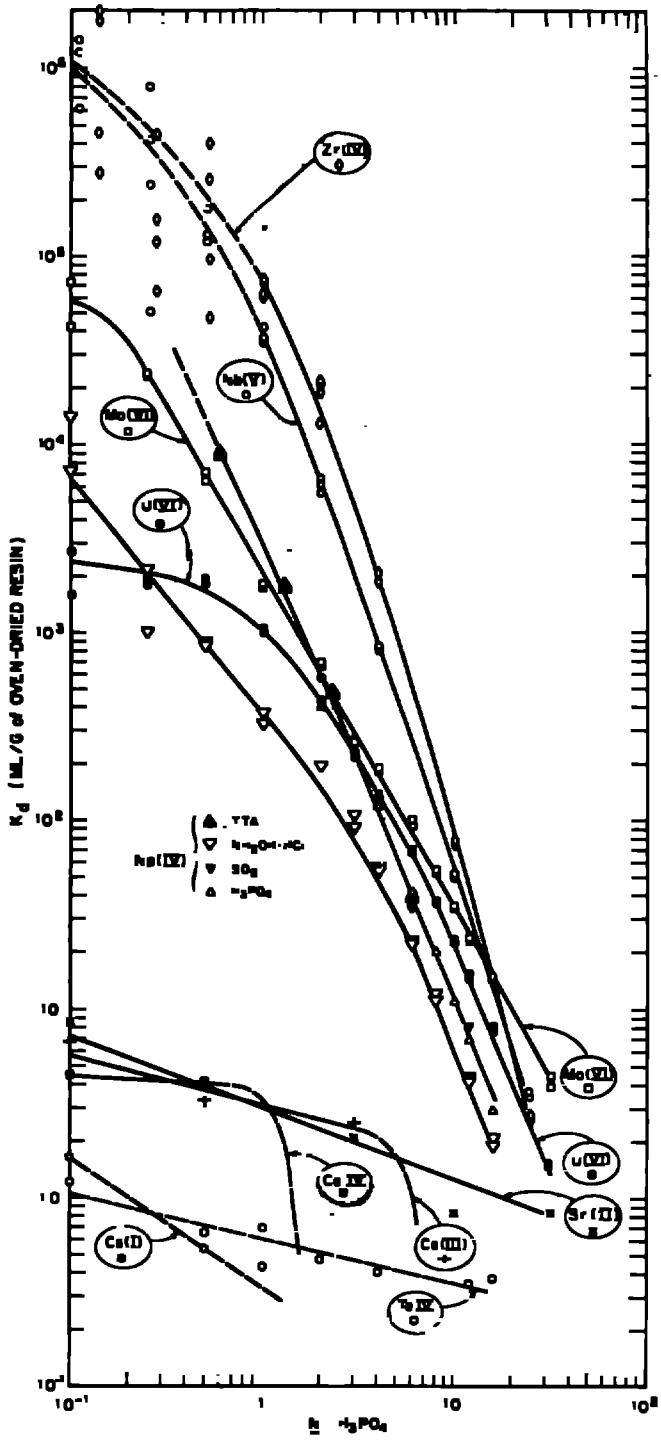


Fig. 94. Equilibrium distribution coefficients of various fission products and actinide elements between H_3PO_4 solution and Dowex-2 at room temperature (153)

IV. 7C-9. Carbonate

Very little work has been done with the rare earths in the anion-exchange resin-carbonate system. Walter[509] reports fairly high distribution coefficients for scandium in dilute sodium carbonate solutions on Dowex-1 resin but states that the results were erratic. The scandium samples failed to approach equilibrium smoothly with increased shaking time and often deposited a large fraction (up to half) of the total activity on the walls of the cellulose acetate vials in which they were shaken, which may be indicative of radiocolloid formation.

Saito and Sekine[403] report that in Dowex-1-sodium carbonate systems the distribution coefficient for yttrium tracer has a maximum value of approximately 3000 in 0.1M Na_2CO_3 solution, decreasing to ≈ 104 in 0.01M Na_2CO_3, and ≈ 6 in 1M Na_2CO_3.

IV. 7C-10. Hydroxide

The rare-earth hydroxides would seem to be analogous to the fluorides and oxalates in that their low solubility prohibits their use with anion-exchange resins. In special cases, however, the low solubility of the hydroxides can be a distinct advantage.

Perkins[362] has reported a procedure for separating Ba^{140}-La^{140} mixtures which involves adsorbing the La^{140} on the hydroxide form of Dowex-1 resin while Ba passes through. Excellent separations can apparently be done very rapidly this way and the author reports that similar results may be obtained with Sr^{90}-Y^{90} mixtures.

IV. 7C-11. Organic Complexes

It seems reasonable to assume that organic complexing agents which are capable of removing rare-earth ions from cation-exchange resins may form negatively charged rare-earth complex ions which might be of interest on anion-exchange resin columns. Huffman and Oswalt[208] have reported successful separation of a mixture of Pm and Eu tracers on Dowex-1 resin with 0.0125M citric acid at a pH of 2.1, while Higgins and Baldwin[196] report good separation of Y-Eu tracers on Dowex-1 columns with 0.16M EDTA at pH 11.7. (With Dowex-1-citrate, Pm elutes before Eu, which is to be expected; but with Dowex-1-EDTA, Y elutes before Eu also, which is quite unexpected.) Higgins and Baldwin state that Y-Eu separation on a Dowex-1-EDTA column is comparable to the separation on the Dowex-50-citrate system (pH 3, room temperature) but slightly inferior to the same system at elevated temperatures. Schonfeld, Wald, and Brund[413] have shown that Sr^{90}-Y^{80} mixtures may be separated on Dowex-1 columns by using a sodium nitrate — (8 hydroxyquinoline-5 sulfonic acid) solution as an eluant.

No data are available on the anion-exchange separation of more complex rare-earth mixtures with any of the organic complexing agents.

Mo(+6), U(+6), Nb(+5), and Zr(+4) and may be of some advantage in effecting separations from those elements.

Subbaraman, Rajan, and Gupta[468] report that the triphosphate complexes of the light rare earths may be adsorbed by Amberlite IRA-400 resin almost quantitatively from $Na_3P_3O_{10}$ solution over the pH range 1-9, and may be eluted with dilute HCl or H_2SO_4. This procedure gave good separation and recovery of Sm, Nd, and Pr while La was retained by the column.

IV. 7C-12. Other Anions

Marcus and Nelson[278] have reported very briefly that the rare earths are adsorbed on Dowex-1 resin from dilute sulfite, nitrite, and thiosulfate solutions, with adsorbability decreasing with increasing electrolyte concentrations, but no further data are available on any of these systems.

IV. 7D. CELLULOSE AND PAPER CHROMATOGRAPHY

Considering the success that has been achieved in separating complex mixtures by this method, it is probably not surprising that a considerable amount of work has been done on the cellulose column and paper chromatographic behavior of the rare-earth elements. For one reason or another, however, the consensus of the published articles in this field seems to be that, for most applications, these techniques are not as good as the synthetic ion-exchange resins for separating complex mixtures of the rare earths.

In paper strip chromatography, for instance, separations are restricted almost entirely to carrier-free samples. Kiba, Ohashi, and Tada,[229] separating Y^{90}-Sr^{90} mixtures on paper strips with an ethyl alcohol-10% NH_4SCN solvent, show that the presence of as much as 0.8 mg of yttrium carrier is enough to distort the shape of the yttrium spot very markedly (Fig. 95).

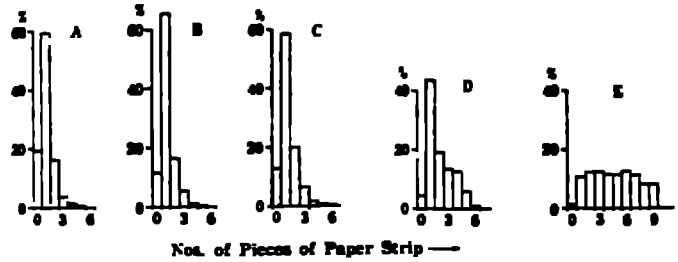


Fig. 95. Effect of yttrium carrier on paper strip chromatography. Solvent, EtOH-10% NH_4SCN aq (5: 2); solvent front, 17.5-18.5 cm; A, Y carrier 5×10^{-5} μg; B, 6×10^{-4} μg; C, 7×10^{-3} μg; D, 7×10^{-2} μg; E, 8×10^{-1} μg (229)

In paper strip chromatography, too, the separation factor between individual rare earths is usually not great enough to permit separation of adjacent elements. This general behavior is illustrated by Fig. 96, which was obtained by Lederer[262] with an ethanol-10% 2N HCl eluant. It is obvious

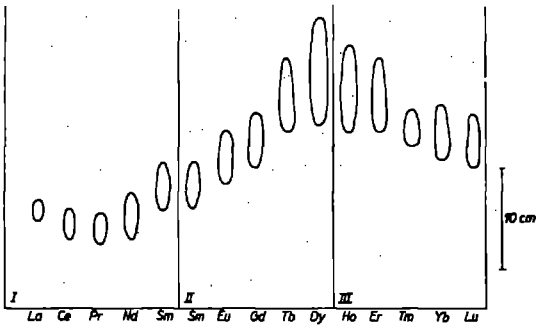


Fig. 96. Paper strip chromatograph of rare-earth chlorides developed for one week with ethanol-10% 2N HCl, placed in order of atomic numbers (262)

that, with this eluant, the paper strip chromatographic method can separate only selected mixtures of rare earths, such as La-Lu, Pr-Eu-Dy, etc., mixtures which are not easily come by in normal radiochemical operations. As a further indication of the current state of the art, Lederer[263] has published data on the movement of Pr, Nd, Sm, Eu, Gd, and Tb with ethanol-HCl-NH_4CNS solvent (Fig. 97) and states that: "In the region of the gadolinium earths this is the best separation so far recorded (1956) by paper chromatographic and electrophoretic methods."

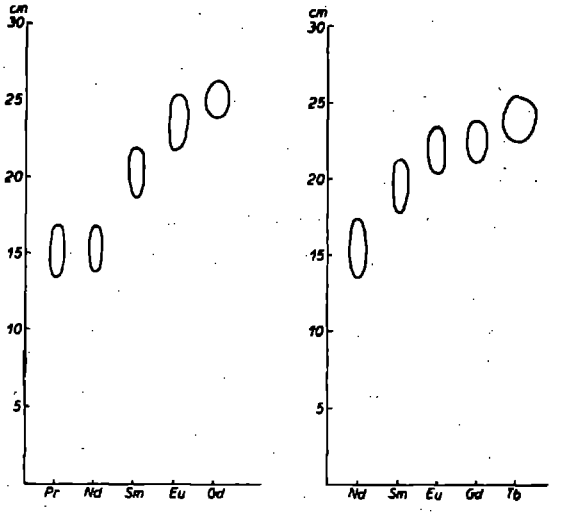


Fig. 97. Paper strip chromatography. The movement of Pr, Nd, Sm, Eu, Gd, and Tb when developed for 48 hours with ethanol (90 ml), 2N HCl (10 ml), NH_4CNS (1 g) (263)

With these very serious limitations in mind, then, additional information on the rare earths with other solvents may be obtained from an excellent review article by Lederer,[264] or articles by Sarma[406] and Danon and Levi.[102]

All indications are that scandium moves more rapidly than any of the rare-earth elements on the paper strip. Thus Lederer[262] shows that very good Sc-rare earth separations may be obtained with ethanol-10% 2N HCl

solvent, and Danon and Levi indicate that a butanol-HNO_3-$LiNO_3$ solvent should work just as well. Presumably this is a general characteristic of scandium, and carrier-free Sc-rare earth mixtures may be separated by a number of other solvents.

Very little information is available relative to the behavior of actinium in paper strip chromatography. One would expect, however, that it would move more slowly than lanthanum, and Danon and Levi have shown, with butanol-HNO_3-$LiNO_3$ solvent at least, that this is indeed the way Ac behaves.

Several authors have reported procedures involving the use of cellulose columns in connection with the rare earths. Center, Henry, and Householder[71] have used columns of activated cellulose to separate small amounts of the rare earths as a group from thorium with an ethyl ether-HNO_3 solvent but give no indication of any separation of individual rare earths.

Pollard, McOmie, and Stevens,[369] on the other hand, have successfully separated macroscopic amounts of rare-earth mixtures on cellulose columns with a butanol-acetic acid-8-hydroxyquinoline solvent. It is difficult to evaluate their method accurately, however, because of the way the data are reported, but their yields of pure products seem to be significantly lower than one would expect from properly run cation-exchange resin columns.

IV. 7E. INORGANIC EXCHANGERS

Inorganic ion exchangers, of course, were among the first ion exchange media to be used for separating mixtures of elements. Very few articles have appeared in the literature, however, to indicate that these materials have significant advantages in separating the rare-earth elements.

Lindner[270] has used columns of Al_2O_3 to purify 4- to 20-mg samples of the light rare earths, but the separations were not clean-cut and the procedure does not compare with present ion-exchange resin techniques.

Nemoda[332] has recently published a very fine article on the separation of fission product mixtures on Al_2O_3 columns. The mixture of elements is placed on the column in weakly acid solution (pH > 2) and successive elutions are then carried out as follows: Cs(0.4$\underline{M}$ NH_4NO_3); Sr, Ba(1.6$\underline{M}$ NH_4NO_3); Mo, Ni, Co(1.6$\underline{M}$ NH_4NO_3 + NH_3); Al, U(0.5$\underline{M}$ Na_2CO_3); Zr, Nb(1$\underline{M}$ $(NH_4)_2CO_3$); Fe, Pb, Cr, Te(1$\underline{N}$ oxalic acid); and the rare earths are eluted as a group with pH 1 HCl.

Vickery[496] has reported the adsorption on activated charcoal of the highly colored Ce^{+4}-p-phenetidine complex and the separation of 10 mg of CeO_2 from 10 g of La_2O_3 by this method.

Schubert[414] has obtained a patent on a process which uses columns of silica gel or fuller's earth to extract rare-earth activities from uranium-organic solvent solutions. The solution is poured through the column and

the rare-earth activities are retained, with fuller's earth being the more efficient of the adsorbents (≈ 99% retention).

And finally, Cornish[87] has attempted to use silica gel columns to separate individual rare earths using a thenoyltrifluoroacetone (TTA)-organic solvent eluant. An elution curve which he obtained with an essentially carrier-free Tb-Eu mixture and a TTA-benzene-methylethyl ketone solvent is shown in Fig. 98. The separation is fairly good but no further work has been done with more complex rare-earth mixtures.

IV. 7F. EXTRACTION-EXCHANGE

An interesting variation of the ion-exchange column technique — so-called "reversed-phase partition chromatography" — has been applied to separation of the rare earths by Siekierski and Fidelis.[553] Fundamentally, the method involves the saturation of a column of inert absorbent — in this case the Kieselguhr "Hyflo Supercel" — with an organic solvent in which the rare earths are soluble. Siekierski and Fidelis use undiluted TBP. The column is pre-equilibrated by washing first with water, then with TBP-saturated HNO_3 of the same concentration that is to be used in the elution, after which the rare earths are introduced into the column and elution is carried out with concentrated HNO_3.

This technique obviously combines features of both extraction- and ion-exchange type operations, but it possesses certain advantages all its own. The most apparent of these is the fact that multistage extraction separations can be carried out automatically with relatively simple apparatus — Siekierski and Fidelis state that they got the equivalent of a 400-plate extraction separation in a column 11 cm long. The eluant is plain nitric acid and does not contain organic complexing agents which sometimes complicate subsequent recovery of the rare earths. Presumably, the eluant could be evaporated to give satisfactory carrier-free samples. Another feature of this method which might be advantageous in certain separations is the fact that the rare earths are eluted in reverse of their "normal" order. With the TBP-HNO_3 system, lanthanum is the first element off the column, followed by the other elements in order of increasing atomic numbers. Yttrium elutes after terbium, presumably in the Dy-Ho region.

As an example of the kind of separations that may be carried out with this technique, Siekierski and Fidelis separated a carrier-free mixture of Ce, Pm, Sm, Eu, Gd, and Tb activities on a 3 mm × 11 cm TBP column with a 15.1 $\underline{M}$ HNO_3 eluant. Cerium was the first element off the column, followed by Pm, Sm, Eu, Gd, and Tb in that order, and all peaks were well separated from their neighbors. Column running time to the Tb peak was approximately 200 minutes.

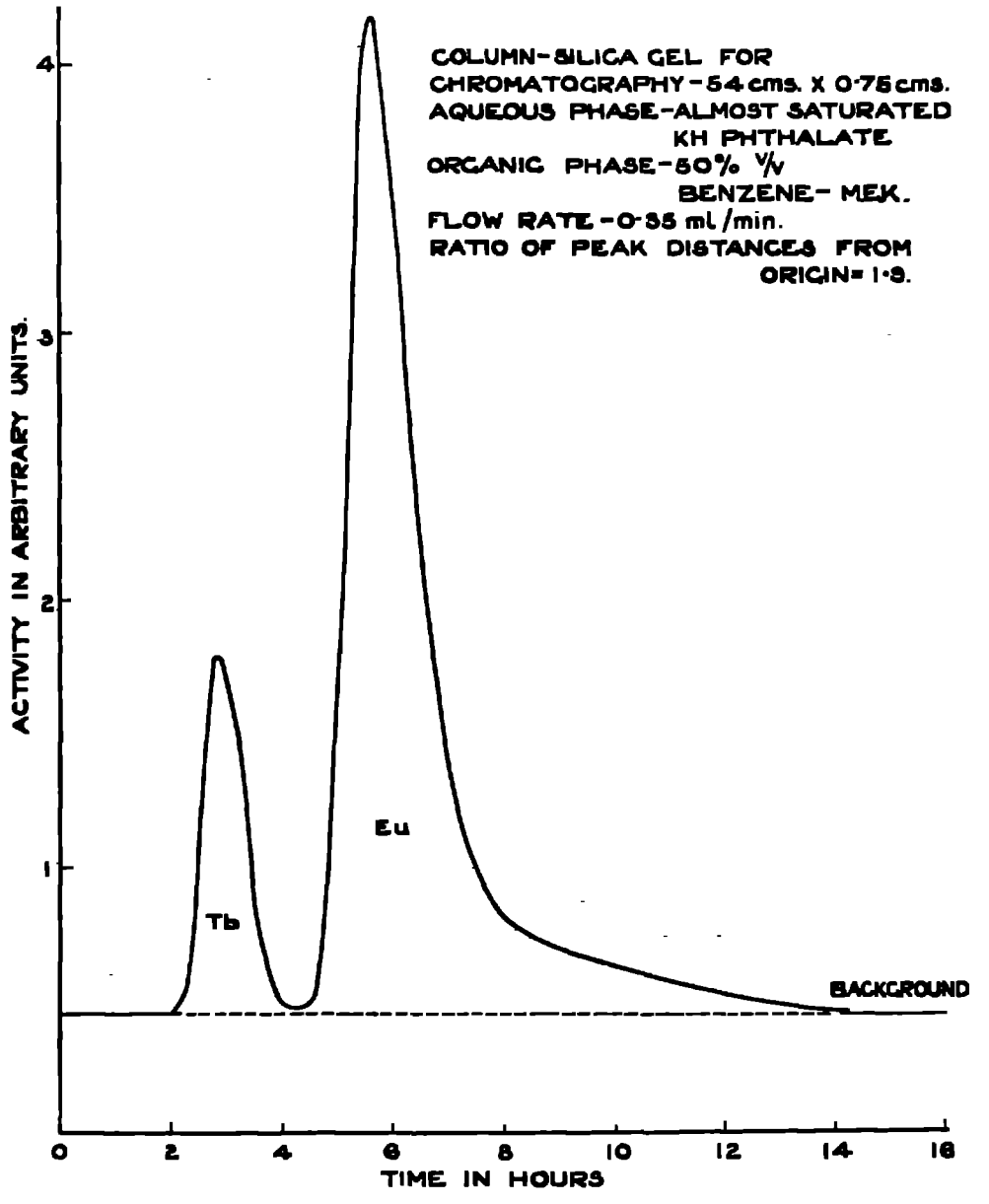


Fig. 98. Elution of carrier-free Tb-Eu activities on a silica gel column. Column dimensions, 54 cm × 0.75 cm diam; "aqueous phase," silica gel + 40% by wt "almost saturated" potassium hydrogen phthalate; eluant, 50% V/V benzene-methyl ethyl ketone + 0.02M TTA; flow rate, 0.35 ml/min (87)

Another way of making up columns for the extraction-exchange type of operation was patented some time ago by Hale,[554] who used styrene-divinyl-benzene beads as absorbing material for the organic solvent. He made no mention of any application to rare-earth separations, but presumably these beads should work as well as Kieselguhr, and it should be easier to make up the columns.

Little data is available on specific extraction-exchange separations, but the method certainly looks interesting enough to warrant considerable attention.

IV. 8. ELECTRIC AND MAGNETIC FIELD SEPARATION

IV. 8A. INTRODUCTION

A variety of electrical and magnetic methods have been applied to the separation of rare earths from each other. With one important exception, the methods are inferior in every way to ion exchange columns for general application. They are either slow, severely limited in the amount of material handled, or give poor separations — usually suffering from at least two of these defects.

IV. 8B. ELECTROPHORESIS

Some separations based on variations in mobility in an electric field have been reported. Sato, Diamond, Norris, and Strain[408] announced successful separation by electrophoresis on filter paper moistened with lactic acid or tartrate-tartaric acid buffer. They used a mixture of Sc, Y, Ce, Pr, Nd, and Pm and obtained (in ≈ 0.1 molar lactic acid) separation into three groups. Sc was the most mobile ion; next were Y and Nd, which did not separate from each other; and least mobile was a group containing Ce, Pr and Pm.

In the tartrate buffer system (0.035 molar tartaric acid-0.015 molar diammonium tartrate) Eu and Pm migrated as anions, Ce as a cation. Running times were from one to two days.

Clusius and Ramirez[82] modified the electrophoresis apparatus to provide a flow of solvent counter to the direction of migration. They were able to separate pure La from Nd and Sm, pure Pr from Sm, and La and Sm from a La-Sm-Eu-Gd-Tb-Dy mixture, but were unable to separate Pr from Nd or Eu from Gd. Their running times were extremely long, on the order of weeks.

Maki[276] studied differential electromigration in citrate solutions of varying pH's containing sodium chloride. She showed that there were two regions where separations were optimized — one at pH 3.05, the ions migrating as anions, and one at pH 2.6, the ions migrating as cations. She was able to get separations between La, Ce, Pr or Nd, and Y, but not between Pr and Nd. Her conditions were: citric acid 0.0125 to 0.050 molar; sodium chloride 0.050 molar; running time about six hours. Ammonium hydroxide or hydrochloric acid were used to change pH as desired.

Lederer[258, 259, 265] has also studied the electromigration of rare-earth ions in citric acid solution. He included yttrium and actinium, but not scandium. His running times were three to four hours. Separations

were fairly good for the lighter rare earths and actinium, but poor for elements heavier than neodymium. By flowing his solvent continuously at right angles to the field, he was able to obtain[259] a continuous electrophoretic separation of actinium from lanthanum, which was quite slow but had the advantage that since very low flow rates and fluid volumes were involved, the final actinium fraction contained much less eluant and hence less dissolved solids than that from an analogous column elution. His data are presented in Fig. 99.

Kertes[225] showed that in 25% thioglycolic acid the migration of gadolinium is much slower than that of many other lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Tb, and Er) and that separation of gadolinium from the rest of the group is possible. He used a paper strip, approximately 4 cm wide by 20 cm long, a voltage of 400 volts, and a running time of two or more hours. The current drawn under these conditions was 3-4 milliamperes. The amount of material separated was of the order of 10-100 micrograms of mixed rare earths.

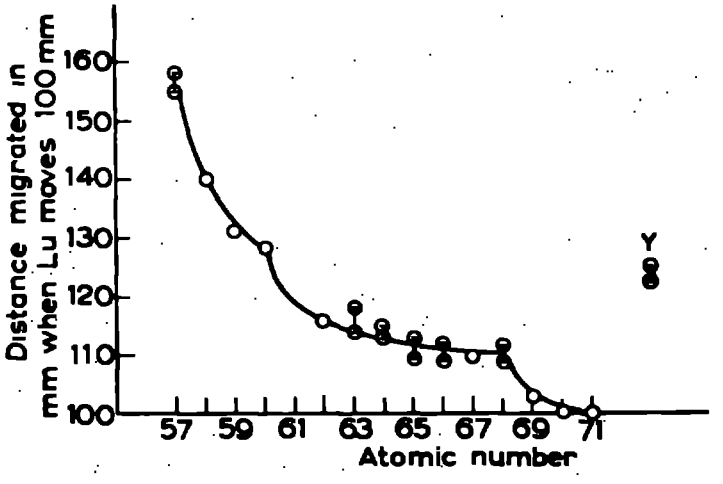


Fig. 99. Relative electrophoretic mobilities plotted against atomic numbers (in 1% citric acid) (265)

IV. 8C. MAGNETOPHORESIS

Noddack and co-workers[339, 342] attempted to use the very high magnetic susceptibilities of some rare earths to separate them from yttrium ($\mu = 0$) in a strongly inhomogeneous magnetic field. He flowed a solution containing Y, Tb, Dy, Ho, and Er perpendicular to the field gradient and permitted the solution to divide into two channels. Some separation of yttrium from the other rare earths was achieved, but the method was not very effective.

IV. 8D. FOCUSING ION EXCHANGE

Schumacher and co-workers[415-421] have developed a technique called by them "focusing ion exchange." This is the only method known to us of separating

individual rare earths (other than Ce, Eu, Sc) in times of the order of five minutes. Although the method is limited to samples of a few micrograms or less, this limitation is unimportant in carrier-free radiochemistry.

Schumacher[415,418] has discussed the theory of the process in great detail. A rather elementary description follows: Fig. 100 is a schematic representation of the apparatus, which consists in essence of two reservoirs connected by a

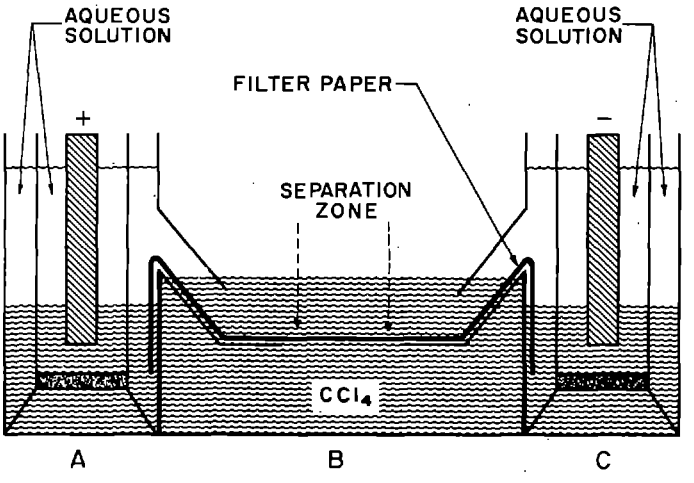


Fig. 100. A schematic representation of the focusing-ion-exchange apparatus of Schumacher and co-workers. A and C are reservoirs containing respectively an anionic complex-forming reagent and a cationic complex-destroying reagent. The central paper strip forms the separation zone (415-421)

moist paper strip. Platinium electrodes (segregated by glass frits) are inserted in the reservoirs and the strip, for cooling, is immersed in a bath of carbon tetrachloride. The only function of the paper is to provide a linear region of electrolyte in which convection and turbulence are minimized.

The reservoir A contains a solution of a complexing anion A^- capable of forming anionic complexes with the cations to be separated. The reservoir C contains a solution of a cation C^+ capable of combining with A^- to form a species which does not have complexing ability. The electrode in A is made the cathode of the system, that in C is made the anode.

Under the influence of the applied field, the species A^- and C^+ migrate toward each other along the paper strip and react as they meet. The result is the establishment of a steady state (or a slowly changing state) in which a gradient of the concentration of A^- exists along the paper.

At a fixed concentration of A^-, an added cationic species M^+ will exist in equilibrium between the complexed, anionic form $(MA)^-$ and the uncomplexed cationic form M^+ (Note: the charge symbols are intended to indicate sign of charge only, and not its magnitude, in the discussion). The reaction M^+ +

$A^- \rightleftarrows (MA)^-$ is assumed to be rapid in both directions. The net motion of the species M in the electric field then will be governed by the relative amounts of M^+ and $(MA)^-$ in solution and by their respective ionic mobilities. If conditions are properly chosen, the concentration of A^- at the positive end of the strip will be low enough so that the cations to be separated will migrate as cations, i.e., toward the center of the strip, while at the negative end of the strip they will migrate as anions. Obviously there exists for each species M a critical concentration of A^- at which the net motion in the field is zero. This concentration of A^- will be found at some particular location along the strip; at positions on either side of the critical location the gradient in concentration of A^- will alter conditions in a manner which will lead to net motion of the species M toward its critical location. The position of the critical point of the species M depends on the ionic mobility of the species M^+ and $(MA)^-$ and on the stability constant of the complex; these factors will in general be different for different species. One would expect, then, that a sample of solution containing a mixture of cations would migrate under the influence of the field into a series of lines, one to each element.

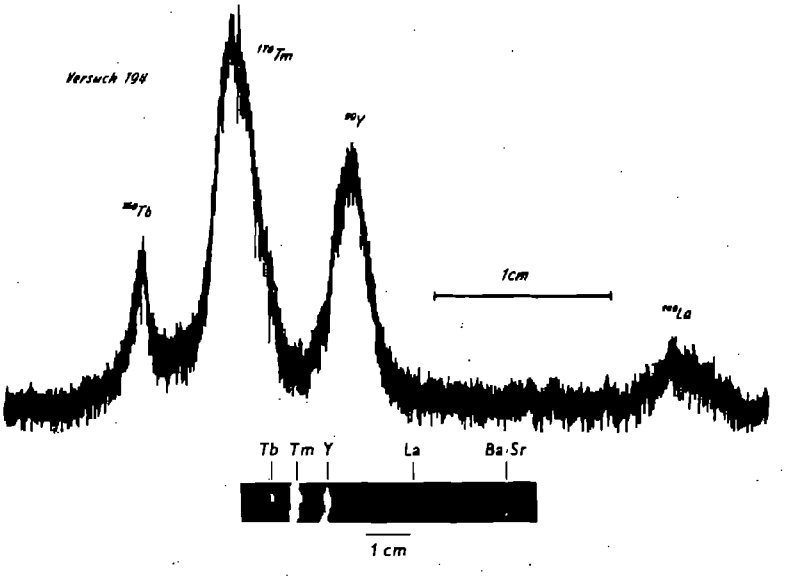


Fig. 101. Autoradiograph and scanning counter results for a typical separation. Conditions: reservoir C, 0.5 molar HCl; reservoir A, 0.3 molar diammonium nitrilotriacetate + sodium trichloroacetate mixture; 500 volts; 8 minutes running time (419)

As can be seen from the accompanying illustration (Fig. 101), the predictions of the theory are verified experimentally.

A detailed theoretical study of the process[418] shows that two effects limit the sharpness of the line obtained and hence the resolution obtainable by the method. One is the effect of diffusion, which tends to broaden the line; this

effect is counterbalanced by increasing the electric field strength (see Fig. 102). The other effect is due to the finite velocity of the chemical reactions involved in the equilibrium between M^+ and $(MA)^-$. The magnitude of this effect depends on the electric field in a sense opposite to that of diffusion (see Fig. 103), increasing with increasing field strengths. In any actual case, both effects must be present to some extent; there exists, therefore, an optimal electric field at which the lines are the sharpest obtainable. In actual practice, the optimal field is often greater than any field which can be utilized. The method depends on the presence of a vast excess of A^- over M^+, so that the concentration gradient on which the separation depends is not seriously perturbed by the presence of the species being separated. Due to the small cross-section of the paper strip, this fact limits the amounts of material being separated to a few micrograms or less. Even so, the amount of power used is quite appreciable: In the example shown in Fig. 101, the voltage used was 600 volts; the current was not stated, but from similar experiments was of the order of several milliamperes. The combination of salt solutions and high voltages require great care in order to avoid dangerous accidents.

Schumacher and Fluhler[420] modified the original system by flowing the solution slowly across the electric field, introducing their test mixture continuously at the upstream side and removing the separated products (copper and cobalt) at the downstream side.

The technique appears to offer great promise and should be thoroughly investigated.

V. DISSOLUTION AND EXCHANGE

V.1. DISSOLUTION

The usual commercial procedures for processing rare-earth ores involve leaching with strong mineral acids. The rare earths are dissolved and separated from insoluble residues by centrifugation or filtration. Spedding's group at Iowa State,[376] for example, leach pulverized xenotime sand with 93% H_2SO_4 at 240-250°C for 6-8 hr to get the rare earths in solution.

On a large scale this type of operation may prove to be undesirable since the handling of hot concentrated acids and slimy sludges is not a pleasant task. Iya[214] has developed a method for opening thortveitite which involves roasting the ore with an excess of carbon for 35-45 min at 1800-2100°C and leaching the scandium out of the resulting carbides with HCl. Vickery[505] obtained essentially the same results by passing a stream of Cl_2 over a thortveitite-carbon mixture at 800-850°C for about 3 to 4-1/2 hours and dissolving the scandium and rare-earth chlorides with 1% HCl. Spedding, Powell, Daane, Hiller, and Adams[456] roasted a mixture of thortveitite and ammonium bi-

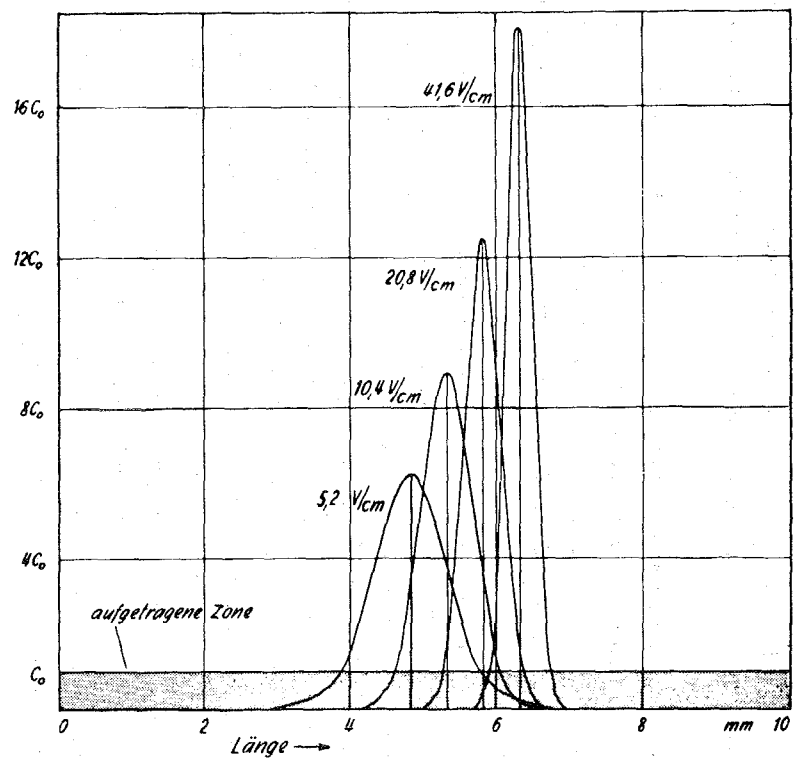


Fig. 102. Line shapes in focusing ion exchange at various electric field strengths: effect of diffusion (parameters arbitrarily selected) (418)

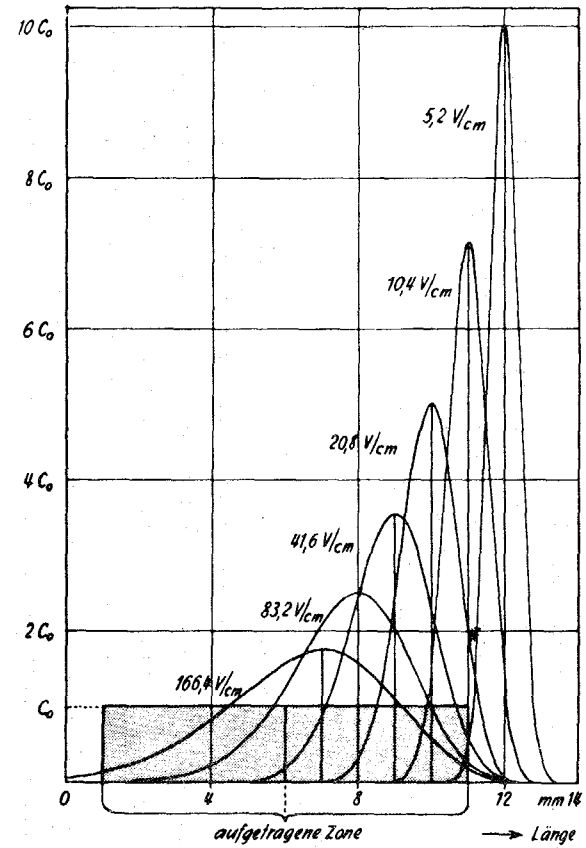


Fig. 103. Line shapes in focusing ion exchange at various electric field strengths: effect of finite reaction velocity (parameters arbitrarily selected) (418)

fluoride overnight at 375-400°C, reduced the ScF_3 to scandium metal with calcium, and dissolved the metal in HCl.

Most rare-earth compounds which are encountered in the laboratory may be dissolved in strong mineral acids, although heating may be required for some of the more recalcitrant species. Organic material may be destroyed by boiling HNO_3-$HClO_4$ or 30% H_2O_2-H_2SO_4 without affecting the rare earths.

V.2. EXCHANGE

In almost all cases the rare earths exist only in the trivalent oxidation state in solution. These trivalent ions form relatively few species in aqueous solution and in mineral acids no special precautions need be taken to ensure exchange between inactive carrier and radioactive isotopes. When strong complexing agents are present the problem of exchange between the free rare-earth ion and the rare-earth complex can be of concern to the chemist. Betts, Dahlinger, and Munro[27] have studied the kinetics of the exchange reaction between rare earth and rare earth-EDTA complexes, and have found that the principal path leading to exchange is the acid-catalyzed dissociation of the $RE(EDTA)^-$ complex. The rate of exchange is given by the expression: $R = k(H^+)^{1.0}(RE(EDTA)^-)^{1.0}(R_{Aq}^{+++})^{0.0}$ and for comparable conditions the rate constants for several rare earths are in the ratio $k_{La}:k_{Nd}:k_{Dy}:k_{Yb}$:: 7700:1200:19:1. At 25°C, $k_{La} = 4.2 \times 10^5$ liters/mole min. Very little is known about the kinetics of the exchange reaction with other strong complexing agents.

A special case of nonexchangeable +3 rare-earth ions is found in the Szilard-Chalmers reaction reported by Herr,[194] in which rare earth-phthalocyanine is irradiated and the reaction products are extracted from quinoline solution by dilute H_2SO_4 without exchanging with the original rare-earth target material.

When the rare earths exist in more than one oxidation state some precautions may have to be taken to ensure exchange. Divalent species of Eu, Sm, and Yb may be prepared in aqueous solution. Of these, only Eu^{++} is reasonably stable; Sm^{+2} and Yb^{+2} oxidize quickly and present no exchange problem. Meier and Garner[305] found that the rate of exchange between Eu^{+2} and Eu^{+3} in chloride solution was measurable. They also found that the reaction is chloride dependent and conclude that in nonchloride systems the reaction might be slow. It would be wise, therefore, to oxidize all Eu^{+2} to Eu^{+3} in any experiment in which europium is to be separated.

Cerium is the only rare earth which can exist in solution in the +4 oxidation state. The tetravalent cerium ion is quite stable and is used in almost all radiochemical cerium separations. The Ce^{+3}-Ce^{+4} exchange reaction

has been the subject of a number of investigations, a good example of which is the paper by Duke and Parchen.[109] The exchange rate is measurable, and, in $HClO_4$ at least, decreases with increasing acid concentration. There seems no doubt but that the exact nature of ceric perchlorate solution is complex, and Kraus, Holmberg, and Nelson[243] conclude that at least some Ce^{+4} is polymerized or hydrolyzed in all concentrations of $HClO_4$. It is not clear that this holds true for all other acids, but to be on the safe side cerium carrier should be oxidized to Ce^{+4} and reduced to Ce^{+3} as a first step in any radiochemical procedure.

There seems to be no problem of the adsorption of rare-earth tracers on container walls. A study of the adsorption on various surfaces in acid solution has been made for carrier-free Pm and Ce,[24] for Ba and La,[426] and for Pm and La[457] and in no case was the adsorption significant.

At higher pH's the carrier rare earths may form radiocolloids which are adsorbed more strongly. Starik and Lambert[457] find the maximum adsorption of Pm and La on quartz occurs at a pH of approximately 6.2, while Belloni, Haissinsky and Salima[24] find the peak to occur at pH 5.6 for Pm. The "percent rare earth adsorbed" that these authors report is quite low even at the maxima of their curves but procedures have been reported in which Sr^{90}-Y^{90} mixtures[427] and Ba^{140}-La^{140} mixtures[426] are separated by adsorption of the rare-earth activities on glass frit filters. The authors report that at pH 7.0 between 90 and 95% of the Y^{90} is adsorbed, while in solutions above pH 6 almost 100% of the La^{140} is retained. Duval and Kurbatov[113] have used the same principle to separate carrier-free scandium from a calcium target by adsorbing the scandium on a filter paper. Maximum adsorption occurs at pH 8.5 and the authors report that eighty percent of the Sc present can be recovered in one hour.

VI. COUNTING TECHNIQUES

In the great majority of cases, samples of rare-earth activities may be counted by using standard β^- and γ counting techniques. As a general rule, however, the authors have found that for the most precise and reproducible results samples should be γ-counted whenever possible. Corrections for self-scattering and backscattering are very much smaller for γ rays than for beta particles and the variation in these corrections between samples of different weight is often undetectable. In many cases, too, the γ counting efficiency is quite comparable to the β^- counting efficiency for the same sample so larger samples are not necessarily needed for γ counting.

Pure β^- emitters, of course, will usually be beta-counted, and in these cases corrections for self-scattering and self-absorption will have to be

made in order to get consistent results between duplicate samples of different weight.[100, 182, 333]

In those cases where absolute disintegration rates must be determined, counting in 4π proportional gas flow counters is often used. A number of papers have been published which deal with details of this technique[179, 291, 292] and, since the rare-earth chemistries given in section VII are ideally suited to the preparation of weightless samples, the preparation of carrier-free rare-earth samples for 4π counting is not too formidable a task. Pascual and Freiling[351] have published a short article giving details of preparing rare-earth samples for 4π counting and the technique developed by Bjornholm, Nielson, and Sheline[32] seems ideally suited to this type of sample. Although the goal for all 4π counting is a sample of zero mass, this ideal is seldom realized and some correction must often be made for self-absorption in the sample. Merritt, Taylor, and Campion[309] and Le Gallic and Thenard[266] have published papers on this subject which enable corrections to be made with some degree of reliability.

In β^- counting it is desirable to have samples of as uniform thickness as is possible. While it may not be directly applicable to counting samples, Bjornholm, Dam, Nordby, and Poulson[33] have developed a method for preparing cyclotron targets which involves the electrophoretic deposition of rare-earth oxides on gold films; they report that uniform layers in the 3- to 10-mg weight range may be prepared by this technique.

The requirements of β-spectroscopy place stringent restrictions on the nature of the active sample so that special techniques are often needed to prepare satisfactory samples for this type of counting. These requirements are usually a weightless sample on a zero area and chemical techniques which have been developed for 4π samples are often just as satisfactory for β-spectroscopy. Hansen and Sheline,[188] and Bjornholm, Nielsen, and Sheline,[32] however, have published several excellent papers which deal specifically with the preparation or rare-earth samples for β-spectroscopic counting. Charpak and Suzor[73] have used vacuum evaporation techniques to obtain erbium samples of approximately 0.5 $\mu g/cm^2$ for β-spectroscopic analysis.

In most routine rare-earth radiochemical analyses the rare earth is finally prepared as a gravimetric compound, weighed, and counted either on a metal plate or on filter paper. For γ counting, rare-earth samples may be counted in solution with satisfactory results. Perey[361] has described a procedure by which this same technique may be used for counting actinium.

For special requirements, the rare earths may sometimes be prepared in thin sources by electroplating. Cotelle and Haissinsky[88] have succeeded in preparing actinium samples by electroplating Ac-La mixtures out of

acetone-ethyl alcohol solutions. Moeller and Zimmerman[317, 318] have obtained samples of Y, La, and Nd by electrolysis in anhydrous ethylenediamine, and Gates and Edwards[166] have used the same technique to obtain point sources of Pm^{147}. The deposit which is obtained is not gravimetric, since Moeller and Zimmerman report that their samples assayed at approximately 50% metal and contained significant amounts of occluded organic material; and the deposits are not stable but are oxidized by air, water, or any other oxidizing agent.

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VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES

RE-1. RARE EARTHS

W. Nervik

The isolation of individual rare-earth activities from any mixture of activities may be considered in two steps: separation of the rare earths as a group from all other elements; separation of the rare earths from one another. The procedure as outlined here has been used in this laboratory for some thousands of mixed rare-earth samples, and gives good results in a reasonable time without undue effort. Most samples consist of 10 mg per element for about five of the rare earths. Initial chemistry on a typical batch of eight samples might be started one morning, the columns loaded in the afternoon, and separated rare earths mounted and counted the following morning.

SEPARATION OF THE RARE EARTHS AS A GROUP FROM ALL OTHER ELEMENTS

The initial solution should consist of the mixed activities and rare-earth carriers in about 20 ml 3M acid (HCl, HNO_3, or $HClO_4$). Excessive amounts of Ca or Th (>200 mg) will interfere and should be removed before the initial chemistry is started. (Th may be extracted from TBP-4M HNO_3 solution, the rare earths may be separated from Ca by TTA extraction at pH 4 to 5; see extraction section for details.) If trans-Pu elements are present which will interfere with the desired rare earths they too should be removed (see the chloride-anion exchange column section).

Procedure

1. Add 3 drops Zr carrier (unless otherwise noted, all carrier solution concentrations are ≈10 mg/ml). Adjust to ≈20 ml 3M HCl. Add 5 drops conc. H_3PO_4. Digest in a hot bath for a few minutes. Centrifuge $Zr_3(PO_4)_4$.
2. Using Lusteroid or polyethylene container, add 2 ml 1.5M $CrO_4^=$ and 1/2 ml conc. HF to supernatant of step (1). Digest in hot bath 5 min. Centrifuge $(RE)F_3$. Wash one time with 20 ml 0.1M HF.
3. Dissolve $(RE)F_3$ in 3 ml saturated H_3BO_3 + 2 ml conc. HNO_3. (Heat and stir well to be sure all the fluoride is dissolved.) Add 5 drops Ba car-

rier, 1 ml 6M H_2SO_4, dilute to 20 ml, digest in hot bath 5 min. Centrifuge $BaSO_4$.

4. Adjust the supernatant of step (3) to pH > 7 with conc. NH_4OH, digest in hot bath for a few minutes, centrifuge $RE(OH)_3$. Wash one time with dilute NH_4OH.

5. Dissolve $RE(OH)_3$ of step (4) in 4 ml conc. HCl and pass through a Dowex A-1 anion-exchange column (6 mm i.d. x 10 cm, 50-100 mesh resin, previously conditioned with 5 ml conc. HCl). The rare earths do not stick and all of the eluant and wash solution is to be collected. Rinse tube with 2 ml conc. HCl, and pass through column; wash resin with 2 ml conc. HCl.

6. Adjust eluate (including rinse and wash solution) of step (5) to pH > 7 with conc. NH_4OH. Centrifuge $RE(OH)_3$. Wash one time with dilute NH_4OH.

7. Dissolve $RE(OH)_3$ of step (6) in 6 drops conc. HNO_3 or conc. HCl. Dilute to 30 ml with boiling H_2O. Add 1.5 ml Dowex-50 resin of the same batch that is to be used for the cation exchange separation. Digest in hot bath 10 min. Centrifuge resin and transfer to the ion exchange column for separation of the individual rare earths.

SEPARATION OF THE RARE EARTHS FROM ONE ANOTHER

The resin from step (7) above is transferred to the top of an ion-exchange resin column.

For these samples (≈ 60 mg total rare-earth carrier), columns 7 mm i.d. × 60 cm long are used. A schematic diagram of the apparatus has been reproduced from ref. 334 and is shown in Fig. 71. Under procedures currently in use at this laboratory, the "low-pH solution" in vessel A is 1M lactic acid adjusted to pH 3.10 with conc. NH_4OH and containing 2 g phenol/liter, and the high-pH solution in vessel B is 1M lactic acid adjusted to pH 6-7 with conc. NH_4OH and containing the same concentration of phenol. The phenol is present to inhibit bacterial growth and a resulting pH change in the solution. W. Hutchins of this laboratory has found that lactate solutions stored in polyethylene containers do not have any bacterial growth and do not require phenol, but we have not as yet changed our glass storage tanks to this type of system. The apparatus of Fig. 71 has been modified to the extent that we have discarded the electrical heating tapes and the water condenser. With prolonged usage we found that some lactate solution invariably spilled on the tapes, where it carbonized and destroyed the fine wires. We now use immersion heaters inserted at an angle of about 20° from the vertical at the bottom of the H_2O bath which surrounds the column. The first units of this design have been in continuous use for about nine months without giving

trouble of any kind. Substitution of a short air condenser for the water condenser in Fig. 71 has proven to give quite satisfactory results. Loss of water from the heating bath is negligible and columns have been run at 90°-95°C for many months without significant change in the water bath level.

In our system reservoir A has a capacity of 5 liters and reservoir B 2 liters. Eight ion-exchange columns are connected to each A reservoir and may be run simultaneously. Each column is 7 mm i.d. × 60 cm long and consists of BioRad AG 50W × 12 cation-exchange resin (Dowex 50W × 12 resin, cleaned, graded, and packaged under their own label by Bio Rad Laboratories, Richmond, Calif.), flow-graded to a settling rate of 0.8-2.4 cm/min in water. Columns are conditioned by passing pH 7, 1M lactate solution through them for at least 8 hours, then pH 3.10, 1M lactate for another 8 hours.

In a "normal" run (10 mg each of Y, Tb, Eu, Sm, Nd) the rare-earth carrier + resin from step (7) above is transferred to the top of the conditioned column with boiling water. With eight columns running, reservoir A should contain 4-5 liters of pH 3.10 1M lactate solution, and reservoir B about 1.5 liters of pH 6-7 1M lactate. Column temperatures are maintained at 90 ± 5°C at all times. With the system closed, the pressure is adjusted until the flow rate out the column is about 15 sec/drop (this operating pressure is usually about 3 psi). Samples of eluant are taken in the collecting tubes over 10-minute intervals. When the columns have been running for about an hour, the magnetic stirrer is started and the high-pH solution is fed into the low-pH solution at a flow rate of about 6-7 sec/drop, and maintained at this rate for the remainder of the run.

Under these conditions Y comes off the column in 4-5 hours, Nd is off in about 15 hours, and Tb, Dy, Eu, Sm, and Pm are eluted in that order at roughly equal intervals between the Y and Nd.

The collecting tubes are assayed for rare-earth carriers by adding a few drops of saturated oxalic acid to each tube. At the end of the run, the oxalate precipitates for each element are combined, washed once with water, once with acetone, ignited over a Meker burner for twenty minutes, and weighed as the oxide.

Note

It cannot be emphasized too strongly that there is no such thing as an "optimum set of conditions" which will be satisfactory for all rare-earth separations. This particular procedure has been designed for separating samples which consist of 10 mg each of Y, Tb, Eu, Sm, and Nd and is an outgrowth of exploratory work by the author on separations of this type.[334]

For other mixtures of rare-earth carriers, either in quantity or in kind, or for slower or faster separations, other conditions could undoubtedly be found which would give better results. The point is that there are so many variables affecting separations of this sort that the chemist should tailor his column operating procedures to fit each separations problem. An obvious drawback, of course, is that information with which this tailoring can be done intelligently is not too plentiful or readily available. The author[334] has shown how factors such as carrier mass and changing pH affect ion-exchange separation of the rare earths, and the section on Ion Exchange discusses a number of other variables as well, while Cabell[68] has published a discussion of the parameters to be considered in operating ion exchange columns. At the present state of the art, however, the best information for setting up "optimum operating conditions" for a given problem is drawn from a little experience in performing these separations. The important point to consider is that the chemical separation of almost any mixture of rare-earth activities is not really difficult and if more radiochemists were aware of this fact perhaps they would be more willing to work with these elements.

RE-2 RARE EARTHS

Bunney, Freiling, McIsaac, and Scadden[62]

Preliminary Isolation and Purification

1. Add the various rare-earth carriers and, if desirable, Pm^{147} tracer to the acid solution containing the activity and stir well.
2. Add 5 mg Ba^{++} holdback carrier, make basic with NH_4OH. Centrifuge, discard supernatant, wash twice with 20 ml H_2O.
3. Dissolve the hydroxide in 5 ml conc. HCl and add 2 drops conc. HNO_3. With sample in water bath (no ice!) saturate with HCl gas.
4. Pass through a bed (6 mm × 10 cm) of Dowex-2 (100-200 mesh) that has been washed with conc. HCl. Pass 5 ml of conc. HCl through to wash out the rare earths.
5. Repeat steps (2), (3), and (4).
6. Make basic with conc. NaOH, centrifuge, discard supernatant, wash with 20 ml H_2O.
7. Repeat steps (3), (4), (6).
8. Dissolve in a minimum amount of HCl or $HClO_4$.

Ion-Exchange Separation

1. Load the boiling solution from the preceding steps onto a bed (10 mm by 60 cm) of Dowex-50 (settles through H_2O at the rate of 0.6-1 in./min) in the NH_4^+ form held at 87°C by the boiling vapors of trichloroethylene. (Ed. Note: These authors have subsequently shifted to electrically heated water baths for maintaining their columns at elevated temperatures.)
2. Rinse twice with an equal volume of boiling distilled water.
3. Elute with degassed 0.87M lactic acid at pH 3.0 until the Ho comes off. (The rare earths elute in reverse order to their atomic number; Y falls between Ho and Dy.)
4. Elute with 1.25M lactic acid at pH 3.0 until the Nd comes off.
5. Elute with 1.25M lactic acid at pH 3.3 until the La comes off.

A flow rate of 10-25 ml/hr is used and fractions are taken every 5-15 min. An automatic fraction collector is a great aid. Where greater purity becomes necessary it is usually less time-consuming to recycle fractions rather than slow down the elution. Among the rare-earth fission products of U^{235} and Pu^{239}, it is usually desirable to recycle Ho, Dy, and Tb, since they are all usually contaminated with Y activity because of the high fission yield of Y relative to the others. This has been found to be true with Tb even in cases where the peak-to-valley ratio of the Y is 10^6 or greater. The elution conditions used here are 0.95M lactic acid at pH 3.10 for Ho and Dy. With Dy it may be necessary to divide the fraction into two parts, a Dy-rich and a Y-rich fraction, and recycle each part. (Ed. Note: A recycled Dy-Y separation may be performed more efficiently by using diethylene-triamine-pentaacetic acid (DTPA). See Ion Exchange Section). The columns used are identical to those previously described. Any rare earth may be further purified by recycling under the elution conditions of its original separation. The usual elution conditions used here for recycling Tb fractions (and Gd, Eu, and Sm) are 1.13M lactic acid at pH 3.10.

Gradient elution has been used at this laboratory with success. There are many variations of molarity, pH, and volumes of eluants that may be used in gradient elutions. The most desirable set of conditions varies with each application. A system that we have found successful with the fission-product rare earths is to connect a reservoir containing 330 ml of 1.10M lactic acid at pH 3.10 to a loaded Dowex-50 column of the type described above and connect a second reservoir containing 1.25M lactic acid at pH 3.25 to the first in such a manner that as a given volume is removed from the first reservoir half that volume is replaced from the second. This set of condi-

tions gives good separation of the fission-product rare earths in about 30 hr.

Sample Mounting

1. Select the appropriate fractions and combine.

2. Precipitate the hydroxide by adding conc. NaOH dropwise until the pH exceeds 9. Centrifuge, discard supernatant. Wash twice with 10 ml H_2O. (Add Nd carrier to Pm.)

3. Dissolve in 2 drops 6N HCl (warming may be necessary), dilute to 5 ml with H_2O, heat to boiling, add saturated oxalic acid dropwise until a precipitate forms. Continue dropwise addition of oxalic acid until 2 ml more has been added. Boil for 1 min. Let cool.

4. Centrifuge, discard supernatant. If rapid analysis is required, transfer to a tared filter paper, wash with H_2O until filtrate does not precipitate with La^{+3}, wash twice with 3 ml of methyl alcohol. Dry at 105°C for 30 min, cool in air 15 min, weigh, mount, and count. (Ed. Note: This drying and cooling procedure requires a minimum of 45 minutes. Direct ignition to the oxide and cooling to room temperature can be done in 10 minutes if speed is required.)

RE-3. NEODYMIUM (RARE EARTHS)

B. E. Cushing[233]

Introduction

In the separation of neodymium from other fission activities, a combination of hydroxide and fluoride precipitations in the presence of neodymium and yttrium carriers is first carried out. The rare earths and yttrium are then placed on a Dowex-50-X12 cation-exchange column in 2M hydrochloric acid. The column is subsequently treated with 1M ammonium lactate (at pH 3.14-3.17) and various fractions are collected in saturated oxalic acid. Yttrium elutes much earlier than neodymium and is recognized by the formation of the white precipitate of the oxalate. Elution of neodymium yields a blue oxalate, which is then converted to the oxide, Nd_2O_3, on ignition. The neodymium is weighed and counted in this form. The chemical yield is about 80% and approximately 24 hours are required to analyze eight aliquots of a sample.

Reagents

Nd carrier: 15 mg Nd_2O_3/ml (added as Nd_2O_3 in 3M HCl), standardized
Y carrier: 15 mg Y_2O_3/ml (added as Y_2O_3 in 3M HCl)
Ba carrier: 10 mg Ba/ml (added as $Ba(NO_3)_2$ in H_2O)
Sr carrier: 10 mg Sr/ml (added as $Sr(NO_3)_2 \cdot 4\ H_2O$ in H_2O)
HCl: 2M
$HClO_4$: conc.
HF: conc.
H_3BO_3: saturated aqueous solution
$H_2C_2O_4$: saturated aqueous solution
NH_3: gas
Ammonium lactate: 1M (note 1)
Ethanol: absolute

Equipment

Centrifuge
Drying oven
Sand bath
Muffle furnace
Steam bath
Blocks for holding centrifuge tubes
Forceps
Mounting plates
Pipets: assorted sizes
Stirring rods
Ground-off Hirsch funnels: Coors 000A (one per aliquot)
Filter chimneys (one per aliquot)
No. 42 Whatman filter paper: 9 cm
No. 42 Whatman filter circles: 7/8 in. diameter, weighed
2-inch, 60° short-stem glass funnels (one per aliquot)
Wash bottle
40-ml conical centrifuge tubes: Pyrex 8320 (one per aliquot)
40-ml Lusteroid centrifuge tubes (one per aliquot)
5-ml conical centrifuge tubes: Pyrex LG 2578
50-ml Pyrex beakers (one per aliquot)
Porcelain crucibles: Coors 00 (one per standardization)
Automatic Fraction Collector (Packard Instrument Company)
Ion exchange columns: The container for the resin bed is of the "condenser" type, 68 cm long, with the inner bore about 1.1 cm in diameter and the outer

jacket about 3.5 cm. The column is heated by means of the vapor of n-propyl alcohol. The Dowex-50-X12 cation resin (200-400 mesh) is placed to a height of 60 cm in the inner column of the "condenser." Prior to actual use, the resin is equilibrated with about 30 ml of 1M ammonium lactate (pH 3.14-3.17).

Preparation and Standardization of Carrier

Dissolve 15.0 g of highest purity Nd_2O_3 (note 2) in 3M HCl and make the solution up to a volume of 1 liter with the acid.

Pipet 5.0 ml of this solution into a 40-ml conical centrifuge tube and add 15 ml of saturated $H_2C_2O_4$ solution. Heat to coagulate the precipitate wich forms and permit to stand for 5 min. Filter the precipitate onto No. 42 Whatman filter paper (9 cm). Transfer the precipitate and paper to a weighed porcelain crucible (Coors 00) and ignite at 800° for 1 hr. Cool and weigh as Nd_2O_3.

Four standardizations are carried out with results agreeing within 0.5%.

Procedure

1. To an aliquot of the sample in a 50-ml beaker, add 1.0 ml of standard Nd carrier, 1 ml of Y carrier and 12 drops of conc. $HClO_4$. Fume to dryness on a sand bath and transfer with 2M HCl to a 40-ml conical centrifuge tube (note 3).

2. Pass in NH_3 gas until precipitation of hydroxides is complete. Centrifuge, discard the supernate, wash the precipitate with H_2O, and centrifuge again. Discard the supernate.

3. Dissolve the precipitate in a minimum of 2M HCl and transfer the solution to a 40-ml Lusteroid centrifuge tube. Add 10 drops each of Ba and Sr carriers and 10-20 drops of conc. HF. Centrifuge the fluoride precipitate and discard the supernate.

4. Slurry the precipitate with 5 drops of saturated H_3BO_3 and add 10 drops of 2M HCl to dissolve the precipitate. Add 10 drops each of Ba and Sr carriers and again precipitate the fluorides with conc. HF. Centrifuge and discard the supernate.

5. Slurry the precipitate with 5 drops of saturated H_3BO_3 and add 10 drops of 2M HCl to complete the solution process. Pass in NH_3 gas until precipitation of hydroxides is complete. Centrifuge and wash the precipitate with H_2O, discarding the supernates.

6. Dissolve the precipitate in a minimum of 2M HCl and add the solution onto the heated Dowex-50-X12 resin bed. Rinse the tube with about 3 ml of 2M HCl and add the rinsings to the column.

7. Allow the last of the HCl solution to reach the top of the resin bed, and then add 15 ml of boiled 1M ammonium lactate. Attach to the ion exchange column a 1-liter separatory funnel containing about 300 ml of 1M ammonium lactate. Allow the lactate to flow under gravity through the resin bed. (The flow rate is adjusted to about 3 ml per 10 min.)

8. Start the Automatic Fraction Collector so that 10-min samples are collected in 5-ml centrifuge tubes each containing 1 ml of saturated $H_2C_2O_4$. The first precipitate to appear is white $Y_2(C_2O_4)_3$; this is discarded. The blue $Nd_2(C_2O_4)_3$ precipitate appears 12-16 hours after the start of elution. There will be 10-15 tubes containing the $Nd_2(C_2O_4)_3$ precipitate. These are heated for 15 min on a steam bath and then filtered through the same No. 42 Whatman filter paper (9 cm), using a 2-in. 60° funnel. The oxalate is ignited to the oxide at 800° for 1 hr.

9. Slurry the Nd_2O_3 with absolute ethanol and transfer to a weighed No. 42 Whatman filter circle (7/8 in. diameter), using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate with ethanol and dry at 110° for 15 min. Cool for 30 min and weigh. Mount and count.

Notes

1. The 1M ammonium lactate solution is made by mixing 420 ml of 85% lactic acid with 3580 ml of H_2O and adjusting the pH to 3.14-3.17 with NH_3 gas. The water is purified prior to use by distillation, followed by passage through a de-ionizer.

2. The Nd_2O_3 was supplied by Research Chemicals, Inc., Burbank, Calif. Spectroscopic examination showed the oxide to be in a high state of purity.

3. If the uranium content of the sample is high (> 1 mg per ml), a purification step is necessary before starting step (2). Removal of uranium is accomplished by saturating the solution at this point with HCl gas and then passing it through a Dowex 1-X8 (100-200 mesh), cloride form, anion exchange column (0.4 cm × 7 cm). The column is rinsed with three 2-ml portions of conc. HCl. The uranium remains on the column.

RE-4. RARE EARTHS (and Cerium)

Green and Mercer[544]

SEPARATION AND PURIFICATION OF INDIVIDUAL RARE-EARTH ELEMENTS FROM FISSION PRODUCTS

1. The elements to be considered are cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, and their analogue yttrium. The isotopic species considered are:

Y-90	61 h (see strontium)
Y-91	57 d
Ce-141	32.5 d
Ce-143	33 h → Pr-143
Ce-144	282 d → Pr-144
Pr-143	13.8 d carrier-free cerium
Pr-144	17.5 m
Nd-147	11.9 d
Sm-153	47 h
Eu-156	15.4 d
Gd-159	18 h
Tb-161	7 d

(Note: 2.7-y Pm-147 is not often determined. If this is needed, a tracer of 50-h Pm-149 may be prepared by irradiation of neodymium in a reactor, with subsequent ion-exchange purification. The presence of some 27-h Pm-151 is immaterial, if a comparison technique is used. If 50-h Pm-149 is required, Pm-147 may be used as tracer in an amount sufficient to swamp that growing from Nd-147. In these cases, samarium carrier is also needed to locate promethium in the ion exchange separation.)

2. It is convenient to divide the separation into two parts: (a) yttrium, terbium, gadolinium, europium, samarium, and (b) yttrium, neodymium, praseodymium, cerium. There are three reasons for making this division: (i) the length of time involved in separating all eight elements in one experiment, (ii) the large differences in fission yield, (iii) the difference in half-lives. Yttrium is included in portion (a) as a "maker" element, and need only be determined in (b). Portion (b) is left for 12 days after fission, to allow complete decay of Ce-143 (see below). To the larger portion the following carriers are added: 0.5 mg each yttrium, terbium, gadolinium, plus 1.0 mg each europium and samarium. To the smaller portion the following carriers are added: 1.0 mg each yttrium, neodymium, praseodymium, cerium, and promethium tracer and samarium carrier if needed.

3. It is possible to separate all the rare earths from yttrium to praseodymium by the use of "graded elution," viz. the slow increase in concentration of the eluant, at a constant pH of 4.00, from 28 g/liter initially to 52 g/liter finally. This produces a more even spacing of the peaks. 0.5-mg quantities of each carrier are used.

4. Outline of Purification Scheme

Two fluoride-hydroxide cycles.

RE passed through Amberlite CG400 in concentrated hydrochloric acid.

RE passed through Amberlite CG400 in 4M hydrochloric acid.

Removal of cerium by precipitation as ceric iodate.

RE separated by elution from ZEO-KARB 225 cation-exchange resin with α-hydroxy-isobutyric acid solution.

5. Procedure

1. Add to the sample 0.5 mg each of required rare-earth carriers and of cerium carrier if not already present; fume down with 0.2 ml perchloric acid and 0.1 ml concentrated nitric acid.

2. Dissolve the residue in 1 ml 1M nitric acid, add 0.5 mg zirconium carrier and 0.5 ml 2M ammonium fluoride solution. Allow the precipitate to stand for 5 minutes and centrifuge.

3. Dissolve the RE fluoride precipitate in 1 drop saturated boric acid + 0.4 ml concentrated nitric acid, add 1 mg barium carrier, dilute to 2 ml, and pass ammonia gas. Centrifuge precipitate and wash once with 2 ml of water.

4. Repeat steps (2) and (3).

5. Dissolve the hydroxide in concentrated hydrochloric acid and evaporate to dryness. Take up the residue in 0.5 ml concentrated hydrochloric acid and transfer to an Amberlite CG400 anion column (4 cm × 5 mm). Wash the column successively with 4 × 0.5 ml concentrated hydrochloric acid.

6. Evaporate the effluent to dryness, take up in 0.5 ml 5M hydrochloric acid and transfer to an Amberlite CG400 column (4 cm × 4 mm). Wash the column successively with 4 × 0.5 ml 4M hydrochloric acid.

7. Evaporate the effluent to dryness and dissolve in 0.4 ml concentrated nitric acid. Add 1 ml 0.35M iodic acid and approximately 10 mg sodium bromate powder. Warm solution and stir well until ceric iodate coagulates. Note time of first separation. Centrifuge ceric iodate and wash with 2 x 1 ml water. Reserve ceric iodate if necessary for further cerium purification [sample (b) only].

8. Evaporate the supernate and washes to dryness. Add 1 ml concentrated hydrochloric acid and re-evaporate. Dissolve the residue in water and pre-

cipitate RE with ammonia. Centrifuge and wash with 2 ml water. Separate by the ion-exchange method below.

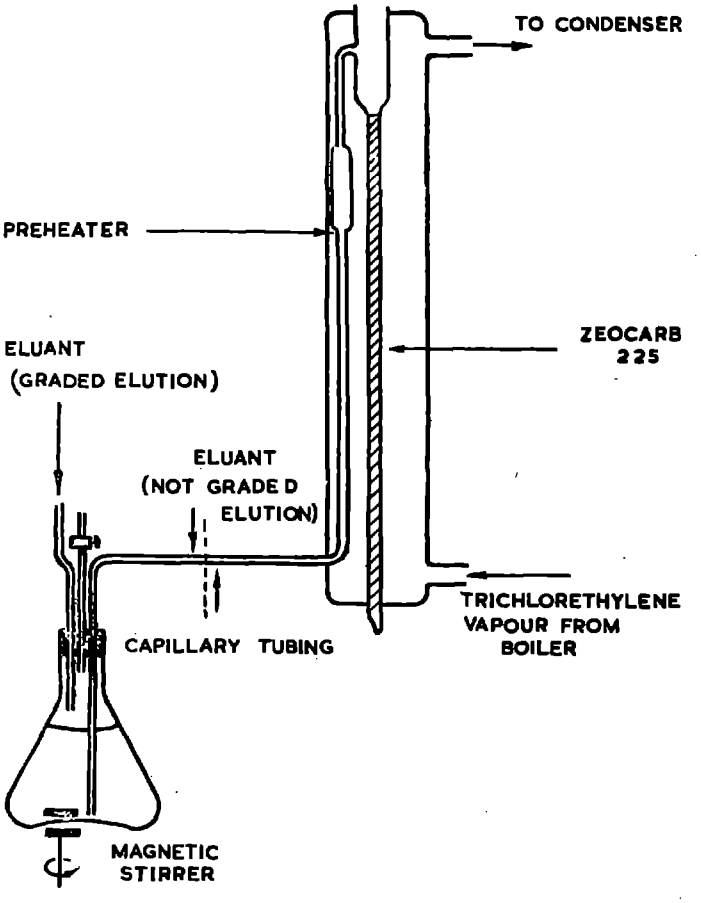

Fig. 104. Ion-exchange column apparatus.

6. Separation Method

6.1. Apparatus. The ion-exchange column apparatus is shown in Fig. 104. The main column of a tube 22 cm long × 6 mm diameter surrounded by a heating jacket. P. V. C. tubing connects the preheater to a gravity feed reservoir. A pressure head of eluant is adjusted to give the correct flow rate. The reservoir is a 40-ml flask with connections as shown.

6.2. Resin. This is ZEO-KARB 225 (20-30 μ) prepared and pretreated as in Section 3C (see ref. 544).

6.3. Column packing. The column is filled with distilled water and this is allowed to attain equilibrium temperature. The conditioned resin is heated on a steam bath, slurried into the column, and allowed to settle with no flow

of water. The resin bed is equilibrated with about 10 ml of eluant followed by 10 ml water, and is then ready for use. When not in use the bed is kept under distilled water. (N.B., the column must be free from bubbles.)

6.4. Eluant

1. For the yttrium, terbium, gadolinium, europium, samarium group the eluant is α-hydroxy-isobutyric acid (3.1 g/liter) adjusted to a pH of 4.00 with concentrated ammonia.

2. For the yttrium, neodymium, praseodymium group the eluant is α-hydroxy-isobutyric acid (42 g/liter) adjusted to a pH of 4.00 with concentrated ammonia.

3. For graded elution, preheater and reservoir are filled with 28-g/liter α-hydroxy-isobutyric acid: a volume of about 30 ml is required for the preheater and a further 40 ml is used in the reservoir. The feed to the reservoir is 52 g/liter α-hydroxy-isobutyric acid. The pH is 4.00 for both solutions.

Dissolve each oxalate precipitate in 0.5 ml nitric acid + 0.5 ml perchloric acid and evaporate to dryness in a 5-ml beaker. Add a further 0.5 ml nitric acid + 0.5 ml perchloric acid and re-evaporate to dryness on a hot plate. (Traces of oxalic acid interfere with chemical-yield determination.) Dissolve residue in 1 ml water and precipitate hydroxide with ammonia. Centrifuge precipitate and wash well with water.

Dissolve in 0.1 ml of 1M hydrochloric acid, dilute suitably and take aliquots for counting and chemical yield.

7. Cerium Purification

7.1. Outline of purification scheme. (As in Section 4, plus two precipitations of ceric iodate.)

1. Dissolve the ceric iodate from Section 5, step (7) by adding 1 drop 1M hydrochloric acid + 1 drop 10 volume % hydrogen peroxide + 0.4 ml concentrated nitric acid. Add 1 ml 0.35M iodic acid solution followed by 10-20 mg sodium bromate. Heat in water bath until precipitate coagulates. Centrifuge precipitate and wash twice with water.

2. Repeat step (1) noting time of the last ceric iodate precipitation, if Ce-143 is to be calculated from the cerium source.

3. Dissolve as in step (1), pass sufficient sulfur dioxide to decolorize iodine, and precipitate cerium as hydroxide with ammonia. Wash once with water.

4. Dissolve in 1 drop 1M hydrochloric acid and make up to convenient volume. Weigh out portions for chemical yield and counting.

8. Source Preparation

Evaporate a weighed portion to dryness on distrene foil in the usual way. Dissolve in 1 to 2 drops of water and precipitate RE in situ either as fluoride or hydroxide. To do this place 1 drop of concentrated hydrofluoric acid or concentrated ammonia solution alongside the main drop and re-evaporate. The method gives a more uniform nondeliquescent source.

6.5. Separation procedure. Almost fill the preheater with eluant, so that it reaches equilibrium temperature. Dissolve the rare-earth hydroxide in 0.1 ml of 1M hydrochloric acid.

Remove excess water plus about 1 cm resin (for use as a tamper) from the top of the bed and place in a test tube on the steam bath. The top of the bed should now be horizontal.

With the first sample tube in position, place the RE solution on the resin bed and allow to percolate under gravity until the meniscus is just above the resin. Wash the test tube which has contained the rare earths with two separate 0.1-ml portions of hot water, and transfer this to the resin in a similar manner. Replace the tamper, allow it to settle and remove any excess water. Introduce the eluant above the surface of the column carefully via the preheater and adjust the height of the reservoir to give a flow rate of 12 ml/hr.

6.6. Elution. Collect the solution in 1-ml fractions using an automatic fraction collector. The break-through volumes for a typical batch of resin are:

α-hydroxy-isobutyric acid (3.12 g/liter, pH 4.00)		α-hydroxy-isobutyric acid (41.6 g/liter, pH 4.00)	
Sc	6 ± 1 ml	Y	5 ± 1 ml
Y	13 ± 1 ml	Nd	38 ± 2 ml
Tb	18 ± 1 ml	Pr	57 ± 2 ml
Gd	30 ± 2 ml		
Eu	43 ± 2 ml		
Sm	65 ± 2 ml		

After collection of these fractions, flush out and reject the resin.

6.7. Treatment of fractions. Add 0.3 ml of saturated oxalic acid to each tube. Each element will then precipitate in one or more tubes. Combine the tubes containing the same element, centrifuge, and wash once with dilute oxalic acid solution. If promethium is being determined, there will be an obvious gap between the precipitates of neodymium and of the samarium used as a marker. Combine the center tubes and add 0.1 mg of neodymium to collect the promethium.

Sc-1. SCANDIUM (β^+ Emitters)

Threshold Detector Group
Radiochemistry
UCRL, Livermore
May, 1958; Revised 10/28/58

This procedure is for trochoidal analyzer samples (B^+ emitters), not β^- pure.

Purification: From a 5-day-old solution containing 1.1×10^{15} fissions only, a sample was obtained which had a beta activity of 2.2×10^4 cpm.

Chemical Yield: About 75%.

Procedure

1. To a 25-ml solution of mixed activities in 6M HCl in a 40-ml glass centrifuge cone, add 10 mg of scandium carrier and ≈10 mg of Ce^{+++}, ≈5 mg of Te^{+4} and ≈2 mg of Zr. Add conc. NH_4OH in excess. Centrifuge the $Sc(OH)_3$ and discard the supernatant. Wash the precipitate twice with ≈15 ml of water to remove salts and especially any Na^+ ions. Centrifuge and discard the wash solutions.

2. Dissolve the precipitate by adding 1-2 ml of 6M HNO_3. Transfer the solution to a 50-ml Lusteroid tube with ≈4 ml of water. Add an equal volume of Na-free 6M NH_4F, making the final solution ≈3M in NH_4F and pH 4-5. Heat in a hot bath for ≈3 minutes. Cool and centrifuge. Pour the supernatant into a new 50-ml Lusteroid tube. Add 10 ml of 3M NH_4F to the precipitate. Heat for 3 minutes. Cool and centrifuge, combining this supernatant with the previous one. Wash the CeF_3 with ≈5 ml of water. Centrifuge and combine supernatants. Discard the CeF_3.

3. To the Sc solution, add 1 ml of sat. $KBrO_3$ soln. and heat in a hot bath for ≈5 min. Then add ≈10 ml conc. HNO_3. The pH should be ≈0.3 (or less). Heat in a hot bath for ≈5 min more. Cool to room temperature. Centrifuge and discard the supernatant. Wash the precipitate with ≈5 ml of water. Centrifuge and discard supernatant. Dissolve the ScF_3 by adding ≈1 ml of 5% H_3BO_3. Mix thoroughly. Heat in hot bath for ≈3 minutes. Add 2 ml conc. HNO_3. Transfer the solution to a 40-ml glass cone using 2 ml 6M $HClO_4$. Heat carefully to strong fumes of $HClO_4$. Dilute to ≈20 ml with water. Precipitate $Sc(OH)_3$ by adding an excess of conc. NH_4OH. Centrifuge and discard the supernatant. Wash the ppt. once with ≈30 ml of water.

4. Dissolve the $Sc(OH)_3$ in ≈20 ml of 0.1M HCl (pH is 1.5-2.0). Transfer the solution to a 60-ml cylindrical separatory funnel. Add ≈30 ml of 0.40M TTA in benzene and stir vigorously for ≈3 minutes. Drain aqueous layer

and wash organic layer four times with ≈ 20 ml of 0.05M HCl for ≈ 3 minutes each time.

Back-extract the scandium with ≈ 20 ml of 2M HCl, stirring for 2 minutes. Allow layers to settle a few minutes before draining aqueous layer.

5. Precipitate $Sc(OH)_3$ with an excess of NH_4OH. Centrifuge and discard the supernatant. Wash the precipitate with ≈ 30 ml of water.

6. Dissolve the precipitate with 0.5 ml of conc. HCl. Add ≈ 30 ml of 1M ammonium tartrate and add conc. NH_4OH dropwise until pH 7-8 (bromothymol blue turns from yellow to blue), then add 4 drops more. Heat in a boiling water bath for ≈ 20 minutes. Cool to room temperature. Centrifuge and discard the supernatant. Wash the scandium ammonium tartrate with 20 ml of water and centrifuge, discarding the supernatant.

7. Dissolve the precipitate in 5 ml of 1M HCl and filter through 9-cm No. 40 Whatman paper. Then add 20 ml 1M HCl and add ≈ 2 ml of 30% H_3PO_2 (hypophosphorous acid) to the filtrate. Heat on a hot (≈ 95°C) bath for 90 minutes. Cool and filter through a tared, 2.5-cm-diameter, No. 542 Whatman filter paper using a filter-chimney setup. Wash with water and methanol. Suck dry for ≈ 2 minutes before removing chimney. Dry in oven at ≈ 110°C for ≈ 10 minutes. Weigh, mount and count β^+'s on trochoidal analyzer.

Sc-2. SCANDIUM (β^- Pure)

Threshold Detector Group
Radiochemistry
LRL, Livermore
1-9-59

This procedure is for β^- pure samples.

Purification: From a two-week-old solution containing 1.1×10^{16} fissions, a sample was obtained which had a beta activity of about 50 cpm (with ≈ 35% geometry).

Chemical Yield: ≈ 65%

Separation Time: ≈ 6 hours

Procedure

1. To a 25-ml solution of mixed activities in 6M HCl in a 40-ml glass centrifuge cone, add 10 mg of scandium carrier, ≈ 10 mg of Y, ≈ 5 mg of

Te^{+4} and ≈ 2 mg of Zr. Add 2 ml of 6% H_2SO_3 and 1 ml of 1M H_3PO_4. Stir and heat on a hot bath for 5 minutes. Cool to room temperature. Centrifuge and discard the precipitate. To the supernatant add ≈ 2 mg Zr and 2 mg Te^{+4} and heat, repeating the Zr phosphate-Te metal scavenge. Discard the precipitate. Pour the supernatant into a 50-ml Lusteroid tube. Add conc. NH_4OH in excess. Centrifuge the $Sc(OH)_3$ and discard the supernatant. Wash the precipitate twice with ≈ 15 ml of water to remove salts and especially any Na^+ ions. Centrifuge and discard the wash solutions.

2. Dissolve the precipitate by adding a few drops of 6M HNO_3. Add 5 ml of water. Add an equal volume of Na-free 6M NH_4F, making the final solution ≈ 3M in NH_4F and pH 4-5. Heat in a hot bath for ≈ 3 minutes. Cool and centrifuge. Pour the supernatant into a new 50-ml Lusteroid tube. Add 10 ml of Na-free 2M NH_4F to the precipitate. Heat for 3 minutes. Cool and centriguge, combining this supernatant with the previous one. Wash the YF_3 with ≈ 5 ml of water. Centrifuge and combine supernatants. Discard the YF_3.

3. To the Sc solution add 1 ml of sat. K BrO_3 soln. and heat in a hot bath for ≈ 5 min. Then add ≈ 10 ml conc. HNO_3. The pH should be ≈ 0.3 (or less). Heat in a hot bath for ≈ 5 minutes more. Cool to room temperature. Centrifuge and discard the supernatant. Wash the precipitate with ≈ 5 ml of water. Centrifuge and discard supernatant. Dissolve the ScF_3 by adding 1 ml of 5% H_3BO_3. Mix thoroughly. Heat in hot bath for ≈ 3 minutes. Add 2 ml conc. HNO_3. Transfer the solution to a 40-ml glass cone using 2 ml 6M $HClO_4$. Heat carefully to strong fumes of $HClO_4$. Dilute to ≈ 20 ml with water. Precipitate $Sc(OH)_3$ by adding an excess of conc. NH_4OH. Centrifuge and discard the supernatant. Wash the precipitate once with ≈ 30 ml of water.

4. Dissolve the $Sc(OH)_3$ in ≈ 20 ml of 0.1M HCl (pH is 1.5-2.0). Transfer the solution to a 60-ml cylindrical separatory funnel. Add ≈ 30 ml of 0.40M TTA in benzene and stir vigorously for ≈ 3 minutes. Drain aqueous layer and wash organic layer four times with ≈ 20 ml of 0.05M HCl for ≈ 3 minutes each time.

Back-extract the scandium with ≈ 20 ml of 2M HCl, stirring for 2 minutes. Allow layers to settle a few minutes before draining aqueous layer.

5. Precipitate $Sc(OH)_3$ with an excess of NH_4OH. Centrifuge and discard the supernatant. Wash the precipitate with ≈ 30 ml of water.

6. Dissolve the $Sc(OH)_3$ with ≈ 8 ml of conc. HCl. Pass the solution (≈ 10 ml total volume) through a Dowex-1 anion-exchange resin column (7 cm in length × 6 mm i.d., 50-100 mesh). Wash the column with ≈ 4 ml of 12M HCl. Collect and combine both solutions.

7. Precipitate $Sc(OH)_3$ with an excess of conc. NH_4OH. Cool, centrifuge

and discard supernatant. Wash the precipitate with ≈ 30 ml of water.

8. Dissolve the $Sc(OH)_3$ with 3 drops of conc. HCL. Add ≈ 15 ml of saturated NH_4SCN solution. Final solution should not be more acid than ≈ pH 0.8. Transfer the solution to a 60-ml cylindrical separatory funnel. Add ≈ 25 ml of ethyl n-butyl ketone (3-heptanone). (Note 1) Stir the layers vigorously for 2 minutes using a motor-driven glass stirring-rod paddle. Drain and discard the aqueous layer. Wash the organic layer three times with ≈ 15 ml of saturated NH_4 SCN solution for ≈ 1 minute per wash. Discard the aqueous layers.

Back-extract the Sc from the ketone using two 7-ml portions of 6M HCl for 1 minute. Discard the organic layer.

9. Precipitate $Sc(OH)_3$ by adding an excess of NH_4OH. Dilute to ≈ 40 ml with water. Cool to room temperature, centrifuge and discard the supernatant. Wash the $Sc(OH)_3$ with ≈ 30 ml of water.

10. Dissolve the precipitate with 0.5 ml of conc. HCl. Add ≈ 30 ml of 1M ammonium tartrate and add conc. NH_4OH dropwise until pH 7-8 (bromothymol blue turns from yellow to blue), then add 4 drops more. Centrifuge and discard any precipitate, broken glass, etc. Heat in a boiling water bath for ≈ 20 minutes. Cool to room temperature. Centrifuge and discard the supernatant. Wash the scandium ammonium tartrate with ≈ 20 ml of water and filter through 7-cm No. 42 Whatman paper. Ignite to Sc_2O_3 in a furnace for ≈ 20 minutes at 800°C in a No. 00 Coors porcelain crucible. Weigh, mount and count in a scintillation counter or beta counter.

Note 1: Ethyl n-butyl ketone is more specific for Sc than is hexone (methyl isobutyl ketone) which might have been used. Therefore this extraction with the washes gives a better separation from thorium and the rare earths.

Sc-3. SCANDIUM (Carrier-Free)

Procedure by: Anders[307]

Target Material: Ti

Type of Bbdt: 7.8-Mev Deuterons

Yield: ≈50%

Degree of Purification: $\approx 10^5$

Time for separation: 4 hours

Equipment Required:

4 Pyrex beakers (50-ml); centrifuge; centrifuge tubes, 40-ml, 15-ml; platinum wire, 6-inch; Erlenmeyer flask, 250-ml; medicine droppers; glass frit filter funnel, coarse; Whatman 42 filter paper; micropipet, 50λ; small ion-exchange column, Dowex-2 resin (200-400 mesh); conductivity water; conc. H_2SO_4, HNO_3, HCl, NH_4OH; 30% H_2O_2; NaOH (solid pellets); $NaHCO_3$ (saturated solution); $KClO_3$ (crystals); HCl-gas tank.

Procedure

1. Place tracer scandium in small beaker, add Mylar substrate. Add 2 ml conc. H_2SO_4 plus a few drops of 30% H_2O_2. Add bombarded titanium foil, heat until dissolved. Oxidize purple solution with few drops of HNO_3 (some TiO_2 precipitates at this point, if solution is too hot, but this does not interfere). (Note 1)

2. Transfer to 50-ml centrifuge cone and precipitate $TiO_2 \cdot aq.$ with several pellets of NaOH. Wash twice.

3. Dissolve with conc. HCl. (If solution is not complete, try adding water and heat gently). Centrifuge and transfer supernate to another centrifuge cone.

4. Add slowly a saturated solution of $NaHCO_3$ until initial precipitate still dissolves on stirring. (Note 2)

5. Heat gently to effect homogeneous precipitation of $TiO_2 \cdot aq.$ Do not permit the pH to rise above about 5.5.

6. Repeat steps (3), (4), and (5) and combine the supernate with that of step (5).

7. Saturate combined supernates with HCl gas (cool!). Centrifuge off the NaCl.

8. Evaporate to 5 ml and repeat step (7).

9. Add a crystal of $KClO_3$, shake and transfer to a small anion-exchange column charged with 1 ml Dowex-2 resin which has been saturated with conc. HCl containing a few mg $KClO_3$ per 100 ml.

10. Permit to absorb. When liquid level reaches the resin bed add 5 drops

of conc. HCl with $KClO_3$ and permit again to reach the bed level. Elute the scandium activity with approximately 12 ml conc. HCl-$KClO_3$.

11. Pour the eluate rapidly into a 250-ml Erlenmeyer flask containing 30 ml of a soln. made of 11 parts 8N NH_4OH and 1 part 30% H_2O_2. Shake vigorously. (Note 3)

12. After fumes subside, cool the clear solution and pass it twice through a double layer of Whatman 42 filter paper positioned over a glass frit funnel. (The scandium activity remains on the filter in radio-colloidal form.)

13. Wash filter paper with 10 ml of the mixture of step (11) to which about 3 ml conc. HCl has been added.

14. Wash with 5 ml alkaline distilled water followed by a wash with 5 ml conductivity water.

15. Elute the scandium activity from the filter paper by passing 5 ml of 4M HCl twice through the filter paper (some of the activity will still remain on the paper, but most of it will be eluted).

16. Evaporate to near dryness and plate for counting.

Note

1. The Mylar is dissolved first, since titanium forms a precipitate in hot conc. H_2SO_4 solution containing peroxide.

2. $Ti(OH)_4$ is precipitated homogeneously from a solution of pH 2, while the $Sc(OH)_3$ precipitates only when pH reaches 7.

3. A sudden increase of the pH in a strongly oxidizing medium transforms any titanium present into the titanate ion whose ammonium salt is soluble, while the trace amount of scandium, being insoluble in the medium, "precipitates" in the form of a radio-colloid.

Sc-4. SCANDIUM

Sattizahn[233]

1. Introduction

The procedure described herein for the determination of radio-scandium in the presence of fission-product material is an alternative to that given in LA-1566, pp. 43-49.

Excellent decontamination of radio-scandium is achieved by six successive applications of the following cycle:

1. Lanthanum fluoride scavenging is done in a medium which is slightly acidic and contains a large excess of fluoride ion. This step gives separation from rare-earth activities; the fluoride ion keeps scandium in solution, presumably as the strongly complexed ScF_4^- ion.

2. Iron hydroxide scavenging is carried out.

3. The destruction of the ScF_4^- complex is accomplished by means of concentrated perchloric acid. This results in the precipitation of ScF_3 which is then dissolved in ammonium hydrogen fluoride solution.

At the end of the final cycle, ScF_3 is dissolved in boric acid solution and is converted to the hydroxide. Scandium is finally precipitated as K_3ScF_6 in which form it is weighed and counted. The chemical yield is about 50%.

2. Reagents

Sc carrier: 15 mg Sc-ml (added as $ScCl_3$ in dilute HCl), standardized
Fe carrier: 10 mg Fe-ml (added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl)
La carrier: 10 mg La-ml (added as $La(NO_3)_3 \cdot 6H_2O$ in very dilute HNO_3)
HCl: 6M
HNO_3: conc.
$HClO_4$: conc.
NH_4OH: conc.
H_3BO_3: saturated aqueous solution
NH_4HF_2: mixture of 2 volumes of 6M NH_4OH and 1 volume of 27M HF
NH_4NO_3: 2% aqueous solution
KF: saturated aqueous solution
Methyl red indicator soln: 0.5% in 90% ethanol
Aerosol: 0.1% aqueous solution
Zapon solution: 6.0 mg Zapon in 25 drops of Zapon-ethanol solution
Methanol: absolute

3. Equipment

Drying oven
Muffle furnace
Centrifuge
Block for holding centrifuge tubes
Mounting plates
Forceps
Pipets: assorted sizes
100-ml beakers (one per standardization)
Ground-off Hirsch funnels: Coors 000A (one per sample)

Filter chimneys (one per sample)
Porcelain crucibles: Coors 00 (one per standardization)
No. 42 Whatman filter circles: 7-8 in. diameter
No. 42 Whatman filter paper: 9-cm
2-in. 60° funnels (one per standardization)
40-ml conical centrifuge tubes: Pyrex 8320 (two per sample)
40-ml Lusteroid centrifuge tubes (13 per sample)
Steam bath
Stirring rods
Wash bottle

4. Preparation and Standardization of Carrier

Dissolve 15.33 g of Sc_2O_3 in a minimum of conc. HCl, add an additional 5 ml of HCl, and make the solution up to a volume of 1 liter with H_2O.

Pipet exactly 5 ml of the above carrier solution into a 100-ml beaker and dilute to 20 ml with H_2O. Add 5 ml of conc. NH_4OH to precipitate $Sc(OH)_3$. Filter the solution through No. 42 Whatman filter paper (9-cm), using a 2-in. 60° funnel. Rinse the beaker with 5 ml of 0.1M NH_4Cl and filter the washings through the paper containing $Sc(OH)_3$. Transfer the precipitate to a weighed Coors 00 porcelain crucible and ignite at 900° for 1 hour. Cool and weigh.

Two standardizations gave results agreeing within 0.3%.

5. Procedure

1. To an aliquot of the sample in a 40-ml conical, glass centrifuge tube add exactly 1 ml of Sc carrier and 4 drops of La carrier and dilute to 20 ml. Add conc. NH_4OH to precipitate $Sc(OH)_3$. Centrifuge and discard the supernate. Wash the precipitate with 30 ml of 2% NH_4NO_3 and discard the washings.
2. Dissolve the precipitate in 6M $HClO_4$. Add 3 ml of NH_4HF_2 solution, 1 drop of methyl red indicator solution, and conc. NH_4OH until the solution is just acidic to the indicator. Make the volume up to 10-12 ml, centrifuge, transfer the supernate to a 40-ml Lusteroid tube, and discard the precipitate.
3. To the solution add 4 drops of La carier, 5 drops of Fe carrier, and 1.5 ml of conc. NH_4OH. Dilute to 20 ml and heat on a steam bath for 2 min to coagulate the $Fe(OH)_3$ precipitate. Centrifuge, transfer the supernate to a clean 40-ml Lusteroid tube, and discard the precipitate.
4. Add 6 ml of conc. $HClO_4$ to the supernate and heat for 5 min on a steam bath. Allow to cool for 10 min, centrifuge, and discard the supernate. (The soluble fluoscandate complex is converted to insoluble ScF_3.)

5. To the precipitate, add 2 ml of NH_4HF_2 solution, 1 drop of methyl red indicator solution, and conc. NH_4OH until the solution is just acidic to the indicator. Add 4 drops of La carrier, make the volume up to 10-12 ml, centrifuge, transfer the supernate to a clean 40-ml Lusteroid tube, and discard the precipitate.

6. Repeat steps (3), (4), and (5) four additional times and then repeat steps (3) and (4).

7. Dissolve the ScF_3 precipitate in 2 ml of saturated H_3BO_3 solution and 3 ml of conc. HNO_3. Dilute to 20 ml and centrifuge. Transfer the supernate to a clean Lusteroid tube. Add 10 ml of conc. NH_4OH to precipitate $Sc(OH)_3$. and discard the washings.

8. Dissolve the $Sc(OH)_3$ in a minimum of 6M HCl, add 5 ml of saturated KF solution and heat on a steam bath for 20 min. Allow to cool for 30 min. Swirl the mixture and transfer to a 40-ml conical, glass centrifuge tube. Wash the Lusteroid tube with 5 ml of saturated KF solution and add the washings to the glass centrifuge tube. Centrifuge and discard the supernate.

9. To the precipitate add 10 ml of absolute methanol, stir, and transfer onto a weighed No. 42 Whatman filter circle, 7-8 in. diameter, contained in a ground-off Hirsch funnel-filter chimney setup. Rinse the centrifuge tube with two 10-ml portions of methanol and pour the washings through the filter. Dry the precipitate in an oven for 10 min at 110°. Cool for 20 min, weigh (Note 1), and mount on two-sided Scotch tape on an Al plate. Add 4 drops of Zapon solution, allow to dry, and cover with Nylon (Note 2).

Notes

1. The scandium is weighed as K_3ScF_6. This formula was established in the following manner. Standard Sc^{46} tracer was added to a known amount of carrier and the scandium was then precipitated by means of a saturated solution of KF. Then step (9) of the procedure was carried out. The sample was counted on a scintillation counter and the chemical yield determined. The weight of precipitate was then corrected for chemical yield. This permitted the determination of the empirical formula of the compound, on the assumption that it contained potassium, scandium, and fluoride. This was found to correspond to K_3ScF_6. Repeated washing of the precipitate with methanol did not change the specific activity of the material.

2. For a discussion of the counting of Sc isotopes, see LA-1566, pp. 48-49.

Sc-5. SCANDIUM

Element separated: Scandium

Procedure by: Batzel[306]

Target material: Copper

Time for sep'n: 1 1/2 hr

Type of bbt: All 60 in. and 184 in.

Equipment required: Standard

Yield: 60%

Degree of purification: Factor of 100 from other activities present.

Procedure

1. Dissolve copper in minimum amount of HNO_3. Boil to remove excess. Add 5 mg of Sc and other carriers. Adjust to 1N in HCl and treat with H_2S (CuS out).
2. Boil to remove H_2S, add NH_4OH and NH_4Cl till ammoniacal. Centrifuge and wash ppt. with hot NH_4Cl solution.
3. Dissolve ppt. in HCl and make 6N in HCl. Extract Fe three times with equal volume ethyl acetate. Add ≈3 mg of Fe carrier and again extract Fe.
4. Make the pH of the solution 2.0 and extract with equal volume TTA (5 ml of 0.5M in benzene). Shake for 10 minutes. Wash TTA layer with three 4-ml portions of water.
5. Extract into 1N HCl with two 3-ml portions.
6. Ppt. the Sc as hydroxide with NaOH. Wash with H_2O. Repeat the extraction with fresh TTA.
7. The scandium can be weighed as Sc_2O_3 after precipitation as $Sc(OH)_3$ and ignition.

Sc-6. SCANDIUM (Carrier-Free)

Element separated: Scandium

Procedure by: Hall

Target Material: Titanium

Time for sep'n: ≈ 5 hours

Type of bbdt: 7.8-Mev deuterons

Equipment required: 250-ml Phillips beaker micro bell jar, No. 00 Hirsch funnels, Whatman No. 50 filter paper, pHydrion (short range) pH paper

Yield: ≈10%

Degree of purification: $\approx 10^2$

Advantages: carrier-free separations for 4π β-counting

Procedure

1. Place 1 ml conc. H_2SO_4 in 250-ml Phillips beaker and add tracer Sc^{46}

(See Remark 2). Introduce the Ti target (≈ 130 mg) and the Mylar substrate. Heat strongly to decompose the Mylar.

2. Cool, add several drops of 30% H_2O_2, and reheat. Repeat until a clear solution is obtained above the unattacked Ti.

3. Add 10 ml 18N H_2SO_4 containing 5% 16N HNO_3. Heat, keeping the HNO_3 replenished until the Ti is all dissolved.

4. Dilute to 100 ml and neutralize to pH 8.5 (use pHydrion paper) with a 1:15 mixture of 30% H_2O_2 and 8N NH_4OH. Add enough excess H_2O_2 to keep the Ti in solution.

5. Filter twice through the same Whatman No. 50 filter paper, using suction. Wash three times with 3N NH_4Cl at pH 8.5.

6. Remove Sc with several portions of hot 3N HCl.

7. Repeat steps (4), (5), and (6) twice, except in final cycle use conductivity water at pH 8.5 to wash the Sc "precipitate."

8. Evaporate to dryness. Destroy organic matter with aqua regia. Take up with water and transfer to 4π plates.

Remarks

1. General reference: J. D. Gile et al., J. Chem. Phys. 18, 1685 (1950).
2. The tracer is added for the purpose of determining the chemical yield.
3. Use conductivity water to make up solutions, etc.

Sc-7. SCANDIUM (Carrier-Free)

K. Lynn Hall and W. W. Meinke
Department of Chemistry
University of Michigan
Ann Arbor, Michigan

Element: Sc-No. 1. (Carrier-free)

Separated from: d-bombarded Ti

Docontamination Factor: ≈ 10^2

Procedure

1. The Ti target (≈ 130 mg) plus the Mylar substrate were placed in a 250-ml beaker, containing 1 ml conc. H_2SO_4 and Sc^{46} tracer (Note 1) and the Mylar decomposed upon vigorous heating.

2. After cooling, several drops of 30% H_2O_2 were added and the solution reheated. The treatment was repeated until a clear solution above the unattacked Ti was obtained.

3. The Ti target was dissolved in 10 ml 18N H_2SO_4 containing 5% HNO_3, with heating; additional HNO_3 was necessary for complete dissolution.

4. The solution was diluted to 100 ml and adjusted to a pH of 8.5 (pH paper) with a 1:15 mixture of 30% H_2O_2 and 8N NH_4OH. Excess H_2O_2 was added to keep the Ti in solution.

5. The solution was filtered twice through the same Whatman No. 50 filter paper with suction, and the filter paper washed three times with 3N NH_4Cl which had previously been adjusted to pH 8.5.

6. Sc was removed from the paper by washing with several portions of hot 3N HCl.

7. Steps (4), (5), and (6) were repeated twice, and the final "precipitate" washed with conductivity water adjusted to pH 8.5.

8. The final solution was evaporated to dryness, any organic matter destroyed with aqua regia, and the residue dissolved in water and mounted for 4π counting.

Notes

1. Sc^{46} was used to determine the chemical yield ($\approx$ 10%).
2. All solutions were made up with conductivity water.
3. The time required was about 5 hours.

References

Gile, J. D., Garrison, W. M., and Hamilton, J. G., J. Chem. Phys. 18, 1685 (1950).

Haskins, J. R., Duval, J. E., Cheng, L. S., and Kurbatov, J. D., Phys. Rev. 88, 876 (1952).

Y-1. YTTRIUM

Threshold Detector Group
Radiochemistry
LRL, Livermore
1-26-59

Purification: From a two-week-old solution containing 1.1×10^{15} fissions, a sample was obtained which had a gamma activity of about 27 γ cpm between 1700 kev and 2000 kev through ≈1100 mg Cu cm^{-2} absorber on a 2-in.-thick × 1-3/4-in.-diameter NaI crystal. For other purification see footnotes.

Chemical Yield: ≈65%

Separation Time: ≈5 hours

Procedure

1. To a 25-ml solution of mixed activities in 6M HCl in a 40-ml glass centrifuge cone, add 20 mg of yttrium carrier and add ≈2 mg each of Sc, Zr, Te^{+4}, and Ce^{+3}. Add conc. NH_4OH in excess. Centrifuge the $Y(OH)_3$ and discard the supernatant. Wash the precipitate twice with ≈20 ml of water to remove salts and especially any Na^+ ions. Centrifuge and discard the wash solutions.

2. Dissolve the precipitate by adding a few drops of 6M HNO_3. Transfer the solution to a 50-ml Lusteroid tube with ≈5 ml of water. Add an equal volume of Na-free 6M NH_4F solution, making the final solution ≈3M in NH_4F and pH 4-5. Check the pH with narrow-range pH paper. Heat in a hot bath for ≈3 minutes. Cool and centrifuge. Discard the supernatant (Sc). Add ≈10 ml of 3M NH_4F to the precipitate. Heat for 3 minutes. Cool and centrifuge, discarding the supernatant (Sc). Wash the YF_3 with ≈5 ml of water. Centrifuge and discard the supernatant, Sc (see Note 1).

3. Dissolve the YF_3 by adding ≈3 ml of saturated H_3BO_3, ≈10 ml of water and an equal volume of 12M HNO_3, making the final solution ≈6M in HNO_3. Add ≈3 ml of 5M HIO_3. Transfer the solution to a 40 ml glass centrifuge cone. Add ≈1 ml of saturated $NaBrO_3$ solution. Stir well and heat in hot bath for ≈25 minutes. Cool to room temperature and centrifuge. Discard the $Ce(IO_3)_4$ precipitate. To the supernatant, add ≈2 mg of Zr carrier while stirring the solution. Centrifuge well and discard the $Zr(IO_3)_4$ precipitate. Repeat the Zr iodate scavenge. After centrifugation, pour the supernatant into a 50-ml Lusteroid tube (see Note 2).

4. Add 12-15 ml of 6M NH_4F (solution is now ≈3M in H^+). Heat on hot bath for 5 minutes. Cool to room temperature in a cold water bath for 5 min. Centrifuge and discard the supernatant (Np^{+6}). Wash the YF_3 with ≈

5 ml of water and discard the wash solution. Dissolve the YF_3 with 2 ml of saturated H_3BO_3. Mix thoroughly and add 3 ml of conc. HCl. Heat on hot bath for ≈ 3 min. Dilute to ≈ 30 ml volume with water and precipitate $Y(OH)_3$ with an excess of conc. NH_4OH. Cool, centrifuge, and discard the supernatant. Wash the $Y(OH)_3$ with ≈ 20 ml of water. Centrifuge and discard wash.

5. Dissolve the precipitate with ≈ 20 ml of ≈ pH 1.0 buffer solution which is 0.5M in Na_2SO_4 and 0.5M $NaHSO_4$ and transfer it to a 40-ml glass cone. Add 5 ml of toluene. Add ≈ 10 ml of $CrCl_2$ solution (Oxsorbent). Add ≈ 10 mg Ba (1 ml of solution as the chloride) dropwise while stirring slowly. Heat in hot bath (≈95°C) for 5 minutes. Cool in a cold water bath for 5 minutes. Add ≈ 10 mg Ba dropwise while stirring slowly. Centrifuge at > 3500 gravities and pour supernatant into a cone containing ≈ 10 mg of Ba. Heat for ≈ 2 minutes in hot bath. Cool in cold bath for ≈ 3 minutes. Add ≈ 10 mg Ba dropwise while stirring slowly, then centrifuge (see Note 3). Pour supernatant into a 50-ml Lusteroid tube containing ≈ 2 ml of conc. HF. Stir, centrifuge, and discard supernatant. Wash the YF_3 with ≈ 20 ml of water and discard the wash solution.

6. Dissolve the YF_3 by adding 1 ml of 5% H_3BO_3. Mix thoroughly. Heat in hot bath for ≈ 3 minutes. Add ≈ 2 ml conc. HNO_3. Transfer the solution to a 40-ml glass cone using 2 ml of 6M $HClO_4$. Heat carefully to strong fumes of $HClO_4$. Cool and dilute to ≈ 20 ml with water. Add an excess of conc. NH_4OH. Centrifuge the $Y(OH)_3$ and discard the supernatant. Wash the precipitate with 30 ml of water.

7. Dissolve the $Y(OH)_3$ in ≈ 15 ml of buffer solution– 0.1M formic acid and 1M Na formate (pH ≈ 4.6). Transfer the solution to a 60-ml cylindrical separatory funnel and extract the Y into ≈ 30 ml of 0.40M TTA in benzene for 3 minutes stirring with a motor-driven glass paddle. Wash the organic layer 3 times with ≈ 15 ml of buffer solution– 0.4M formic acid and 1M Na formate (pH ≈ 4.0)– for 3 minutes (see Note 4). Back-extract the Y into ≈ 20 ml of 0.05M HCl for 3 minutes. Let layers settle for several minutes and then drain the aqueous layer into a 40-ml glass cone. Centrifuge and discard any precipitate, broken glass, etc.

8. Add ≈ 5 ml of saturated oxalic acid and stir vigorously. Let stand for 5 minutes then centrifuge and discard the supernatant. Wash the yttrium oxalate with a few ml of 0.2M oxalic acid and filter through 7-cm No. 42 Whatman paper. Ignite at ≈ 900°C for ≈ 20 minutes in a Coors No. 00 porcelain crucible. Weigh, mount on aluminum hat, and count 1.85-Mev gamma ray on 2-in. NaI scintillation counter (slit width 1.7-2.0 Mev) with 1186 mg Cu cm^{-2} as absorber to stop betas.

Notes

1. Steps (2), (7), and (8) have an over-all separation factor of $\approx 4 \times 10^5$ of Sc from Y.

2. Steps (3) and (7) have an over-all separation factor of $> 10^6$ of Ce from Y.

3. Step (5) has a separation factor of $\approx 10^4$ of Eu tracer from Y. Nd, Pr and other cerium earths, if carrier-free, will separate from Y in step (5) also.

4. Three washes in step (7) will separate La away from Y by a factor of ≈ 100. More washes will give a greater separation factor but there is about a 5% loss of Y per wash.

Y-2. YTTRIUM (Y^{88})

Threshold Detector Group
Radiochemistry
LRL Livermore
August 1958

Procedure by: W. H. Hutchin

Purification: See Note 1

Chemical yield: ≈ 80%

Procedure

1. To a solution of the activity in 20 ml of 6M HNO_3 in a 40-ml glass cone add ≈ 1 mg Ce^{+3}, ≈ 2 mg Zr and 10 mg Y, all as the nitrate. Add 1 ml of a saturated solution of $NaBrO_3$. Stir and heat in a hot water bath for ≈ 5 min. Add 3 ml of 5M HIO_3, and stir. Centrifuge and discard ppt., pouring supernatant into a 50-ml Lusteroid cone.

2. To the supernatant add ≈ 20 ml 6M NH_4F. Stir, centrifuge, and discard supernatant. Wash one with ≈ 20 ml water.

3. Dissolve in 5 ml of a saturated solution of H_3BO_3 and 5 ml HNO_3. Dilute to ≈ 20 ml and add NH_4OH until basic. Centrifuge and discard supernatant. Wash once with 20 ml water.

4. Dissolve in 2 or 3 ml conc. HCl and pass through anion column (Dowex-1

× 8, 50-100 mesh) that has been equilibrated with conc. HCl, catching eluate in a 40-ml glass cone. Wash col. with ≈ 4 ml conc. HCl.

5. Dilute eluate with water and make basic with NaOH. Centrifuge and discard supernatant. Wash ppt. once with ≈ 20 ml water.

6. Dissolve ppt. in 25 ml of 0.5M H_2SO_4-0.5M Na_2SO_4 solution. Add ≈ 5 ml toluene and ≈ 8 ml of a fresh solution of $CrCl_2$ by introducing it under the organic layer. While stirring add ≈ 10 mg Ba (as Cl^-). Stir carefully, avoid mixing any air with the aqueous phase or forming a vortex in the solution. Heat in a hot water bath (100°C) for 10 minutes. After heating period, transfer to a room temperature bath and cool to room temperature. After cooling add another 10 mg Ba while carefully stirring. Centrifuge strongly and pour supernatant into a cone containing ≈ 10 mg Ba. Heat in a hot water bath for 10 minutes. Cool to room temperature in a room-temperature water bath and add ≈ 10 mg Ba while carefully stirring. Centrifuge strongly and pour supernatant into a 50-ml Lusteroid tube. Add ≈ 2 ml conc. HF. Stir, cool, and centrifuge, discarding supernatant. Wash once with ≈ 20 ml water (see Notes 2 and 3).

7. Repeat step (3).

8. Dissolve $Y(OH)_3$ in 6M HNO_3 and transfer to a 40-ml glass cone. Make volume up to 20 ml with 6M HNO_3. Add ≈ 2 mg Zr and 1 ml of a saturated soln. of $NaBrO_3$ and stir. Heat for 5 min in a hot water bath. Add 3 ml of 5M HIO_3 and stir. Centrifuge and pour supernatant into a new glass cone containing ≈ 2 mg Zr. Stir, centrifuge, and discard ppt., pouring supernatant into a 50-ml Lusteroid cone (see Note 4).

9. Repeat steps (2) and (3).

10. Dissolve ppt. in HCl, dilute to ≈ 20 ml volume and make basic with NH_4OH. Filter through a No. 42 filter paper. Ignite at ≈ 900°C for ≈ one hour. Count 1.85-Mev gamma ray on 2-in. NaI scintillation counter using 1186 mg Cm^{-2} Cu as absorber to stop betas. (Lower discriminator is set at 1.7 Mev and upper at 2.0 Mev.)

Notes

1. This procedure does not separate from Sc Quantitatively. If Sc^{46} is present as one of the activities, it will interfere in the counting of the sample.

2. When opening a new bottle of $CrCl_2$, it is best to put a benzene layer over the $CrCl_2$ as soon as it is opened and to add to the benzene layer as $CrCl_2$ is used.

3. This step gives a separation factor from Eu of ≈ 2×10^5.

4. This step gives a separation from Ce of ≈ 4×10^4.

Y-3. YTTRIUM (Carrier-Free)

Procedure by: Anders[307]

Target material: Zr

Type of bbdt: ≈ 7.8-Mev deuterons

Yield: ≈ 85%

Degree of purification: $\approx 10^5$

Time separation: 3 hours

Equipment required: 4 pyrex beakers (50-ml); centrifuge ; centrifuge tubes, 40-ml, 15-ml (Pyrex); Lusteroid tube (10-ml); micro pipette 50; platinum wire; small anion-exchange column; medicine droppers; calcium carrier (10 mg-ml); zirconium carrier (10 mg-ml); Dowex-2 (200-400 mesh); conductivity water; conc. H_2SO_4, NH_4OH, HCl, 30% H_2O_2; HCl-gas tank.

Procedure

1. Cut the tracer yttrium, deposited on Zapon film, from aluminum sample plate and place in small beaker; add bombarded zirconium foil plus Mylar substrate. Add 1.5 ml conc. H_2SO_4 and a few drops 30% H_2O_2. Heat to fumes until dissolved (cool and add more H_2O_2 at intervals). (Note 1)

2. Transfer clear solution to a 40-ml centrifuge tube, add 30 ml H_2O and precipitate zirconium hydroxide with conc. NH_4OH. Stir with platinum wire; centrifuge and wash twice.

3. Dissolve precipitate with a minimum amount of conc. HCl, add 3 mg calcium carrier and one drop $NbCl_5$ carrier (10 mg-cm^3). Transfer to 10-ml Lusteroid tube.

4. Precipitate CaF_2 (and YF_3) with 3 ml conc. HF. Centrifuge (water in centrifuge cups!) and wash twice.

5. Transfer precipitate to a 15-ml centrifuge cone, centrifuge, decant, add 0.5 m. conc. H_2SO_4.

6. Heat to fumes to drive off HF. Cool. Add 3 mg Zr carrier and dissolve residue in 10 ml warm water.

7. Precipitate zirconium hydroxide with conc. NH_4OH. Wash three times with conductivity water. (Note 2)

8. Dissolve precipitate with a few drops conc. HCl and saturate with HCl gas.

9. Transfer solution to a small anion-exchange column charged with I ml Dowex-2 resin saturated with conc. HCl.

10. Adsorb zirconium onto the resin slowly. After liquid level reaches resin bed add 5 drops of conc. HCl and permit to soak in. (Note 3)

11. Elute carrier-free yttrium reaction product with 5 ml conc. HCl at a rate of 1 drop in 7 seconds. (Note 4)

12. Collect eluate when activity starts coming through. Evaporate to near dryness and plate for counting.

Note

1. A homogeneous solution is obtained under rather severe conditions. Complete isotopic interchange between the Y^{88} tracer and the reaction product is thus accomplished.

2. This washing removes the calcium carrier and must be done thoroughly, if carrier-free yttrium is to be obtained.

3. Try to wash the walls of the column free of activity with these 5 drops.

4. The yttrium is not absorbed by the resin in hydrochloric acid but is easily eluted, while zirconium and niobium are strongly absorbed from a conc. HCl medium.

Y-4. YTTRIUM

C. W. Stanley[233]

Introduction

The separation of radioyttrium from rare-earth fission products is accomplished by extraction of the nitrate from concentrated nitric acid solution with tributyl phosphate (TBP) dilute with Gulf Solvent BT. The yttrium is back-extracted into water. Two extractions give excellent separation from europium and samarium. The method, therefore, is superior to other procedures in current use.

Reagents

Y carrier: 10 mg Y-ml (see Preparation and Standardization of Carrier)
Zr carrier: 10 mg Zr-ml (added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1M HNO_3)
HCl: 6M
HNO_3: conc.
HF: conc.
H_3BO_3: saturated solution
NH_4OH: conc.
$(NH_4)_2C_2O_4$: saturated solution

Tributyl phosphate
(TBP) reagent: 60% by volume TBP, 40% Gulf BT; freshly equilibrated with conc. HNO_3
CH_3OH: anhydrous

Equipment

Centrifuge
Block for holding centrifuge tubes
Forceps
Mounting plates
Porcelain crucibles: Coors 000 (one per sample)
Porcelain crucibles: Coors 00 (one per standardization)
Ground-off Hirsch funnels: Coors 000A (one per sample)
Filter chimneys: (one per sample)
Filter flasks
No. 42 Whatman filter circles: 7-8 in. diameter
Pipets: assorted sizes
50-ml Lusteroid tubes: (one per sample)
40-ml conical centrifuge tubes: (three per sample, one per standardization)
125-ml separatory funnels: (two per sample)
2-in., 60° funnels: (one per standardization)
Steam bath
Ice bath
Stirring rods
Muffle furnace

Preparation and Standardization of Carrier

Dissolve 43 g of $Y(NO_3)_3 \cdot 6H_2O$ in H_2O, add 5 ml of 6M HNO_3, and dilute to 1 liter. To 5.00 ml of the carrier solution in a 40-ml centrifuge tube add 20 ml of H_2O, heat to boiling, and add 20 ml of saturated $(NH_4)_2C_2O_4$ solution with stirring. Heat for 10 min on a steam bath and then cool in an ice bath for 4 min. Centrifuge the $Y_2(C_2O_4)_3$ and decant the supernate. Take up the precipitate in 10 ml of H_2O and filter through a 2-in., 60° funnel. Wash the precipitate with H_2O, transfer to a porcelain crucible, burn off the paper, and ignite at 800° for 1 hour. Cool and weigh as Y_2O_3.

Four standardizations are carried out with results agreeing within 1%.

Procedure

1. To the sample in a 50-ml Lusteroid tube, add 2.0 ml of standard Y carrier and make the solution 2M in HNO_3. Add 2 ml of Zr holdback carrier and

make the solution 4M in HF. Centrifuge the YF_3 precipitate and discard the supernate. Wash the precipitate with 10 ml of 5M HF.

2. Dissolve the YF_3 in 2 ml of saturated H_3BO_3 solution and 2 ml of conc. HNO_3, and dilute 10 ml. Add 2 ml of Zr carrier and enough conc. HF to make the solution 4M with respect to this acid. Centrifuge the YF_3, decant the supernate, and wash the precipitate with 10 ml of 5M HF.

3. Dissolve the precipitate in 2 ml of saturated H_3BO_3 solution and 2 ml of conc. HNO_3. Dilute the solution to 10 ml and precipitate $Y(OH)_3$ by the addition of conc. NH_4OH. Centrifuge and discard the supernate.

4. Dissolve the $Y(OH)_3$ in 50 ml of conc. HNO_3 and transfer the solution to a 125-ml separatory funnel. Add 10 ml of TBP reagent and shake the solution for 5 min. Discard the aqueous layer and wash the TBP phase twice by shaking for 2-min intervals with 50 ml of conc. HNO_3. Remove the Y from the TBP by shaking for 1 min each with three 10-ml portions of H_2O. Combine the water extracts in a 40-ml centrifuge tube and precipitate $Y(OH)_3$ with conc. NH_4OH. Centrifuge and discard the supernate.

5. Repeat step (4).

6. Dissolve the $Y(OH)_3$ precipitate in 2 ml of 6M HCl and dilute the solution to 10 ml with H_2O. Transfer the solution to a clean 40-ml centrifuge tube and reprecipitate $Y(OH)_3$ with conc. NH_4OH. Centrifuge and discard the supernate. Dissolve the precipitate in 2 ml of 6M HCl and dilute to 15 ml with H_2O. Heat the solution on a steam bath and add 20 ml of saturated $(NH_4)_2C_2O_4$ solution. Continue heating for 10 min and then cool in an ice bath for 4 min. Centrifuge the $Y_2(C_2O_4)_3$ and discard the supernate. Take up the precipitate in 10 ml of H_2O and pour onto a 7/8-in.-diam No. 42 Whatman filter circle in a standard chimney arrangement with the suction off. Allow the precipitate to settle for a minute or two and then apply suction. Wash the precipitate with anhydrous CH_3OH and transfer to a porcelain crucible. Ignite at 800° for 1/2 hour. Cool, weigh, and mount on an Al plate in a centered depression 5/16 in. in diameter and 1/32 in. deep. Beta-count (Note 1).

Notes

1. The isotopes counted are 65-h Y^{90} and 61-d Y^{91}.

Ce-1. CERIUM

Procedure by: H. G. Hicks[271]

Decontamination: 5×10^{13} Atoms of Ce^{143} isolated from a 1-day-old solution containing 10^{15} fissions showed no trace of a foreign radioactivity when followed through three half-lives.

Yield: About 60%.

Separation time: About eight hours for four samples.

Procedure

1. To an acid solution of the activities, add 10 mg cerium carrier, about 3 mg Zr^{IV}, and about 1 mg lanthanum carrier. Make the solution ammoniacal. Centrifuge the precipitate and wash once with water.

2. Dissolve in 8 ml conc. HNO_3. Add one drop 30% H_2O_2 (to reduce Ce^{IV} to Ce^{III}) and 20 ml 0.35M HIO_3. Let stand two to three minutes, cool in ice. Centrifuge and discard the precipitate.

3. To supernatant add 2 ml 1M $NaBrO_3$, digest at room temperature five to ten minutes and cool in an ice bath. Centrifuge and discard supernatant. Wash with 20 ml of a solution of two parts 0.35M HIO_3 and one part conc. HNO_3; then once with 20 ml water.

4. Dissolve the precipitate in 2 ml cold conc. HCl and pass through Dowex A-1 column. Wash column with an additional 2 ml conc. HCl.

5. Add 3 mg Zr^{IV} to eluate (no La) and repeat steps (1) through (4).

6. Dilute eluate and adjust to pH 2-3. Precipitate cerium oxalate with saturated $H_2C_2O_4$, wash twice with H_2O, once with acetone, dry, ignite at red heat for 20 minutes, weigh as CeO_2.

Ce-2. CERIUM

LRL Livermore
G. M. Iddings

Procedure

1. To the active solution add 10 mg of Ce^{+3} and ≈ 1 mg of Y and ≈ 1 mg of Zr. Add conc. NH_4OH to precipitate $Ce(OH)_3$. Centrifuge and discard the supernatant. Wash the $Ce(OH)_3$ once with water.

2. Dissolve the hydroxides in ≈ 25 ml of 6M HNO_3. Add 1 drop of 30% H_2O_2 (to keep Ce in the +3 state). Add 3 ml of 5M HIO_3 to precipitate

$Zr(IO_3)_4$. Centrifuge and discard the precipitate. While vigorously stirring the supernatant, add 1 mg of Zr carrier. Centrifuge and discard the precipitate.

3. To the supernatant add 1 ml of saturated $NaBrO_3$ solution and heat in hot bath for ≈ 3 minutes. Cool to room temperature and centrifuge the $Ce(IO_3)_4$. Discard the supernatant.

4. Dissolve the $Ce(IO_3)_4$ in 25 ml of 6M HNO_3. Add 1 mg of Y holdback carrier, 1 ml saturated $NaBrO_3$ solution and 3 ml of 5M HIO_3. Heat in hot bath for ≈ 3 minutes. Cool to room temperature and centrifuge. Discard the supernatant.

5. Repeat step (4).

6. Dissolve the $Ce(IO_3)_4$ in ≈ 10 ml of conc. HCl and pour it through a Dowex-1 anion-exchange column (7 cm long and 6 mm i.d., 50-100 mesh). Wash the column with ≈ 3 ml conc. HCl. Discard the resin column.

7. Partially neutralize the HCl solution of Ce with conc. NH_4OH. Cool and add 1 ml 6% H_2SO_3 solution. Make basic with NH_4OH. Centrifuge and discard the supernatant. Wash the precipitate once with water.

8. Dissolve the $Ce(OH)_3$ with ≈ 15 ml of ≈ pH 4.5 buffer solution (0.1M formic acid - 1M Na formate). Transfer the solution to a 60-ml cylindrical separatory funnel containing 30 ml of 0.4M TTA in benzene. Extract by stirring for ≈ 3 minutes. Discard the aqueous layer. Wash the organic layer twice with ≈ 15 ml of pH 4.5 buffer solution for ≈ 3 minutes. Discard aqueous solutions.

9. Back-extract the Ce^{+3} with ≈ 15 ml of pH ≈ 4.0 buffer solution (0.4M formic acid - 1M Na formate) for 3 minutes. Repeat the back-extraction and combine the aqueous layers in a 40-ml centrifuge cone.

10. Add 3 ml of conc. HCl. The pH is now ≈ 0.4. Add 5 ml of saturated oxalic acid. Stir vigorously to precipitate cerium oxalate. Heat on hot bath for ≈ 3 minutes, then cool to room temperature. Centrifuge and discard the supernatant. Wash the precipitate with a few ml of 0.2M oxalic acid. Filter through 7-cm No. 42 Whatman paper. Ignite. Weigh, mount, and count.

Ce-3. CERIUM

The procedure for the determination of cerium in fission-product material was developed by D. P. Ames and is based on a method described by N. E. Ballou, CN-2815 (June 30, 1945).[233]

Introduction

In the analysis for radiocerium, exchange between carrier and fission-product cerium is effected by a Ce (III)-Ce (IV) oxidation-reduction cycle. Cerium (III) and other rare earths are separated from other fission product by precipitation as fluorides with hydrofluoric acid. Cerium is then oxidized to the +4 state and separated from other rare earths by precipitation as the iodate, $Ce(IO_3)_4$. Cerium is converted to the +3 state and zirconium, plutonium (IV), and thorium activities are removed by zirconium iodate scavenging. Precipitation of $Ce(OH)_3$ separates cerium from alkaline earth activities. Cerium is finally precipitated as the oxalate and ignited to the oxide CeO_2, in which form it is weighed and counted. The chemical yield approximates 75%. Quadruplicate analyses can be performed in about 7 hours.

Reagents

Ce carrier: 10 mg Ce/ml (added as $Ce(NO_3)_3 \cdot 6H_2O$ in H_2O), standardized
La carrier: 10 mg La/ml (added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O)
Zr carrier: 10 mg Zr/ml (added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1M HNO_3)
HCl: 6M
HCl: conc.
HNO_3: conc.
HF: conc.
H_3BO_3: saturated aqueous solution
HIO_3: 0.35M
NH_4OH: conc.
$NaBrO_3$: saturated aqueous solution
$(NH_4)_2C_2O_4$: saturated aqueous solution
H_2O_2: 30%

Equipment

Muffle furnace
Centrifuge
Block for holding centrifuge tubes
Forceps
Mounting plates
Pipets: assorted sizes
Hirsch funnels: Coors 0000 (one per sample)

Filter flasks (one each per standardization and sample)
No. 42 Whatman filter paper: 11-cm
No. 42 Whatman filter cirlces: 1/2-in. diameter
2-in., 60° filter funnels (one per standardization)
100-ml beakers (one per standardization)
Porcelain crucibles: Coors 00 (one per standardization)
Porcelain crucibles: Coors 000 or 0000 (one per sample)
50-ml Lusteroid tubes (two per sample)
40-ml conical centrifuge tubes: Pyrex 8320 (three per sample)
Ice bath
Steam bath
Stirring rods.

Preparation and Standardization of Carrier

Dissolve 31.0 g of $Ce(NO_3)_3 \cdot 6H_2O$ in H_2O and dilute to 1 liter. To obtain cerium free from other rare earths it may be necessary to purify by two $Ce(IO_3)_4$ precipitations (see steps 4 and 5 of Procedure).

Pipet 5 ml of the cerium carrier solution into a 100-ml beaker and dilute to about 20 ml with H_2O. Warm on a steam bath and add about 50 ml of saturated $(NH_4)_2 C_2O_4$ solution. Continue heating on the steam bath until the precipitate has coagulated. Cool in an ice bath for 15 min and filter through a filter funnel, using a No. 42 Whatman filter paper (11-cm). Ignite in a porcelain crucible at 800° for 30 min, cool, and weigh as CeO_2.

Four standardizations, with results agreeing within 0.5%, are carried out.

Procedure

1. To a 40-ml centrifuge tube, add 2 ml of Ce carrier and 5 ml of conc. HNO_3, and pipet in the sample for analysis. Add 1 ml of saturated $NaBrO_3$ solution and heat on a steam bath for 10 min (Note 1).

2. Remove the tube from the steam bath and add 30% H_2O_2 dropwise with vigorous stirring (Note 2) until the solution has a light reddish-brown color. Heat on the steam bath until the Br_2 color disappears, adding a drop or two of H_2O_2 if necessary.

3. Add 2 ml of La carrier and 2.5 ml of Zr holdback carrier and transfer the solution to a 50-ml Lusteroid tube. Add 3 ml of conc. HF to precipitate CeF_3 and LaF_3. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of 5M HF, centrifuge, and discard the supernate.

4. To the precipitate add 1 to 2 ml of saturated H_3BO_3 solution and suspend the precipitate by stirring. Then add 4 ml of conc. HNO_3 and stir vigorously

until a clear solution is formed. Transfer to 40-ml glass centrifuge tube and add 4 ml of conc. HNO_3 and 1 ml of saturated $NaBrO_3$ solution. Heat on a steam bath for about 10 min.

5. Add 20 ml of 0.35M HIO_3 and stir vigorously. Cool for 5 to 10 min in an ice bath. Centrifuge and discard the supernate, retaining the $Ce(IO_3)_4$ precipitate (Note 3).

6. Suspend the precipitate in a solution made up by the addition of 8 ml of H_2O, 3 ml of conc. HNO_3, and 3 ml of 0.35M HIO_3. Centrifuge and discard the supernate. Repeat this washing step twice, suspending the precipitate each time.

7. Add 1 ml of La carrier to the precipitate. Add 4 ml of conc. HNO_3 and a drop or two of conc. HCl and slurry the $Ce(IO_3)_4$ by stirring vigorously. Add 0.2 ml of 30% H_2O_2 and stir until dissolution of $Ce(IO_3)_4$ is complete. Add 1 ml of saturated $NaBrO_3$ and 4 ml of conc. HNO_3. Reoxidize Ce (III) to Ce (IV) as in step (4).

8. Repeat step (5).

9. Repeat step (6), washing the precipitate three times. (All other rare earths have now been removed from the cerium.)

10. Add 1 ml of Zr carrier to the precipitate from step (9) and dissolve the precipitate as in step (7), using 8 ml of conc. HNO_3, 0.2 ml of conc. HCl, and 0.2 to 0.3 ml of 30% H_2O_2. Add 20 ml of 0.35M HIO_3 to clear solution to precipitate $Zr(IO_3)_4$ (Note 4). Centrifuge and transfer the supernate to a 50-ml Lusteroid tube, discarding the $Zr(IO_3)_4$ precipitate.

11. Add 5 ml of conc. HF to precipitate CeF_3. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of 5M HF. Centrifuge and discard the supernate.

12. Dissolve the CeF_3 by making a slurry in 1 ml of saturated H_3BO_3 and adding 2 ml of conc. HNO_3. Transfer to a 40-ml centrifuge tube. Heat on a steam bath for 5 min to insure complete dissolution.

13. Dilute to 10 ml with H_2O and make strongly basic with conc. NH_4OH to precipitate $Ce(OH)_3$. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of H_2O. Centrifuge and discard the supernate.

14. Dissolve the $Ce(OH)_3$ in 1 to 2 ml of 6M HCl. Heat on the steam bath to insure complete dissolution.

15. Add 25 ml of saturated $(NH_4)_2C_2O_4$ to precipitate $Ce_2(C_2O_4)_3$. Allow the precipitate to coagulate before removing the tube from the steam bath (3 to 5 min).

16. Cool the precipitate for 15 min in an ice bath. Filter on a No. 42 Whatman filter circle, 1/2 in. diameter, using a Hirsch funnel.

17. Transfer the precipitate to a porcelain crucible and ignite at 800° for 30 min. Cool for 30 min and weigh as CeO_2 (Note 5).

18. Mount on an Al plate in a centered depression 5/16 in. in diameter and 1/32 in deep, and count (Note 6).

Notes

1. In strongly acid (HNO_3) medium, BrO_3^- ion oxdidizes Ce (III) to Ce (IV).

2. Ce (IV) is reduced by H_2O_2 in acid medium. The oxidation-reduction cycle performed in steps (1) and (2) promotes exchange between radiocerium and carrier.

3. If the concentration of HNO_3 is low, $La(IO_3)_3$ will also precipitate at this stage.

4. The $Zr(IO_3)_4$ scavenging step removes any Th and Pu isotopes which may be present, as well as active Zr.

5. CeO_2 should be white. If it is not white at this stage, decontamination from other rare earths is not complete.

6. If it is desired to obtain the mass 144 chain, count the samples immediately through 217 mg Al/cm^2 to cut out the 32.5d Ce^{141} and the 290d Ce^{144} betas. This gives only the activity from the 17.5m Pr^{144}. To eliminate 33h Ce^{143}, one should allow 20 days from the end of bombardment before beginning the analysis. If it is desired to determine Ce^{141}, it is best to count with no added absorber and use a least-squares separation of the Ce^{141} and Ce^{144} activities.

Ce-4. CERIUM

Glendenin, Flynn, Buchanan, and Steinberg[174]

Procedure

1. To the aliquot (1-5 ml) taken for analysis add 1 ml (10 mg) of standardized Ce carrier, 2 ml of 2M $NaBrO_3$, and sufficient conc. HNO_3 to make the solution 8-10M in HNO_3.

2. Transfer to a separatory funnel containing 50 ml of methyl isobutyl ketone (which has just been equilibrated with 50 ml of 9M nitric acid containing 2 ml of 2M $NaBrO_3$) and shake for 15-30 seconds. Withdraw the aqueous phase and wash the methyl isobutyl ketone phase twice with 1 ml of 9M HNO^3 containing a few drops of 2M $NaBrO_3$. (Caution: Combine the aqueous phase and washings, and neutralize with NH_4OH before discarding.)

3. Back-extract the cerium by shaking the methyl isobutyl ketone phase with 5 ml H_2O containing 2 drops of 30% H_2O_2. (Caution: Wash the methyl isobutyl ketone three times with 50 ml of H_2O before discarding).

4. Neutralize the aqueous phase by adding concentrated NH_4OH (3-5 ml) until a precipitate just appears, and acidify with 1.5 ml of 6M HNO_3. Dilute the solution to 15 ml with H_2O, heat just to boiling, and add 15 ml saturated $H_2C_2O_4$. Cool for 2-3 minutes in running water or ice bath, centrifuge, and wash the precipitate with water.

5. Dissolve the precipitate in 1 ml 6M HNO_3 (warming if necessary) and dilute to 15 ml with H_2O. Repeat the oxalate precipitation, centrifuge, and filter with suction on a weighed filter-paper disc in a small funnel, transferring and washing with three 5-ml portions of H_2O. Wash three times with 5 ml of ethyl alcohol, three times with 5 ml of ether, and place in a vacuum desiccator. Evacuate for 2 min, release and evacuate again for 5 min. Weigh the cerium oxalate, mount, and count.

The yield of cerium through the above procedure is usually about 80%, and the time required is approximately 1 hour.

Eu-1. EUROPIUM

The procedure described below for the analysis of radioeuropium in fission-product material is essentially that developed by R. N. Keller at the Argonne National Laboratory.[233]

Introduction

The separation of europium from the other rare earths present in fission-product solutions is based upon its reduction from the +3 to the +2 state by zinc dust, followed by precipitation of the unreduced rare earths as hydroxides. Samarium, the other rare earth in fission products which is capable of existence in the +2 state, is not reduced by zinc dust. Barium and strontium activities are removed as sulfates prior to the reduction process. Separation of the rare earths from other activities is effected by fluoride precipitations in the presence of zirconium holdback carrier; this separation is also carried out prior to the reduction by zinc. After reduction of europium and precipitation of the +3 rare earths as hydroxides, the europium is oxidized to the tripositive state and precipitated as the oxalate, in which form it is

weighed and counted. The chemical yield is 55 to 65%. A set of eight samples can be analyzed in about 8 hours.

Reagents

Eu Carrier: 10 mg Eu/ml (added as $EuCl_3$ in dilute HCl solution), standardized
Ba carrier: 10 mg Ba/ml (added as $Ba(NO_3)_2$ in H_2O)
Sr carrier: 10 mg Sr/ml (added as $Sr(NO_3)_2 \cdot 4H_2O$ in H_2O)
Zr carrier: 10 mg Zr/ml (added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1M HNO_3)
Ce carrier: 10 mg Ce/ml (added as $Ce(NO_3)_3 \cdot 6H_2O$ in H_2O)
HCl: 6M
HNO_3: conc.
H_2SO_4: 6M
HF: conc.
H_3BO_3: saturated aqueous solution
$H_2C_2O_4$: saturated aqueous solution
NH_4OH: conc.
NH_4OH: conc. (Free From O_2 and CO_2)
NaOCl: 6% solution
Zn dust
Aerosol: 1% in H_2O
Methanol: anhydrous
N_2: tank

Equipment

Bunsen burner
Drying oven
Centrifuge
Block for holding centrifuge tubes
Forceps
Mounting plates
Pipets: assorted sizes
Ground-off Hirsch funnels: Coors 000A (one per sample)
Filter chimneys (one per sample)
Filter flasks
60-ml sintered glass crucibles: fine porosity (one per standardization)
No. 42 Whatman filter circles: 7/8-in. diameter, wieghed
40-ml conical centrifuge tubes: Pyrex 8320 (four per sample)
40-ml narrow neck, round bottom centrifuge tubes: Pyrex 8420 (four per sample)

100-ml beaker (one per standardization)
Ice bath
Wash bottle
Stirring rods.

Preparation and Standardization of Carrier

Dissolve 23.1 g of Eu_2O_3 in 50 ml conc. HCl and make the solution up to a volume of 1 liter with H_2O. If the initial reaction of acid and oxide is too violent use an equivalent amount of dilute acid in place of the concentrated acid.

Pipet 5 ml of the above carrier solution into a 100-ml beaker and add 10 ml of H_2O and 15 ml of saturated $H_2C_2O_4$ solution. Heat the solution on a steam bath for 15 to 20 min and then cool to room temperature. Filter on a weighed 60-ml sintered glass crucible (fine porosity). Wash the europium oxalate precipitate several times with small quantities of H_2O and once with anhydrous CH_3OH. Dry at 100° for 1 hour and then permit the crucible to cool for 20 to 30 min. Weigh.

Two standardizations, with results agreeing to within 0.5%, are performed.

Procedure

1. Mix 1 ml of Ba and Sr carriers and exactly 2 ml of Eu carrier in a 40-ml short-taper conical centrifuge tube. Add an aliquot of the active sample.
2. Heat the solution on a steam bath for 5 min and add 5 drops of 6M H_2SO_4 and a few drops of aerosol solution. Centrifuge the $BaSO_4$ precipitates and decant the supernate to another 40-ml centrifuge tube. Discard the precipitate.
3. Add 1 ml each of Ba and Sr carriers to the supernate and heat for 5 min on a steam bath. After precipitation is complete ($SrSO_4$ forms somewhat slowly), centrifuge thoroughly. Transfer the supernate to another 40-ml tube and discard the precipitate. (It is frequently necessary to recentrifuge this supernate and decant from the small amount of precipitate which has floated over.)
4. To the supernate add 3 ml of conc. HNO_3, 4 ml of Zr carrier, and 3 ml of conc. HF to precipitate EuF_3 and other rare-earth fluorides. Centrifuge and wash the EuF_3 with 10 ml of 0.1M HF, discarding both supernate and washings. (If the analysis is being run on samples containing U or Pu, place the supernate and washings in the appropriate waste bottle.)
5. Dissolve the EuF_3 precipitate in 1 ml of saturated H_3BO_3 and 1 ml of conc. HNO_3 and dilute to 20 to 30 ml. Precipitate $Eu(OH)_3$ with 2 ml of conc. NH_4OH. Centrifuge and discard the supernate.

6. Dissolve the precipitate in 3 ml of conc. HNO_3 and dilute to 20 ml with H_2O. Add 4 ml of Zr carrier and reprecipitate and wash EuF_3 as in step (4). Dissolve the precipitate in 1 ml of H_3BO_3 and 1 ml of conc. HCl and dilute to 20 to 30 ml with H_2O.

7. Precipitate $Eu(OH)_3$ by the addition of 2 ml of conc. NH_4OH. Centrifuge and discard the supernate.

8. Dissolve the precipitate in 2 ml of 6M HCl and transfer the solution to a 40-ml narrow-neck centrifuge tube. Precipitate $Eu(OH)_3$ as in step (7). centrifuge and discard the supernate.

9. Dissolve the precipitate in 2 ml of 6M HCl and dilute to 20 to 30 ml with H_2O. Add 2 ml of Ce^{+3} carrier (Note 1) and again precipitate $Eu(OH)_3$ with conc. NH_4OH (Note 2).

10. Dissolve the precipitate in 7 to 10 ml of 6M HCl, dilute with H_2O to 15 to 20 ml, and add approximately 0.5 g Zn dust.

11. Heat the tube in a steam bath for 10 min with stirring, using as a stirring device a 4-mm tube through which is passing a stream of CO_2-free and O_2-free N_2 (Note 3).

12. With the N_2 still bubbling through the solution, quickly plunge the centrifuge tube into an ice bath and chill for 2 to 3 min. Add an excess of O_2-free and CO_2-free NH_4OH from a dropping bottle to precipitate $Ce(OH)_3$ (Note 4). Immediately stopper the tube, swirl, and centrifuge. Decant the supernate at once into another narrow-neck centrifuge tube and add 0.5 ml of 6% NaOCl to the decantate to oxidize Eu^{+2} to the +3 state and thus precipitate $Eu(OH)_3$.

13. Centrifuge and discard the supernate. Dissolve the precipitate in 2 ml of 6M HCl and reprecipitate $Eu(OH)_3$ with 2 ml of conc. NH_4OH.

14. Repeat steps (9)-(13).

15. Repeat steps (9)-(11) and also the precipitation and centrifugation of $Ce(OH)_3$ and decantation of supernate (see step 12) as before. Transfer the decantate into a clean 40-ml narrow-neck centrifuge tube. (This is to remove any $Ce(OH)_3$ which has floated over in the original decantation.) Stopper immediately and centrifuge. Transfer the supernate to a regular 40-ml centrifuge tube containing 0.5 ml of NaOCl solution. Centrifuge and discard the supernate.

16. Dissolve the $Eu(OH)_3$ in 2 ml of 6M HCl, dilute to 20 ml with H_2O, and centrifuge. Discard any precipitate which forms. Reprecipitate $Eu(OH)_3$ by the addition of 2 ml of conc. NH_4OH. Centrifuge and discard the supernate.

17. Wash the precipitate once with H_2O, dissolve it in 1 ml of 6M HCl, and dilute to 15 ml with H_2O. Add 15 ml of saturated $H_2C_2O_4$ solution and place the tube in a steam bath for 10 to 20 min. Cool to room temperature, cen-

trifuge, and discard the supernate. Transfer the precipitate by means of a stream of H_2O onto a No. 42 Whatman (preweighed) 7/8-in.-diameter filter circle in a ground-off Hirsch funnel mounted in a chimney. As soon as the precipitate has been transferred and has partially settled, turn on the suction. Filter and wash the precipitate and also the outside of the chimney twice with small quantities of H_2O and once with CH_3OH. Dry at 110° for 15 min. Let the precipitate cool for 12 to 15 min, weigh, and mount (Note 5).

Note

1. The Ce^{+3} carrier is added to act as a scavenger for rare earths after Eu has been reduced to the +2 state. $Ce(OH)_3$ is precipitated and carries down unreduced rare earths.

2. A number of $Eu(OH)_3$ precipitations are carried out for the purpose of removing H_3BO_3 and HNO_3 prior to the reduction of Eu^{+3} with zinc dust.

3. CO_2-free and O_2-free N_2 is obtained by passage of the gas through a U-tube containing Ascarite, then through fresh $CrCl_2$ solution (Oxsorbent) contained in a wash bottle with a sintered glass dispersing disk, and finally through a spray trap, such as a Kjeldahl trap.

4. O_2-and CO_2-free NH_4OH is obtained by the transfer of the base from a freshly opened bottle to a 500-ml graduated dropping funnel, made with two ground joints at the top--one to lead N_2 in and the other, which is fastened to a glass check valve, to permit N_2 to go through the funnel over the surface of the NH_4OH and prevent air from backing up into the funnel.

5. For the determination of 15.4d Eu^{156}, which has a 10h Sm^{156} parent, the chemistry is performed 4 days after bombardment time so that the Sm parent will have decayed. Counting is done 6 days after bombardment to permit the decay of 15.4h Eu^{157}.

Eu-2. EUROPIUM

Element separated: Europium

Target material: Thorium (metal)

Type of bbdt: 60-in. α's

Procedure by: Newton[306]

Time for sep'n: 4 hours

Equipment required: Tank N_2 (O_2 and CO_2 free)

Yield: 40%

Degree of purification: 10^6 except from RE; $\approx 10^4$ from RE.

Procedure: The Th metal is dissolved in conc. HCl + a few drops of 0.2M $(NH_4)_2SiF_6$ solution to clear up the black residue. The HCl is diluted to 2N and an aliquot taken.

1. To aliquot add 10 mg Eu^{+++} and 10 mg Ce^{+++} carriers. Add 8 ml conc. HNO_3 and 20 ml 0.35M HIO_3 soln. Ppt. $Th(IO_3)_4$. Discard ppt.
2. To centrifugate add 19M NaOH, ppt. $Ce(OH)_3$ and $Eu(OH)_3$. Centrifuge and wash ppt. once with H_2O.
3. Dissolve ppt. in 8 ml conc. HNO_3, add 2 ml Zr and 20 ml HIO_3, ppt. $Zr(IO_3)_4$. Centrifuge and discard ppt.
4. Add 19M NaOH to ppt. $Eu(OH)_3$ and $Ce(OH)_3$. Discard supernate. Wash ppt. once with H_2O.
5. Dissolve hydroxides in 1 ml 6N HCl. Add 10 mg each Ba and Sr carriers. Pass in CO_2-free NH_3, ppt. hydroxides.
6. Repeat (5).
7. Dissolve ppt. in 1 ml HCl. Add Cb and Zr carrier and 3 ml 27N HF. Ppt. CeF_3 + EuF_3. Wash ppts. once.
8. Dissolve ppt. in 1 ml 6N HCl and 1 ml sat. H_3BO_3. Dilute, pass in NH_3, ppt. $RE(OH)_3$.
9. Dissolve $RE(OH)_3$ in 1 ml 6N HCl. Pass in NH_3, ppt. $RE(OH)_3$.
10. Dissolve $RE(OH)_3$ in 1 ml 6N HCl. Add 0.5 g Zn(Hg). Dilute to 5 ml, pass in pure N_2 through stirring rod. Heat, stirring with rod through which gas is passing. Place in ice bath and pass in NH_3 to ppt. $Ce(OH)_3$. Stopper tube and centrifuge. Pipette off supernate to another tube.
11. Dissolve ppt. in 1 ml 6N HCl, dilute, and repeat step (10).
12. To combined supernates of steps (10) and (11) add 1 drop NaOCl (6%) or pass in ozone. Ppt. $Eu(OH)_3$. Centrifuge. Dissolve in 6N HCl and repeat steps (10), (11), and (12).
13. Dissolve $Eu(OH)_3$ from step (12) in 1 ml 6N HCl. Dilute to 10 ml. Heat. Add 10 ml saturated $H_2C_2O_4$ and place in ice bath 10 min. Filter on weighed filter paper and wash three times with 5 ml H_2O, three times with 5 ml EtOH and three times with 5 ml Et_2O. Evacuated and weigh.

Remarks

1. N_2 gas must be Free From O_2 and CO_2.
2. Save all Eu residues, active or not. Eu is extremely rare and hard to get.

This method has been described previously in Phys. Rev. 75, 17 (1949).

Preparation of Europium Carrier

About 1.5 g of europium oxalate originally prepared by McCoy was puri-

fied. There are both α and β activities associated with this Eu and it is necessary to separate it in order to obtain a good carrier solution. The process is given below.

1. $Eu_2(C_2O_4)_3$ ignited and dissolved in HCl.
2. NH_4OH passed to ppt. $Eu(OH)_3$.
3. $Eu(OH)_3$ dissolved in 10 ml 16N HNO_3, Zr^{+4} carrier added.
4. HIO_3 added ppt. $Zr(IO_3)_4$ carrying all Th impurities.
5. 19N NaOH added to ppt. $Eu(OH)_3$.
6. $Eu(OH)_3$ dissolved in 6N HCl. Ba^{++} added and H_2SO_4 added while hot to ppt. $BaSO_4$, carrying Ra and MsTh activities.
7. $Eu(OH)_3$ pptd. with NH_4OH, washed and dissolved in dilute HCl.
8. Zn(Hg) added to reduce Eu with N_2 bubbling through solution. Then NH_3 passed into ppt. RE and Ac hydroxides. Ppt. redissolved in acid and recycled since some Eu not reduced.
9. Eu^{++} oxidized with NaOCl and pptd. as hydroxide, washed and dissolved in HCl as carrier.

Standardization of Carrier

Take 2 ml carrier solution, heat and ppt. oxalate with $H_2C_2O_4$. Cool 10 min in ice bath, filter. Wash three times with 5 ml H_2O, three times with 5 ml EtOH and three times with 5 ml Et_2O. Dry by evacuation. Weigh as the oxalate. Ignite to oxide and weigh as the oxide.

$Eu_2(C_2O_4)_3 \cdot 10\ H_2O$ (24.6 mg per 10 mg Eu).

Eu-3. EUROPIUM

Element separated: Europium

Procedure by: Goeckermann[306]

Target material: ≈ 1 g Bi metal

Time for sep'n: few hours

Type of bbdt: 184-in., all particles

Equipment required: Centrifuge, tubes, Lusteroid cones, H_2S tank, NH_3 tank, ozone generator

Yield: Eu approx. 15%

Degree of Purification: Eu decontamination factor > 10^4 from non-RE fission and spallation products.

Advantages: Good for separating small amounts of Ce and Eu activity from large amts. of non-RE activities.

Procedure: Cerium and Europium were purified together and then separated from the other rare earths.

1. To aliquot of HNO_3 soln. of target add 20 mg Ce, Eu, and Y. Make 2N in HCl with Zr, Cb, and Sr present and precipitate RE fluorides.
2. Dissolve and reprecipitate RE fluorides from 2N HNO_3 with Zr and Cb present.
3. Scavenge twice with Bi_2S_3 and RuS from 0.5N HCl.
4. Precipitate RE hydroxides twice with NH_3(CO_3^{-2}-free) and Sr present.
5. Precipitate RE fluorides from 2N HCl twice with Zr and Cb present.
6. Scavenge with Bi_2S_3 and RuS from 0.3N HCl.
7. Precipitate RE Hydroxides with NH_3 three times with Sr present.
8. Precipitate RE oxalates from dilute HCl.
9. Precipitate RE fluorides from HNO_3.
10. Repeat step (7).
11. Displace air with N_2 that is free of O_2 and CO_2, reduce with Zn amalgam, precipitate $Y(OH)_3$ and Ce $(OH)_3$ with NH_3. Dissolve and reduce again, reprecipitate hydroxides.
12. Oxidize supernatants from hydroxide precipitations with ozone, precipitate $Eu(OH)_3$ with NH_3. Dissolve in HCl, add Ce, reduce to Eu^{+2} and precipitate $Ce(OH)_3$. Repeat separation cycle three times. Precipitate $Eu_2(C_2O_4)_3$ like $Y_2(C_2O_4)_3$ and treat similarly. Weigh as $Eu_2(C_2O_4)_3 \cdot 10H_2O$ (24.6 mg per 10 mg Eu). See (58-2) for cerium separation from the same target.[306] In these bbdts., the amount of Y activity produced was 10^3 times the RE activity. 1-2 mg of holdback carriers or scavengers are used.

Ac-1. ACTINIUM

G. M. Iddings (LRL, Livermore)

5-17-60

Actinium can be mildly purified and mounted weightless by the following procedure:

1. To the Ac tracer in mixed activities add ≈ 5 mg of pure Lu carrier. Precipitate $Lu(OH)_3$ with NaOH at pH > 13 (see Note 1). Wash the precipitate once with water.

2. Dissolve the Lu(Ac) in ≈ 5 ml of buffer solution— 0.1M acetic acid and 1M sodium acetate— which is ≈ pH 5.7. Transfer the solution to a 60-ml cylindrical separatory funnel and extract the Ac and Lu into ≈ 30 ml of 0.40M TTA in benzene for 3 minutes, stirring with a motor-driven glass paddle. Wash the organic layer twice with ≈ 15 ml of pH 5.7 buffer solution.

3. Back-extract the Ac (but not the Lu) into ≈ 10 ml of pH 4.5 buffer solution made of 0.1M formic acid and 1M sodium formate. Repeat the back-extraction and combine the solutions (see Note 2).

4. Adjust the pH of the solution to ≈ 5.7 with saturated sodium acetate solution. Extract the Ac into a new batch of 0.40M TTA in benzene. Wash the organic layer with pH 5.7 buffer solution. Wash out the buffer solution with water without stirring.

5. Back-extract the Ac into a few ml of 0.05M HCl. Repeat the back-extraction with a new portion of 0.05M HCl.

6. Evaporate the combined solutions of Ac on a Pt plate under a heat lamp. Ignite gently and count.

Notes

1. Ac carries much better on Lu at pH 13 or 14 with NaOH than at pH 8 or 9 with NH_4OH.

2. The pH 4.5 back-extraction is a good separation of Ac from Y earths and the heavier Ce earths. There is only a partial separation of Ac from La.

Ac-2. ACTINIUM (From Its Daughters)

Cabell[67]

Chemical Purification of Irradiated Actinium

Cation- and anion-exchange chromatography were used to purify the irradiated actinium.

Each cation column consisted of 1.00 g (dry weight) of 200-400 mesh Dowex-50 (hydrogen form) contained in a glass tube 10 cm long and 6 mm in diameter sealed onto a reservoir 10 cm long and 3 cm in diameter. Both column and reservoir were jacketed at 60°. Before they were loaded, the columns were prepared by washing with water.

Each anion column contained 0.25 g of 200-400 mesh Dowex-1 (chloride form) in a tube 6 cm long and 6 mm in diameter sealed onto a reservoir 5 cm long and 1.5 cm in diameter. The anion columns, which were operated at room temperature, were washed with 5 ml of 10M hydrochloric acid before loading.

The irradiated actinium sample was dissolved in 5 ml of 2M hydrochloric acid and the solution was warmed to 80° before it was fed to a cation exchange column without application of pressure. When the feed had passed, the column was eluted successively with 5 ml of hot 2M hydrochloric acid (to remove bismuth, lead, and francium) and 20 ml of hot 3M nitric acid (to remove radium). Finally the column was eluted with 25 ml of hot 6M nitric acid; the first 5 ml of eluated was rejected and the remainder, which contained the purified actinium, was collected in a centrifuge tube. The Th^{227} daughter of the actinium was left on the column.

The progress of this separation is illustrated in Fig. 105 (each peak was identified by separate experiments using only one of the five components each time).

Three drops of a ferric nitrate solution (10 mg iron per ml) were added to the eluate obtained from the cation column; the solution was neutralized with ammonia, cooled to room temperature, and the ferric hydroxide precipitate, which carries the actinium, was collected by centrifuging. The precipitate was dissolved in 2 drops of concentrated hydrochloric acid, diluted to 20 ml, and the iron was precipitated again with ammonia. This solution-precipitation cycle was then repeated.

The precipitate was next dissolved in 1 ml of concentrated hydrochloric acid and fed to an anion exchange column at the rate of 0.2 ml/min to remove the iron carrier. After the feed had passed, the column was eluted with 1 ml of 10M hydrochloric acid and the total eluate was collected in a small platinum crucible and evaporated to dryness under an infrared lamp. The crucible was then heated in a furnace at 700° for 5 minutes and cooled; 2 ml concentrated nitric acid was added and the solution was again evaporated to dryness under an infrared lamp. Finally the residue, which was invisible to the naked eye, was dissolved in 1 ml concentrated nitric acid and the resulting solution was used for making sources on thin films for counting.

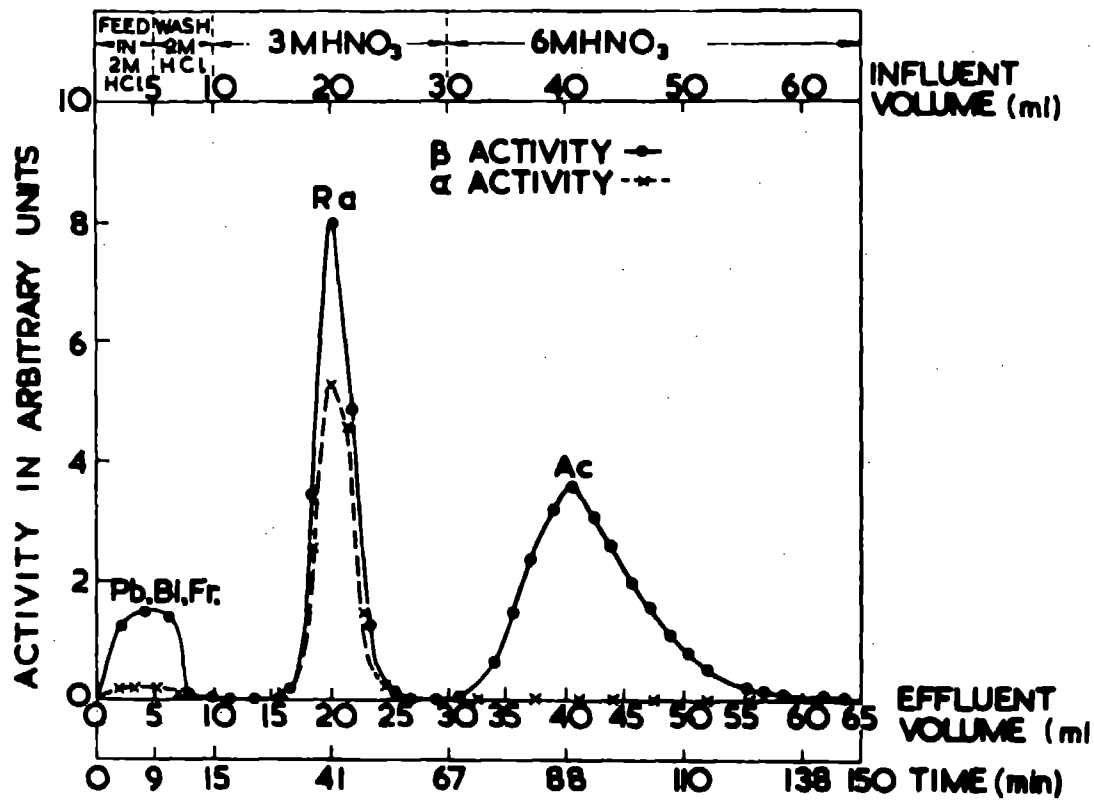

Fig. 105. The separation of Ac^{227} from its daughters by cation-exchange chromatography (67)

Ac-3. ACTINIUM

Element separated: Actinium (procedure designed for Ac^{225} and Ac^{226})

Procedure by: Hyde[306]

Target material: Thorium metal about 25 g (two 25-mil foils 1-1/2 in. square bombarded on edge)

Time for sep'n: 24 hours

Type of bbdt: Protons from 184-in. cyclotron

Equipment required: beakers, centrifuge cones, 250-ml separatory funnel, resin column, automatic sampler, pH meter

Yield: Not known, estimated 75%

Degree of purification: Complete separation from all other elements by factor of at least 10^4.

Procedure

1. Dissolve thorium in hot conc. HNO_3. Add 1 drop 1N HF occasionally to catalyze dissolution.

2. Evaporate solution nearly to crystallization. Cool. Transfer to 250-ml pear-shaped separatory funnel. One which has been modified to provide a side funnel as shown in Fig. 1[306] is recommended.

3. Add 1-2 volumes pentaether (dibutoxytetraethylene glycol).* Stir. Let settle. Drain aqueous layer into original beaker. Drain pentaether layer into bottle for storage.**

4. Return aqueous layer to funnel. Add solid ammonium nitrate with stirring until solution is saturated. Add 2-3 volumes pentaether. Stir. Drain aqueous into 50-ml centrifuge cone. Drain pentaether layer into storage bottle.

5. Repeat pentaether extraction once again after adding 0.5 ml conc. HNO_3 to replace that extracted by solvent.

6. Centrifuge aqueous layer in 50-ml centrifuge cone to separate last cc's of pentaether, which are pipetted off.

7. Add NH_4OH to ppt. last amounts of thorium as $Th(OH)_4$. This serves to carry the actinium out of the salted solution. Wash twice with H_2O.

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*It is quite important that the solution be cool before the solvent is added as pentaether is rapidly decomposed by hot nitric acid.

**Pentaether is used to extract the bulk of the thorium away. The thorium serves as its own salting agent in the first pass which extracts the bulk of it and reduces the aqueous volume greatly. Subsequent extractions must be aided by NH_4NO_3 salting.

8. Dissolve mixed hydroxides in minimum amount HCl. Dilute to 5 ml. Adjust pH to 1.5-2.5,*** check with Beckman pH meter using 1-drop glass electrode. Add 10 ml 0.15M TTA in benzene. Stir. Recheck and if necessary readjust pH. Stir well 10-20 minutes.

9. Centrifuge. Pipet off benzene layer containing thorium.

10. To aqueous add 10 ml fresh TTA. Stir, check pH. Stir 10-20 minutes. Centrifuge. Pipet off benzene layer.

11. To aqueous layer containing actinium, rare-earth, and other activities add NH_4OH to adjust pH to 5.5-7.0.***

12. Add 10 ml TTA-benzene. Stir. Recheck pH. Contact 20 minutes.

13. Pipet benzene layer containing actinium and rare earths into clean 50-ml centrifuge cone. Re-extract activity into 2.5 ml 0.1N HCl by 2 minutes of stirring. (At this point the only likely impurities are rare-earth fission products. If these do not interfere, this solution may be considered the final solution. If separation from rare earths is desired the following resin separation is recommended.)

14. Add a few mg of ammonium-form, colloidal Dowex-50 resin to the dilute HCl solution. Warm to ≈ 60°C in water bath for 2-3 minutes. Centrifuge.

15. If assay of supernate indicates nearly complete adsorption on resin, pipet the resin on to the top of a short resin column. Elute with 5% citrate solution of pH 3.8-4.0. Use a mechanical sampler to take samples every 20 minutes.

The rare-earth and actinium peaks cannot be predicted accurately enough to eliminate the necessity of alpha and beta counts to determine their location. The rare-earth fractions come off in the first samples as indicated by the beta counts. The actinium peak is located by the alpha counts of Ac^{225}. The solution of Bi^{213} and its associated Po^{213} daughter alpha activity in the early fractions obscures the location of the actinium peak unless samples are pulse-analyzed or unless the 47-minute Bi^{213} is allowed to decay before counting.

My experience with a column 6 cm × 2 mm of colloidal resin eluted with pH 3.9 citrate at a rate of 1 drop per 2.5 minutes was that the rare-

***An equal volume of TTA-benzene will extract thorium essentially completely from an aqueous solution of pH>1. Actinium extraction is 0 at pH 2.5 or less, is 10% at pH 4, and rises sharply to essentially complete extraction at pH 5.5 or greater. See Hagemann, AECD-1933.

earth fraction came off within two hours and the actinium fraction, well separated from the rare earths, started to come off after 5 hours and was spread over 2-3 hours. Others (Orth and Street) report much more rapid elution under essentially the same conditions.

Ac-4. ACTINIUM

Element separated: Actinium

Parent material: Tracer Pa^{230}

Milking experiment

Procedure by: Meinke[306]

Time for sep'n: 3-4 hours

Equipment required: Standard, centrifuge

Yield: ≈ 40%

Degree of purification: Factor of at least 10^7 from Pa, U, and Th.

Advantages: Can separate very small amounts of Ac from large amounts of Pa, U, and Th activity. In one experiment separated 500 d/m Ac^{226} from 10 total d/m of Pa^{250} and about equivalent amounts of U and 30-minute Th^{226}

Procedure: Pa^{230} in 6N HNO_3 after DIPK extractions (procedure 91-1).[306]

1. Take 10 cc of Pa soln. and add 1/4 mg La^{+3} and 5 mg Ce^{+3} carriers.
2. Add 10 drops of conc. HF to ppt. the fluorides. Centrifuge.
3. Metathesize ppt. to La and Ce hydroxides and wash once with 5 ml alkaline water.
4. Dissolve ppt. in few drops 6N HCl and dilute to 5 cc.
5. Add 1/4 mg Zr^{+4} carrier and H_3PO_4 to make 3N PO_4^{-3}. Discard ppt.

Steps (2) through (5) are repeated alternately or consecutively until the desired degree of purification is obtained. For the purifications noted above, 10 fluoride pptns. and 9 phosphate pptns. were made. After the 10th fluoride ppt. had been metathesized to the hydroxide, the following procedure was used:

6. Dissolve hydroxide ppt. in 10M HNO_3, make .01M Fe^{+3} and oxidize Ce^{+3} to Ce^{+4} with solid sodium bismuthate (warm to speed up reaction). (Ce^{+4} will now carry on the $Zr_3(PO_4)_4$ ppt.)
7. Repeat step (5).
8. Repeat steps (2) and (3).
9. Dissolve ppt. in few drops 6N HCl, dilute to known volume and plate aliquot for counting.

Remarks:

The fluoride cycles decontaminate primarily from Pa, the phosphate from Th. If further purification is required include more cycles in procedure.

Only one milking can be made from a given batch of Pa by this procedure since it is difficult to again get the Pa into an extractable form once fluoride ion has been added.

It has been found that the $LaCl_3$ solution makes a more adherent and thinner plate than the LaF_3 ppt. The amount of La^{+3} carrier used in step (1) should be determined by the amount of bulk that can be tolerated on the final plate.

Ac-5. ACTINIUM

Element separated: Actinium (procedure designed for Ac^{226})

Procedure by: Hall[306]

Target material: Thorium metal (≈ 0.5 g 5-mil foil)

Time for sep'n: ≈ 24 hours

Type of bbdt: 340-Mev protons

Equipment required: Beakers, resin column, automatic sampler, pH meter, stirrer

Yield: Not known, probably at least 75%.

Degree of purification: Factor of at least 10^4 from other elements.

Advantages: TTA separation of Th target material faster and cleaner than pentaether extraction.

Procedure

1. Dissolve thorium in hot concentrated HCl in 50-ml beaker. Add 1 drop only of 0.2M $(NH_4)_2\ SiF_6$ (more causes Si to precipitate).
2. Evaporate to dryness to expel most of the HCl.
3. Take up residue with water and adjust the pH meter and glass and calomel electrodes, Nos. 1170 and 1190.
4. Extract the thorium away with an excess of 1M TTA in benzene, previously washed first with acid then with water.
   (a) Add ≈ 25 ml TTA.
   (b) Adjust pH throughout extraction period to 1.0-2.0.
   (c) Stir 20 minutes.

(d) Pipet off the aqueous layer and transfer to a clean beaker.

5. Repeat the thorium extraction three times using clean stirrers, beakers, etc., each time. Smaller portions of TTA may be used.

6. Similarly, extract the actinium and rare earths into the benzene phase at pH of 6.0-7.0, using ≈ 5-ml portions of TTA. Repeat if necessary.

7. Finally, extract the actinium and rare earths into the aqueous phase using ≈ 3 ml 0.1M HCl. Repeat if necessary.

8. Transfer the activity to a resin column and complete the actinium separation as indicated in steps (14)-(15) of Hyde's procedure.

Sp-1. SCANDIUM

Determination of Chemical Yield of Scandium

This is a spectrophotometric method depending on the color of the 8-hydroxyquinoline complex in amyl acetate solution.[544]

Reagents

Carrier solution, 10 mg scandium/g: Weigh out 0.768 g Johnson Matthey Specpure scandium oxide (Sc_2O_3) into a platinum dish and add 5 ml of 16M nitric acid and a few drops of 1M hydrofluoric acid. Heat under the lamp until dissolved and then evaporate off most of the acid. Add more nitric acid and again evaporate nearly to dryness. Dilute to 50 g.

Dilute scandium standard: About 200 μg/g prepared by accurate dilution of the carrier solution.

8-hydroxyquinoline (oxine): 1 g dissolved in 100 ml 95% alcohol.

Procedure

Transfer the sample containing 20-60 μg of scandium in dilute acid solution* to a 40-ml centrifuge tube and bring the final volume to about 5 ml with water. Add 2.0 ml of the oxine reagent, and 0.5 ml of 6M ammonium hydroxide. Add 10.0 ml of Analar-grade amyl acetate and stir the layers together mechanically for 5 min. Centrifuge and transfer some of the top (amyl acetate) layer to a 1-cm cell. Measure the absorbancy against a blank solution, similarly prepared, at 380 mμ. (This is not the peak wavelength,

*The sample taken must contain less than 1 milliequivalent of free acid.

which is below the range of the SP600 but the absorbancy is changing quite slowly with wavelength over the range 395-375 mμ and there is adequate sensitivity for the purposes of this analysis.)

Carry out similar determinations on accurately measured portions of the dilute scandium standard solution.

The Beer-Lambert law is obeyed.

Under the above conditions 50 μg of scandium give an absorbancy of about 0.6.

Reference: The method was developed by J. Herrington at AWRE. [544]

Sp-2. RARE EARTHS

Determination of Chemical Yield of Cerium, Praseodymium, Neodymium, Samarium, Europium, Gadolinium, Terbium, and Yttrium

This is a spectrophotometric method depending on the blue colors of the complexes with bromopyrogallol red. [544]

Reagents

Carrier solutions: 5 mg element/g in 0.1M nitric acid.

Cerium: Dissolve 1.96 g Analar-quality ceric ammonium nitrate in 5 ml 0.5M nitric acid and add sufficient 100-volume hydrogen peroxide to decolorize the solution. Dilute to 5 g.

Praseodymium: 1.54 g praseodymium nitrate $Pr(NO_3)_3 \cdot 6H_2O$ in 100 g solution. Standardize gravimetrically, using duplicate 10-g portions, by evaporating nearly to dryness in a tared silica crucible, adding a little cellulose powder to absorb the solution, igniting carefully at 800-900°C, and weighing as Pr_6O_{11}.

Solutions of the other elements are prepared by dissolving weighed amounts of Johnson Matthey "Specpure" oxides in 5 ml of 6M nitric acid, evaporating to about 0.5 ml, and then diluting quantitatively to 50 g. The following weights of oxides are needed.

Neodymium	0.291 g Nd_2O_3	Gadolinium	0.288 g Gd_2O_3
Samarium	0.290 g Sm_2O_3	Terbium	0.288 g Tb_2O_3
		Yttrium	0.318 g Y_2O_3

Dilute standards: About 200 μg/g prepared by accurate dilution of the carried solutions.

Bromopyrogallol red: 0.05% w/v solution in 50% ethyl alcohol.
Sodium acetate: 54 g $CH_3COONa.3H_2O$ per 100 aqueous solution.
Sodium bicarbonate: 5 g per 100 ml aqueous solution.
Hydrochloric acid: 0.2M.
Ascorbic acid: 1 g per 100 ml aqueous solution, freshly prepared.

Procedure

Yttrium and rare earths. Transfer the sample containing 15-35 μg yttrium or 20-50 μg of rare earth, in acid solution, to a 25-ml measuring flask. Dilute to 15-16 ml with water. Add 2.0 ml of the bromopyrogallol red reagent and then sodium bicarbonate solution dropwise, until one drop produces a permanent blue color. Wash down the neck of the flask with water and then add 0.2M hydrochloric acid dropwise, until the blue color is discharged, leaving a clear red solution. Add 0.5 ml of the sodium acetate solution, and stand the flask in a boiling water bath for 10 min. Cool and dilute to the mark with water. Measure the absorbancy of the solution against water, in 1-cm cells at 660 mμ.

The color is quite stable and obeys the Beer-Lambert law. Carry out similar determinations on accurately measured portions of the diluted carrier solution. Plot a calibration curve of absorbancy against concentration of rare earth. Obtain the blank from the value of the intercept of the calibration line with the absorbancy axis (about 0.005).

Under the above conditions, 40 μg of rare earths give an absorbancy of about 0.56, 30 μg of yttrium give an absorbancy of about 0.66.

Cerium. As for yttrium and rare earths (above) except that 0.2 ml of 1% ascorbic acid is added before the bromopyrogallol red, and the final solution is measured is measured at 680 mμ. Under the above conditions, 40 μg of cerium give an absorbancy of about 0.64.

Interfering Ions

The most serious interference is occasioned by the presence of Zr^{4+}, Fe^{2+}, and Fe^{3+}. The first two increase the absorbancy and Fe^{3+} decolorizes the solution. Peroxide interferes and must be eliminated from samples by careful evaporation to dryness before adding any reagents.

Reference

Both of these procedures were developed at AWRE by J. Herrington and K. C. Steed.[544] The use of bromopyrogallol red as a chromogenic reagent was suggested by its use as an indicator for rare-earth titrations with EDTA (see A. Jenickova, V. Suk, and M. Malat: Chem. listy 50, 760 (1956).

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