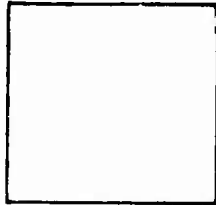


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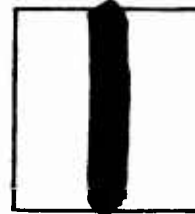
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IN LOW-ALLOY CONSTRUCTIONAL STEELS

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METHODS OF SEPARATION OF TOTAL RARE EARTHS
IN LOW-ALLOY CONSTRUCTIONAL STEELS

WAL 120/73

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The over-all objective of this project is to develop a method for the separation of total rare earths in low-alloy constructional steels. The work is being conducted for the Ordnance Corps of Watertown Arsenal through the Chicago Ordnance District.

This bibliography was prepared by Mrs. Ann Wennerberg, Research Literature Chemist, under the direction of Dr. Otto Reinmuth, Supervisor of the Chemistry Literature Section. Mr. W. A. Dupraw, Research Analytical Chemist, was responsible for the technical evaluation and selection of the references in this bibliography.

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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
I. GENERAL - REVIEWS-BOOKS-UNCLASSIFIED ARTICLES . . .	2
II. EXCHANGE RESINS	15
III. EXTRACTIONS	46
IV. PRECIPITATIONS	52
V. AMALGAMATIONS	80
VI. CHROMATOGRAPHY	83
VII. IONIC MIGRATION	88
VIII. COLORIMETRIC AND VOLUMETRIC METHODS	91
IX. POLAROGRAPHY	97
X. ELECTROMETRIC AND CONDUCTOMETRIC STUDIES	101
XI. COMPLEX FORMATIONS	103
XII. SOLUBILITY STUDIES	126
XIII. SPECTROGRAPHIC STUDIES	129
XIV. PARAMAGNETIC SUSCEPTIBILITY	137
XV. ACTIVATION AND X-RAY STUDIES	148

METHODS FOR SEPARATION OF TOTAL RARE EARTHS IN LOW-ALLOY CONSTRUCTIONAL STEELS

INTRODUCTION

A comprehensive survey was made of the technical literature pertaining to the rare earths. Selections for the bibliography were limited to references on chemical methods of separation, fractionation, and determination. Studies of chemical, and physical properties of rare earths and rare-earth compounds were also included wherever it appeared that they might suggest a basis for new or improved analytical schemes.

In view of the availability of the experience of the Manhattan Project, it was decided not to extend the search farther back than 1940. The survey was necessarily based upon secondary sources, although in some instances primary sources were consulted.

References in this bibliography were compiled from the following sources.

<u>Title</u>	<u>Abbreviation</u>	<u>Coverage^o</u>
Chemical Abstracts	CA	1940 - August 1954
Metallurgical Abstracts	Met. Abstr.	1949 - 1952
Analytical Abstracts	Anal. Abstr.	Jan - July 1954
Crerar Metal Abstracts	Crerar Met. Abstr.	Aug. 1952 - July 1954
Nuclear Science Abstracts	Nuclear Sci. Abstr.	Jan. 1953 - July 1954
Industrial Arts Index	IAI	1953 - July 1954
Engineering Index	Eng. I	1953

The bibliography is classified according to subject matter, as indicated in the table of contents; references are listed within each section alphabetically by author. The abbreviations follow, as closely as possible, the style used by Chemical Abstracts.

Out of a total of 638 references, 250 were judged not pertinent to the objectives of this bibliography. Evaluation was limited to the selection of pertinent references; no attempt was made to appraise the merits of the various methods of analysis.

^o Dates inclusive.

I GENERAL - REVIEWS - BOOKS - UNCLASSIFIED ARTICLES

1. Barthauer, G. L., and Pearce, D. W. Analytical chemistry of the rare earths. The active oxygen determination. Ind. Eng. Chem., Anal. Ed. 18, 479-80, 1946; cf. CA 37, 6483. CA 40, 6362.8, 1946. Place a weighed sample of the oxide or mixture of oxides in a Kjeldahl flask fitted with a reflux condenser terminated with a Bunsen valve. The valve dips under the surface of a KI solution. Add a 10% aqueous solution of KI and concentrated HCl to the oxide and heat until the solid has dissolved. Iodine equivalent to the O in excess of that equivalent to the sesquioxide is freed by the reaction. Titrate the liberated I with standard $\text{Na}_2\text{S}_2\text{O}_3$ solution. Data are given to show that Pr_6O_{11} is the formula of the oxide obtained by ignition of the oxalate in the air at 955° and to show the active O content of La_2O_3 - CeO_2 mixtures. The active O in CeO_2 is unaffected by admixture and ignition with La_2O_3 .
2. Bock, R. Recent progress in the separation of the rare earths. Angew. Chem. 62A, 375-82, 1950 CA 45, 55a, 1951. A review covering processing of minerals and separation of Th and Ce; separation of individual rare earths from mixtures; the position of Y in the series of the rare earth elements; and systematic separation methods, i.e., fractional crystallization and precipitation fractional distribution (extraction), adsorption, and ion-exchange methods. Over 100 references
3. Brantley, J. C., et al Investigations of rare earth problems. March 1 - June 1, 1948. University of Illinois, Urbana. ATI 86 703. UNCLASS. The investigation of the effects of added anions upon the absorption spectra of the rare earths elements has been continued. The effects of tartrate in both acid and basic solution are reported. Results of studies involving rare earth ions only are discussed. Reductions of the rare earths to divalence included polarographic studies and amalgam reduction. Further studies were made of methods of concentrating praseodymium, and analysis and analytical requirements were investigated. Investigation of the phosphoric acid derivatives of the rare earths was undertaken to determine the mechanism of the existing methods for opening up monazite ores and to improve analytical

procedures for thorium and the rare earths.

4. Brantley, J. C , et al. Investigations of rare earth problems December 1, 1948. (Quarterly Progress Rept.) University of Illinois, Urbana. ATI-86 704. UNCLASS Progress report contains information pertaining to rare earth problems, and results of the various investigations are discussed in detail. The absorption spectrum of cerium (III) chloride has been measured in the ultra-violet. A study of the effects of excess perchlorate ion on erbium perchlorate solutions has been made, and a procedure for preparing virtually acid-free solutions for analysis is given. A proposed quantitative approach to determining the stability and composition of the complexes is outlined. The procedure involved in the purification of Dowex 50 resin was developed. The stabilization of the higher valence states of praseodymium, and composition and structure of the oxides and hydrous oxides of praseodymium were studied. Other investigations included hypophosphate studies and 8-hydroxyquinoline and substituted derivatives of the rare earth elements
5. Charlot, G. Some reagents for the ions of the aluminum group. Anal. Chim. Acta 1, 218-48, 1947. CA 42, 7192g, 1948. New reagents, or the application of existing reagents which have been proposed since the 1st and 2nd Reports of the International Committee on Analytical Reactions and Reagents for Al, Be, Ti, Zr, Ga, In, Sc, Yt, the rare earths, and Tl were studied, besides a number of unpublished reagents and methods.
6. Connick, R. E. Oxidation states of the rare earth and actinide elements. J. Chem. Soc. (Suppl. Issue No. 2), S235-41, 1949. CA 44, 8274h, 1950. The oxidation potential for a given couple in acidic aqueous solution is given by $-E^{\circ} = \Delta F_4^{\circ} - \Delta F_2^{\circ} + I + A$, where E° is the oxidation potential, ΔF_4° the free energy of hydration of the gaseous ion in the higher oxidation state, ΔF_2° the free energy of hydration of the gaseous ion in the lower oxidation state, I the ionization potential of the gaseous ion in the lower oxidation state, and A a constant. For the rare earth elements the quantities determining E° , the ionization potentials and hydration energies of the 4f electrons, are such that the +3 oxidation state is stable in aqueous solution. This same conclusion

cannot be reached from electronic structures (Meggers, CA 41, 4714d). The +2 and +4 oxidation states which exist for the rare earth elements are stable because of the changes in binding energy for the 4f electrons as the shell is filled. Since 5f electrons, which should have different values for I and $\Delta F_4 - \Delta F_2$, are involved in the oxidation of the actinide elements, there is no reason to expect the +3 oxidation state to be stable for these elements in aqueous solution. The stability of the +5 and +6 oxidation states in aqueous solution, which is greater than expected, is related to the existence of MO_2^+ and MO_2^{++} ions rather than simple hydrated cations. The d electrons reported for Th^{++} and Th^{3+} (de Bruin, et al., CA 37, 311.3; 39, 2253.1) are comparable to the d electron in Ce^{3+} (Lang, CA 30, 7451.2). The reactivity of +2 and +3 Th compounds with H_2O is expected for either d or f electrons, and the intense color of ThI_2 and ThI_3 can be explained for a structure with f as well as d electron. The probable existence of a +4 oxidation state for Pa (Bouissieres and Haissinsky, J. Chem. Soc. (Suppl. Issue No. 2), S256, 1949) indicates f electrons are involved in the Pa 4-5 couple since Ta, with d electrons, is difficult to obtain in the +4 state.

7. Dialer, K. The question of bonding in the rare earth hydrides. Monatsh 79, 311-15, 1948. CA 43, 2883a, 1949. A review. It is not inconsistent with present results to call the first two H atoms in these compounds ionically bound and the last H atom held by solution-like forces.
8. Dutt, N. K. Chemistry of the rare earths. III. Estimation of rare earths in uranium minerals. J. Indian Chem. Soc. 22, 75-6, 1945. CA 40, 2086.3, 1946. Various methods for the separation of U and the rare-earths were tested and compared. Precipitation of the rare-earth oxalates is satisfactory up to $UO_3-R_2O_3$ ratios of 25. At higher ratios, complex oxalate formation causes low results for the rare earths. The precipitation of oxalates in the presence of salicylic acid is satisfactory up to the same ratio as above. The hydroxylamine method of Jannasch and Schilling (J. prakt. Chem. 72, 26, 1905) is good but tedious. HF precipitation works well but is time-consuming. The removal of most of the $UO_2(NO_3)_2$ by solution in ether and preci-

pitating the rare-earths with oxalic acid works well even up to a $\text{UO}_3\text{-R}_2\text{O}_3$ ratio of 400

9. Dutt, N. K. Chemistry of rare earths. VI. Double thiosulfates of rare earths. J. Indian Chem. Soc. 26, 405-14, 1949, cf. CA 40, 4307.8 CA 44, 2400h, 1950. The compositions of several double thiosulfates of rare earths were investigated by Dutoit's thermometric method (Ca 16, 3041) and Job's method of continued variation (CA 22, 2120), involving conductometric titrations. Thermometric titration plots showed the existence of normal thiosulfates, $\text{R}_2(\text{S}_2\text{O}_3)_3$, in which R stands for La, Ce, Pr and Nd, addition of further $\text{Na}_2\text{S}_2\text{O}_3$ gave a break corresponding to $\text{R}(\text{S}_2\text{O}_3)_4^{5-}$, while for the K and NH_4 thiosulfates the break corresponded to a complex ion $\text{R}(\text{S}_2\text{O}_3)_3^{3-}$. In contrast to the elements of the Ce group the yttrium salt gave only a single break, indicating $\text{Y}_2(\text{S}_2\text{O}_3)_3$. No evidence was obtained for the existence of any complex salt. Conductometric data gave evidence for the existence of the normal thiosulfates and the complex ion $\text{R}(\text{S}_2\text{O}_3)_4^{5-}$, showing that at the dilutions studied only one type of complex and no molecular species such as $\text{R}(\text{S}_2\text{O}_3)_3^{3-}$ existed. In the solid state two molecule forms were isolated. The independence of the maximum composition from the concentrations of the primary solutions was demonstrated by the identity of the results obtained with different but equimolecular concentrations. Procedures are given for the preparation of solid $\text{Na}_5\text{R}(\text{S}_2\text{O}_3)_4$, $\text{K}_3\text{R}(\text{S}_2\text{O}_3)_3$ and $(\text{NH}_4)_3\text{R}(\text{S}_2\text{O}_3)_3$. These compounds were analyzed by decomposition with concentrated HCl, precipitation of the rare earths with ammonia, solution of the precipitate in dilute HCl, and precipitation as oxalate followed by ignition to the oxides. The filtrates from the ammonia precipitation were evaporated to dryness, NH_4 salts removed by ignition, and the alkalis converted to sulfates and weighed. Sulfur was determined on a separate sample as BaSO_4 after oxidation with ammoniacal H_2O_2 and separation of the rare earth hydroxides. NH_4 was determined by Kjeldahl's method.
10. Dutt, N. K. Chemistry of rare earths. VII. Dissociation constants of the thiosulfates of rare earths. J. Indian Chem. Soc. 27, 191-4, 1950; cf. CA 44, 2400g. CA 45, 2351b, 1951. Dissociation constants are calculated for the thiosulfates of La, Ce, Pr, Nd, and Sm by the

method of Job. The mean values obtained for K range from 2.35×10^{-9} for $\text{La}_2(\text{S}_2\text{O}_3)_3$ to 5.50×10^{-12} for $\text{Sm}_2(\text{S}_2\text{O}_3)_3$.

11. Dutt, N. K., and Gupta, A. K. Chemistry of the rare earths. IX. Dissociation constants of the double thiosulfates of the rare earths. J. Indian Chem. Soc. 29, 105-11. 1952; cf. CA 46, 4945d. CA 46, 7407c, 1952. The transference numbers and dissociation constants of solutions of Ce and La thiosulfate were determined. In the transference experiments, the metal ions were present in both cases in the anode compartment in a ratio $\text{R}:\text{S}_2\text{O}_3::1:3$ which indicates an ionic species of $\text{R}(\text{S}_2\text{O}_3)_3^{-3}$. The dissociation constant for the $\text{La}(\text{S}_2\text{O}_3)_3^{-3}$ double salt was 3.01×10^{-1} and for the $\text{Ce}(\text{S}_2\text{O}_3)_3^{-3}$ double salt, 7.2×10^{-2} for the equation $\text{R}_2(\text{S}_2\text{O}_3)_3 + 3\text{S}_2\text{O}_3^{-2} \rightleftharpoons 2[\text{R}(\text{S}_2\text{O}_3)_3]^{-3}$.
12. Fernelius, W. C. Ed. Inorganic Syntheses. 294 pp., 1946. McGraw-Hill Co., New York. cf. CA 36, 2485.5-93.7. CA 40, 6009.5-6012, 1946. Chapter 11. Pearce, D. W. p. 29-38. The rare earth elements and their compounds. Chapter 12. Pearce, D. W., Hanson, R. A., and Butler, J. C. The extraction of rare earth minerals I. Monazite and xenotime. Chapter 13. Pearce, D. W., Russell, R. G., and Butler, J. C. The extraction of rare earth minerals. II. Allantite, cerite, and gadolinite (separation of cerium and yttrium earths by the double sulfate method). p. 44-7. Chapter 14. Pearce, D. W., and Butler, J. C. Separation of cerium from rare earth mixtures. p. 48-51. Chapter 15. Pearce, D. W. Fractional crystallization. The magnesium-rare earth nitrates. p. 52-8. Chapter 16. Pearce, D. W., Barthauer, G. L., and Russell, R. G. The average atomic weight of rare earth elements in a mixture. Method based on the ratios oxalate: oxide and oxalate: permanganate. p. 58-61. Chapter 17. Pearce, D. W., and Russell, R. G. Rare earth bromates. p. 62-5. Chapter 18. McCoy, H. N. Europium amalgam. Separation of europium from rare earth mixtures. p. 65-9.
13. Hernandez-Gutierrez, F. Sulfamic acid-properties, determination, and use in analysis. Inform. quim. anal. (Madrid) 4, 168-77, 1950. CA 45, 5059f, 1951. A review. After HCl hydrolysis BaCl_2 is added to precipitate BaSO_4 , and the crystal pattern used for identification. The volumetric method with HNO_2 is a better procedure than the

gravimetric or the gasometric determination. Ibid. 205-13. $\text{-HSO}_3\text{NH}_2$ can be readily made of high purity. It is useful as an acidimetric standard, having a flat titration curve from pH 4 to 9; as a protein precipitant; to destroy nitrites rapidly and quantitatively at temperature below 50° ; for colorimetric determination of amino compounds; for determination of dissolved O in H_2O ; in electroanalysis where nitrites interfere; to identify nitrite in highly colored solutions; to separate the rare-earths from metals; and the Pb salt is a stable, neutral density standard ($D_4^{25} = 2.18$ for saturated solution of 68.5 g per 100 ml at 25°).

14. Hufferman, L. Separation of rare earths and application of the method to other elements. Chem Weekblad 48, 441-6, 1952. CA 46, 9004a, 1952. Methods of separation and purification of the rare earths are reviewed Trombe's method of basic precipitation with NH_3 (CA 38, 3211.9) is discussed in detail. T.'s method is applied to separating Al-Fe and Al-Zn. Diluted NH_3 gas was passed during 5 hours through 40 ml of a solution containing 0.1 gram ion per liter of Fe and Al. The pH of the solution was measured regularly in order barely to precipitate quantitatively the less-basic component. The solution was then boiled and the $\text{Fe}(\text{OH})_3$ precipitate filtered off. The $\text{Fe}(\text{OH})_3$ precipitate contained 0.6% Al, the filtrate 0.4% Fe. Similar results were obtained for the Al-Zn separation. 32 references.
15. Ingles, J. C. Chemical determination of thorium in ores. Can. Chem. Process Inds. 35, 397-8, 400, 402, 404, 406, 1951. CA 45, 7914h, 1951. Various methods for determining Th in ores and for the separation of the rare earths are described. Methods are given for determining Th and Ce colorimetrically, for fluoride separation of Th, U ore decomposition, methyl oxalate separation of Th, mandelic acid separation of Th from Zr, separation of Th from rare earths, and mesityl oxide separation of Th nitrate from other nitrates. A detailed, recommended procedure for determination of Th in ores is given.
16. Lortie, L. The rare earths. Can. Chem. Process Inds. 27, 213-16, 1943. CA 37, 4207 6, 1943. The history, occurrence, separation, properties and applications of the 16 elements constituting the so-called rare earths are briefly considered.

17. Marsh, J. K. The relation of yttrium to the lanthanons. A study of molecular volumes. J Chem Soc p 1084-6, 1947. CA 42, 831i, 1948. cf. CA 41, 4056e. The Y(III) ion has almost the same size as the Ho(III) ion, and as a result Y normally concentrates near HO in a fractional crystallization series. Sometimes, however, Y shows a behavior indicating a resemblance to Nd and Sm, which elements have a larger ion size than Ho. It has been suggested that Y on passing from the ionic to the covalent state undergoes a relatively larger increase in size than the lanthanons do under the same conditions. Direct evidence that Y has at times a larger volume than Ho was sought by measurement of molecular volumes. Four series of rare earth salts were prepared, the acetates, basic nitrates, ferricyanides, and acetylacetonates of La, Nd, Sm, Gd, Dy, Y, Er, and Yb. The rare earth acetates $(R.E. (C_2H_3O_2)_3 \cdot 4H_2O)$ were prepared by evaporation of a solution of the normal acetates in a desiccator, or by crystallization from warm neutral solutions. The basic nitrates $(R.E. O_5(NO_3)_8 \cdot 20 H_2O)$ were obtained by evaporating the normal nitrates to dryness and then heating until some decomposition occurred. The vitreous melts were then poured into cold H_2O to give clear hot solutions, from which crystals deposited overnight. The ferricyanides $((R.E.)Fe(CN)_6 \cdot 4 H_2O)$ were prepared by adding cold saturated $K_3Fe(CN)_6$ dropwise to a neutral chloride solution 100 grams of oxide per liter at 40-50°. The precipitate was washed and dried. The acetylacetonates $R.E. (CH(COCH_3)_2)_3$ were prepared by adding acetylacetone (3 g in 10 ml of EtOH) to an equivalent of R.E. acetate in 50 ml of cold H_2O to which aqueous NH_3 was then added dropwise. The precipitates were pressed well on a filter paper and dried in a desiccator. These precipitates all appeared to be slightly basic and did not give clear melts unless one or two drops of acetylacetone was added before fusion. The molecular volumes of these compounds were calculated from the densities, which were determined in the following manner. In the case of the acetates, the crystals were suspended in mixtures of $CHCl_3$ and $CHBr_3$, the densities of which were determined by a Westphal balance. For the basic nitrates and ferricyanides the densities were determined by the loss in weight of

a sample in CHCl_3 . The fused acetylacetonates were weighed in H_2O . A Pt bucket of 2 ml capacity and a 0.5 g sample were used in the last 3 cases. The molecular volumes for the series of acetates placed Y in the position normally associated with its ionic position. The crystalline basic nitrates and ferricyanides also had molecular volumes which placed Y in the same order as the ionic radii, even though these two salts were good examples of a case in which Y was rapidly accumulated with Nd and Sm in a fractionation series. The crystals were, therefore, regarded as polar in nature, and since the nitrates were regarded as existing in non-ionizing solvents only, these data suggested that a transition from the nonionic to ionic state occurred upon crystallization. The compounds formed with acetylacetone gave molecular volumes which placed Y in series with Nd and Sm, and this was taken as evidence of a covalent Y compound. Molecular volumes of the acetylacetonates were La 283, Y 275, Nd 273, Sm 271, Gd 271, Yb 269, Dy 269.

18. Marsh, J. K. The separation of the lanthanons (rare earth elements). Quart. Rev. (London) 1, 126-43, 1947. CA 42, 3276h, 1948. A review.
19. McBride, D. L. Minerals and metals advisory board report on use of rare earths in stainless steels, low alloy steels and magnesium. June 18, 1952. National Academy of Sciences, National Research Council, Washington, D.C. (Report No. MMAB-23-M) ATI-156 306. CONFIDENTIAL. A discussion is presented on use of rare earths in stainless steels, low alloy steels and magnesium.
20. Meier, D. J., and Garner, C. S. The exchange reaction between europium (II) and europium (III) in hydrochloric and perchloric acid solutions. J. Am. Chem. Soc. 73, 1894-5, 1951. CA 45, 7457 g, 1951. The change in half time as a function of the Eu concentrations showed that the reaction is of first order for both Eu (II) and Eu (III). The rate is independent of pH in the range 0.3-1.0 f. The exchange rate, R, is given by $R = k[\text{Eu(II)}][\text{Eu(III)}][\text{Cl}^-]$. The value for k at $39 \pm 4^\circ$ is 0.102 - 0.108.
21. Moeller, T., et al. Investigations of rare earth problems. (Final Rept.) Sept 1950. University of Illinois, Urbana. ATI-95 406. UNCLASS

This chemistry task, No. VII, is the final report on investigation of rare earth problems.

- 22 Morgan, R. Lanthanide series of rare earths. A bibliography U.S. A.E.C. TID-3029, 8pp., 1952. Crerar Met. Abstr. 1, No. 2, 29, 1952. An annotated list of unclassified references which includes a list of bibliographies and books, and AEC depository libraries. Subdivisions include rare earths in general with a separate section devoted to each element
- 23 Neunhoeffer, O. Simple and sensitive test for rare earths. Z. anal. Chem. 132, 91-4, 1951. CA 45, 3289e, 1951. Donau's test for Bi (CA 7, 3445) is based upon the fact that CaCO_3 impregnated with a Bi compound after ignition and cooling gives, by contact with the lower edge of a small H flame, a blue coloration. Sb or Mn in place of Bi give greenish blue or yellow colors. If a little $\text{Ca}(\text{NO}_3)_2$ is added to a rare earth solution free from halide and then some $(\text{NH}_4)_2\text{CO}_3$, the resulting CaCO_3 can be tested for rare earths with the flame. The test is so delicate that nearly all commercial Ca salts show the presence of traces of rare earths so that the $\text{Ca}(\text{NO}_3)_2$ solution should be purified by adding $\text{Fe}(\text{NO}_3)_3$, ammonia, and filtering. The $\text{Fe}(\text{OH})_3$ precipitate will contain the rare earth impurities. About 1 g of Ca as nitrate should be used in the test. Strong luminescence was obtained by the action of the electrons in the H flame, when Y, La, Ce, Pr, Nd, Sm, Dy, or Tm is present. In all cases, positive tests are obtained if 1% of rare earth element is present in the CaCO_3 . The colors shown are as follows: Y is pale, blue violet; La is brick red; Ce is yellowish green; Pr is red; Nd is orange red; Sm is yellowish green; Dy is pale green; and Tm is yellowish green.
24. Quill, L. L. Researches in rare earth chemistry. Record Chem. Progress 11, 151-63, 1950. CA 45, 1827e, 1951. Chemical and physical methods of separating rare-earth compounds are reviewed, with detailed attention to the ion-exchange method. Data on oxidation states and crystal structure are presented. 26 references
25. Quill, L. L., and Rodden, C. J. Scandium, yttrium, and the rare earths. Natl. Nuclear Energy Ser., Div. VIII, 1, Anal. Chem. Manhattan Project, 494-508, 1950. CA 45, 1908e, 1951. Since the

rare earths occur as fission products, considerable attention has been paid to their separation and subsequent radiochemical determination. The separation of the individual rare earths is not considered in this chapter but group separations are given. The actual determination of each rare earth was usually made with the spectroscope. Details are given for (a) precipitating the oxalates, (b) precipitating the fluorides, (c) hydroxide precipitation, (d) various other methods, (e) the peroxide precipitation of U, (f) the use of carriers, (g) the formation of complexes with UO_2^{2+} . Extraction of $\text{UO}_2(\text{NO}_3)_2$ with ether and the extraction of Th salicylate in an NH_4NO_3 -AcOH mixture with 90% EtOAc and 10% Et_2O are described as well as the volatilization of rare earth chlorides in a stream of S_2Cl_2 when present with Th and U. 36 references.

26. Ryabchikov, D. I. and Terent'eva, E. A. Methods of separation of rare earth elements. *Uspekhi Khim* 16, 461-89, 1947. CA 42, 2200i, 1947. A critical review; 118 references.
27. Ryabchikov, D. I., Terent'eva, E. A., and Sklyarenko, Uy. S. Analytical chemistry of the rare earths and accompanying elements. *Trudy Komisii Anal Khim., Akad. Nauk S.S.S.R.* 3, 23-88, 1951. CA 47, 2629a, 1953. A comprehensive review of the atomic structure, occurrence, mineralogy and predominantly of the analytical properties of elements 57-71 and of Sc, Y and Th. 243 references.
28. Vickery, R. C. The rare earths. *Metallurgia* 30, 130-4, 215-20, 1944. CA 38, 5741.5, 1944. A survey of the chemistry of the rare earth elements, including methods of separation identification and determination.
29. Vickery, R. C. Separation of the rare earth elements by chloride volatilization. *J. Soc. Chem. Ind.* 65, 388-90, 1946. CA 41, 3007d, 1947. The volatilization temperatures of the chlorides of La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er, and Yb were found to be, respectively, 950°, 900°, 930°, 925°, 895°, 865°, 730°, 780°, 925°, and 930° at 760 mm.; and 476°, 400°, 425°, 425°, 410°, 395°, 360°, 370°, 420°, and 425° at 1 mm. The following binary mixtures containing 0.4 g of each chloride were fractionally volatilized: La-Nd, Ce-Tb, La-Yb, Tb-Er, Pr-Gd. The volatilization temperatures were, respectively,

430°, 375°, 450°, 390°, 410°. The following residues were obtained, respectively: 0.385 g free of Nd, 0.392 g free of Tb, 0.404 g with traces of Yb, 0.368 g with traces of Tb, and 0.400 g free of Gd. The following ternary mixtures containing 0.3 g of each chloride were fractionally volatilized: La-Ce-Yb, Pr-Nd-Sm, and Tb-Dy-Er. The 1st fractions were volatilized at 415° and 360°, respectively, and were 0.307 g with Yb, 0.315 g with Pr and Nd, and 0.304 g with Dy, respectively. A 2nd fraction was obtained from the 1st and 3rd ternary mixtures at 440° and 400°, respectively, and were 0.292 g free of La and 0.295 g with Tb, respectively. The 3 residues were, respectively, 0.296 g free of Yb and Ce, 0.586 g free of Sm, and 0.298 g free of Dy and Tb. From a monazite sand, and a rare earth-bearing residue, metals of Groups I and II and Th were removed, the residues were converted into chlorides and fractionated at 380° and 420°. The 1st fraction contained Cd, Tb, Dy, and some Ce and Y. The 2nd fraction contained Ce, Sm, Er, Tm, Y, and some Pr, Nd, and Yb. The residue had Pr, Nd, Yb, and La.

30. Vickery, R. C. Production analysis and applications of the lanthanons. *Ind. Chemist* 29, 291-4, 1953. *CA* 47, 8429b, 1953. A review with 56 references.
31. Vickery, R. C. Recent advances in lanthanon chemistry. *Ind. Chemist* 29, 260-5, 291-4, 1953. *Eng. J.* p. 911, 1953. Methods of separation and preparation; uses and applications, such as in glass, glazes, ceramics as polishing powder and metal alloy. Bibliography.
32. Vickery, R. C. Chemistry of the lanthanons. 296 pp., 1953. Butterworths Scientific Publications, London and Academic Press, Inc., New York. *Creat. Met. Abstr.* 2, No. 8, 40, 1954. The historical development, modes of occurrence, structure, spectroscopy and properties of the light and heavy lanthanons are covered in different chapters of this authoritative work. The separation techniques considered include precipitation, crystallization, oxidation-reduction, solvent extraction, ion exchange, and thermal reactions. A complete separation scheme of individual lanthanons is given. Analytical methods and purifications are described. Among the uses of the lanthanons which are enumerated are neodymium for purple glass and

artificial gems, cerium in ferrous metallurgy, and several lanthanons for catalysts and alkaline phosphors.

33. Weaver, B. Separation factor; criterion for evaluation of fractional separation processes. Anal. Chem. 26, 474-5, 1954. CA 48, 7479c, 1954. The separation factor in fractional separation is the ratio between two elements in one fraction divided by their ratio in the other fraction. It is independent of the original composition and of the extent of the separation process. More use should be made of the separation factor as a criterion for determining the effectiveness of a single stage in a division of a mixture into two fractions. The literature dealing with separation of the Hf-Zr pair and the rare-earth group was surveyed as a means of evaluating separation methods. Separation factors have been calculated and compiled from the small amount of useful data.
34. West, T. S. Separation methods in metallurgical analysis. Metallurgia 43, 41-6, 1951. CA 45, 5560e, 1951. A review of recent progress in extraction and precipitation methods, covering extraction of Fe, Sb, U, Au, Ca, Li, separation of the Cu and As groups, separation of Sr, Ba, and Pb from Ca and other metals, separation of Ca from Mg, of Bi from Pb, of Fe, Al, Cr, U, Tl, and Zr from Mn, Co, Ni and the alkaline earths by use of pyridine, separation of Th, Zr-Hf, Ce and quadrivalent from trivalent Pu by use of m-nitrobenzoic acid, separation of Ce and Th, Th from the rare earths, Al and Be, Cd and Zn, and separation of the Pt metals. 63 references.
35. Wilkinson, G. and Grummitt, W. E. Chemical separation of fission products. Nucleonics 9, No. 3, 52-62, 1951. CA 46, 6965b, 1952. Long-lived fission products from thermal neutron bombardment of natural U and U^{233} are chemically separated. The procedure involves the separation of elements from Ge to Pr. Long-lived isotopes of Sr, Y, Zr, Nb, Mo, Ru, Sn, Sb, Te, I, Cs, Ba, Ce, and Pm are found; short-lived activities of Rh, I, and La are present as daughter products of longer-lived parents. Aliquots of a solution of the bombarded U sample dissolved in HNO_3 are used for separation of one or a small group of ions. Appropriate carrier for the element (2-10 mg.) and "hold back" carriers are added and the solution is subjected to oxida-

tion-reduction cycles to facilitate radiochemical exchange. Usual semimicro techniques are employed. The separated element is finally precipitated as a stoichiometric compound which is suitably mounted for weighing and counting. Samples of satisfactory radiochemical purity are separated from fission-product solutions containing 10^4 - 10^6 times the activity of the separated product. Distillation methods are used for Ge, As, Se, Ru, Tc, Sn, Sb; solvent extraction methods for Mo, I, Br; precipitation methods for Rb, Sr, Y, Zr, Nb, Rh, Pd, Cd, In, Te, Cs, Ba, La, Ce, and other rare earths; electrochemical separations are used for Ag and Sb.

36. Wylie, A. W. Composition of some Australian monazites. Australian J. Appl. Sci. 1, 164-71, 1950. CA 45, 987f, 1951. In the total light lanthanons ("cerium-group" elements), in 8 Australian monazites, the range of composition was: La_2O_3 21-30%; Ce_2O_3 43-48%; Pr_2O_3 4.8-6.1%; Nd_2O_3 18-24%; Sm_2O_3 3.7-5%. An approximate method is described of correcting for contamination of the heavier lanthanons ("yttrium-group" elements) with the lighter lanthanons in fractional precipitation with Na_2SO_4 .
37. Wylie, A. W. The rare earths or "lanthanons". Roy. Australian Chem. Inst. J. and Proc. 17, 377-97, 1950. CA 45, 3210b, 1951. A review. The atomic molecular volumes, x-ray diffraction and magnetic properties, oxidation states, and optical and absorption spectra are interpreted in terms of the electronic configurations and energy states of the individual elements. The chemistry of the metals and of individual groups of compounds, viz. the hydroxides, oxides, chlorides, nitrates, sulfates, and other oxy-salts of these elements is also discussed, and published methods for separating the elements from one another are reviewed in detail.

II. EXCHANGE RES'NS

38. Ayres, J. A. Purification of zirconium by ion exchange columns. J. Am. Chem. Soc. 69, 2879-81, 1947. CA 42, 1522c, 1948. Zr nitrate produces in water colloidal solution, the Zr exists not as an ion but rather as the hydrous oxide with no ionic charge. Since Zr is not charged it will not be removed if the solution is poured through an ion-exchange column. This should serve as the basis for a separation of Zr from impurities that are present as charged ions. Experiments were carried out to determine (a) the recovery of Zr in the effluent when a solution is poured through a column filled with ion-exchange resin; (b) the degree of purification from other elements of interest such as Fe, Ti, Be, and the rare earths, and (c) the efficiency of this method in extracting Zr from ores. The cation exchanger was Amberlite IR-100, and the anion exchanger was Amberlite IR-4. When solutions containing 10 g $\text{ZrO}(\text{NO}_3)_2$ were poured through the H-form of Amberlite IR-100 at a rate of 5-6 ml per minute 98% of the Zr remained in the effluent. With the Na-form of the resin 99% of the Zr passed through. The capacity of the resin for Zr is 0.00084 mole/100 cc of resin. This small capacity is attributed to true surface adsorption. Two grams of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to 200 ml of the Zr stock solution and passed through the column. Essentially all the Zr passed through; about 98% of the iron was absorbed. A similar experiment was carried out for mixtures of Ti and Zr. Essentially all the zirconium passed through whereas about 5/6 of the titanium was absorbed. A mixture of a solution of 1.4 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 40 ml water and 200 ml of Zr stock solution was tested. Practically all the Zr passed through, but the amount of La in the effluent was less than 1%. Beryllium was completely removed by the ion-exchange resin. A procedure is presented for obtaining a purified solution of Zr salt from a typical ore (alvite).
39. Boyd, G. E., Adamson, A. W., and Myers, L. S., Jr. Ion charge and exchange rates with ion-exchange polymers. J. Am. Chem. Soc. 72, 4807-8, 1950, cf. CA 42, 1781g. CA 45, 2286d, 1951. The equilibrium exchange rates for uni-, bi-, and trivalent cations on

Amberlite IR-1 in dilute HCl diminish rapidly as ionic charge increases. Na^{24} , U^{233} , and Ce^{144} exchange by film diffusion from 0.001 N, 0.003 N, and 0.1 N HCl, respectively, whereas they exchange by particle diffusion from 0.1 N, 0.3 N, and 0.5 N HCl, respectively. Diffusion through the exchange polymer is slower than in aqueous solution and depends only on the nature and composition of the exchanger, the temperature, the ionic strength of the external solution, and the charge of the diffusing ion.

40. Bregman, J. I., and Murata, Y. Phosphonous and phosphonic cation-exchange resins. *J. Am. Chem. Soc.* 74, 1867-8, 1952, cf. *CA* 42, 9008h; 45, 9994e, *CA* 45, 4524i, *CA* 47, 6217e, 1953. The resins are the first to show a selectivity for Na over K. Potential applications of the resins include Na depletion in physiological applications, rare earth separations, and use in mixed-bed and reverse demineralization units.
41. Dolar, D., and Draganic, Z. Separation of traces of rare earth elements from uranium with Amberlite IR-120 resin. *Rec. trav. inst. recherches structure matiere* 2, 77-83, 1953, (in English). *CA* 47, 6816b, 1953. After adsorption in the column, UO_2^{++} is eluted with N oxalic acid. Ce, Eu, and Y can then be eluted with 5N HCl.
42. Duncan, J. F., and Lister, B. A. J. Ion-exchange studies. II. The determination of thermodynamic equilibrium constants. *Discussions Faraday Soc.* No. 7, 104-14, 1949; cf. *CA* 44, 9770i, *CA* 45, 19i, 1951. Batch equilibrium methods and column methods for the Ba-H and La- NH_4 exchange systems were used to evaluate the activities of ions in an exchanger. Radiochemical tracer methods were applied in this critical examination of the postulates used by different authors for this type of determination. The assumption that the activities in the exchanger are proportional to the molar concentrations gives an approximate constant value for the mass product, but even here the mass product varies by about 50%, rising to a maximum at an equivalent fraction of about 1/3 for the multivalent ion in the exchanger. The activities in the exchanger may have been incorrectly evaluated because of the effect of some secondary process, such as adsorption, solution of the ions in the exchanger, or swelling of the resin.

43. Fitch, F. T., and Russell, D. S. Separation of the rare earths by ion-exchange procedures. *Can. J. Chem.* 29, 363-71, 1951. *CA* 46, 373i, 1952. The NH_4 salts of the iminodiacetic acids from complex ions with the rare-earth elements involving both one and two iminodiacetate ions. These acids were examined as possible complexing agents in the chromatographic separation of the rare earths with cation-exchange resins since the stability of the rare-earth complex increases with atomic number. Methods which greatly reduce the time and material requirements for the separation of the Ce group elements with nitrilotriacetic acid are given.
44. Fitch, F. T., and Russell, D. S. Determination of lanthanum in rare earth mixtures. *Anal. Chem.* 23, 1469-73, 1951. *CA* 46, 58i, 1952. With a suitably prepared resin bed supported on sand or ground glass, it is possible to remove rare-earth cations. Then by elution with a weak solution of hydrazinodiacetic acid, all rare earths except La can be removed and finally the La cations can be stripped from the bed by a 1% solution of the acid in a solution containing 2% NH_4Cl at pH 7.5-8. Finally the La can be precipitated as oxalate and the washed precipitate heated at 800° to get La_2O_3 . Good results can be obtained in determining 80-100 mg. of La_2O_3 .
45. Freiling, E. C., and Bunney, L. R. Ion exchange as a separation method VII. Near optimum conditions for the separation of fission product rare earths with lactic acid eluant at 87° . *J. Am. Chem. Soc.* 76, 1021-22, 1954. *Crerar Met. Abstr.* 2, No. 9, 35, 1954. Lactic acid, more selective than citric acid, has been studied for separation of the lanthanons up to and including terbium. 1 M lactic acid at pH 3 gives a complete separation at 87°C of europium and samarium in a reasonable time. A discontinuous gradation in eluant strength (0.85 to 10 M) gave good results with separating terbium and gadolinium from europium. Data are tabulated.
46. Fulmer, F. H., et al. The separation of rare earths by ion exchange III. Pilot-plant-scale operations. U.S. AEC, ATI-23915. UNCLASS. Detailed procedures have been given for the large-scale separation of the rare earths, using Amberlite IR-100 and 0.5% citric acid-ammonium citrate solutions as the eluant. The process employed

24 columns 4 inches in diameter and with 8 ft. of resin bed length. The pH of the citrate eluant was 3.9. The growth of mold was eliminated by the use of 0.1% phenol. Large samples of rare earths of high purity were obtained by these procedures, portions of which have been furnished to other activities of the Manhattan Project. Examples of the quantity and quality of several fractions on hand are included.

47. Futterknecht, A. Use of ion exchange resins in analytical chemistry. *Chim. anal.* 32, 306-8, 1950. *CA* 45, 2361g, 1951. Ion-exchange resins can be used for separating most inorganic ions, for separating many organic compounds and furnish the only means for rapidly isolating radio-isotopes. Two experiments are described to illustrate their use.
48. Harris, D. H., and Tompkins, E. R. Ion-exchange as a separations method. II. Separations of several rare earths of the Cerium group. (La, Ce, Pr, and Nd.) *J. Am. Chem. Soc.* 69, 2792-2800, 1947. *CA* 42, 1835g, 1948. Experiments with mixtures of Y and Ce showed that Dowex 50 is much superior to the Amberlite resins IR-1 and IR-100 for the separation of rare earths by the citrate elution technique. With Dowex 50 it was possible to get essentially complete separations between several rare earths of the Ce group in a single adsorption-elution cycle. Pr was separated in trace and in bulk amounts from Ce. Ce was separated from La. In one run a mixture of nearly equivalent quantities of Nd, Pr, and Ce was separated into its constituent elements. The impurities were below a detectable level (probably less than 0.1%). III. Equilibrium studies of the reactions of rare earth complexes with synthetic ion-exchange resins. Tompkins, E. R. and Mayer S. W. *Ibid.* 2859-65. For any given composition of solution the distribution coefficient of a rare earth between the two phases does not change as the ratio of the weight of Dowex 50 resin to the solution volume is varied. The exchange reaction between a rare earth ion and the NH_4^+ resin compound follows the relation predicted by the mass law. The exchange constants for several rare earths, equilibrated with the NH_4^+ compound of Dowex 50 resin, vary. This shows that some separation of rare earths is possible without

the use of complexing agents when this resin is employed. A study of the citrate complexes showed that the one in which three H_2Cit^- ions are combined with a rare earth ion is responsible for the relatively large separation factors between these elements. A preliminary, comparative study of the effectiveness of several exchangers (Dowex 50, Dowex 30, Duolite C, and Amberlite IR-1) and complexing agents (citric acid, tartaric acid, lactic acid, sulfosalicylic acid, ethyl acetoacetate, acetylacetone, oxalic acid, citric acid in 50% EtOH) was made. Since the NH_4^+ ion concentration, the total rare earth concentration, the citrate concentration and the pH are interdependent variables, it should be possible, from the results of these equilibrium studies, to choose a number of sets of "optimum conditions" for a column separation. When Dowex 50 is used in the column, the concentration of the rare earth ions in the solution cannot exceed 3×10^{-4} M without adversely affecting the separation. With Amberlite IR-1, this concentration must be below 10^{-6} M. The pH of the citrate solution should not be greater than 3.2, since appreciable concentrations of the citrate ions HCit^{2-} and Cit^{3-} interfere with the separation.

49. Heijde, van der, H. B., and Aten, A. H., Jr. Adsorption curve of a rare earth in an ion-exchange column. *J. Phys. and Colloid Chem.* 55, 740-4, 1951. CA 45, 6896d, 1951. The distribution curves of activated dysprosium ions on the resin (and interstitial solution) along an exchange column after the initial adsorption and also after two different phases of elution with NH_4 citrate solution were determined. The results agree well with predictions made on theoretical grounds by Boyd, et al. (CA 42, 1782d)
50. Higgins, G. H., and Street, K., Jr. Note on ion-exchange separation of europium, gadolindium and terbium. *J. Am. Chem. Soc.* 72, No. 11, 5321-2, 1950. CA 45, 2286i, 1951. The elution of Y, Eu, Gd, and Tb from Dowex-50 by 5% NH_4 citrate at 97° was studied by use of radioactive tracers to check the work of Ketelle and Boyd (CA 42, 1782h) with which unpublished work did not agree. Spectrographic measurements supplementary to the activity measurements showed the sample was separated into 3 fractions corresponding to Y, Tb, and Eu and Gd, respectively. Apparently K. and B. identified the Tb

activity as Gd. The more marked separation of Tb from Gd than Eu from Gd is related to the half-filled 4f configuration.

51. Higgins, C. E., and Baldwin, W. H. The separation of yttrium and europium with anion exchange resins. April 3, 1951. Union Carbide and Carbon Corp., Oak Ridge, Tenn. ATI-96 278. UNCLASS. The separation of yttrium and europium tracers by selective elution from cation exchange resins depends upon the formation of anionic complexes of these metals. The separation of such metals as niobium and tantalum, zirconium and niobium by selective elution of their anionic complexes from the anion exchanger.
52. Higgins, C. E., and Baldwin, W. H. The separation of yttrium and europium with anion exchange resins. U. S. AEC ORNL-894, 4pp., April 3, 1951. *Crerar Met. Abstr.* 2, No. 4, 53, 1953. The experimental procedure made use of Y^{91} and natural europium bombarded in the ORNL reactor as tracers. The resin employed was Dowex-1 and the complexing agent was Versene (EDTA). The yttrium peak activity occurred at 30 columns. This separation compares with elution from Dowex-50 with citrate buffer at pH 3.0.
53. Huffman, E. H., and Oswalt, R. L. Rare-earth separation by anion exchange. *J. Am. Chem. Soc.* 72, 3323-4, 1950. *CA* 46, 3904c, 1952. A separation of Pm^{137} and Eu^{154} in tracer quantities has been carried out by development of their citrate complexes at pH 2.1 on an anion-exchange column containing Dowex A-1 resin, the original chloride form of which had been treated with citrate solution of the same concentration and pH as that containing the rare earths to be separated.
54. Huffman, E. H., and Oswalt, R. L. (to U. S. AEC.) Rare earth separation by anion exchange. U. S. 2,636,044, April 21, 1953. *CA* 47, 7744i, 1953. See preceding abstract.
55. Jeng-Tsong, Y. Separation of traces of actinium²²⁷ from large amounts of lanthanum by ionic exchange. *J. chim. phys.* 47, 805-6, 1950; cf. *CA* 44, 6333c. *CA* 45, 3746g, 1951. Ac^{227} (3.12 millicuries) was separated from 160 mg of La in a column of ion-exchange resin (Amberlite IR-100) with an eluent of 5% NH_4NO_3 (pH 5.5). In a single manipulation, a product was obtained whose activity was 5.31 millicuries per mg.

56. Jeng-Tsong, Y. Radionography. Specificity of ion exchangers. Separation of lanthanum and yttrium. Anal. Chim. Acta 4, 59-67, 1950. CA 44, 6333c, 1950. Two French adsorbing resins have been studied by means of radioactive tracers, and their specificity was found to be very satisfactory. The adsorbing power in g ions is inversely proportional to the valence of the adsorbed ion, though constant to the ionic concentration. The elution and separation of La and Y have been performed ionographically.
57. Johnson, C. M. Rapid determination of cerium in steel. Iron Age 169, No. 3, 94-6, 1952. CA 46, 2444f, 1952. To determine the Ce group in high-Cr steels, weigh 2- and 3-g samples into 600-cc beakers, dissolve in 100 cc of 6 N H_2SO_4 , boil down to 70 cc, cool, add about 12.5 g of dry Na_2O_2 with stirring, dilute to 100 cc, boil down to 70 cc, add 40 cc H_2O , stir in a little low-ash filter-paper pulp, and filter the precipitate. Do not wash. Dissolve the precipitate off the filter with 30 cc of hot 4.5 N H_2SO_4 , added in 5 cc portions. Dilute the filtrate to 300 cc, add 50 cc of 5% $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution and NH_4OH until the solution turns brown and slightly cloudy, stir well, and add 1 g of $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Let the white $\text{Ce}(\text{C}_2\text{O}_4)_2$ settle over night and then filter and wash 40 times with a solution containing 50 cc of the 5% oxalate solution and 1 g of $\text{H}_2\text{C}_2\text{O}_4$ in 500 cc of H_2O . Ignite and weigh the red CeO_2 .
58. Johnson, W. C., et al. Rare earths separation developed on Manhattan Project. Chem. Eng. News 25, 2494, 1947. CA 41, 7305b, 1947. The methods for separating the rare earths by adsorption on Amberlite resins are outlined chronologically. Credit for certain developments is assigned to individuals and groups.
59. Johnson, J. W. The ion exchange process. Fairchild Engine and Airplane Corp., NEPA Div., Oak Ridge, Tenn. July 1948. ATI-31640. UNCLASS. A discussion is given on an ion exchange process, to summarize the applications of ion exchange to the separation of mixtures of rare earth and related elements. The report includes a review of the factors affecting adsorption and elution, followed by a section devoted to experimental data dealing with separations of mixtures of rare earth and the effect of varying conditions. The adsorp-

tion band width has been shown to vary with the properties of the resin, concentration of adsorbate ions, flow rate, and temperature. The nature of the resin (i.e. fibrous structure) determines the ease with which solution can infiltrate into the interior of the particle, and thus affects diffusion time and the extent of approach to equilibrium. The elution process, on which the efficiency of the separation is primarily dependent, has been shown to depend on complexing agent, hydrogen ion concentration, flow rate, bed length, particle size, and temperature.

- 60 Ketelle, B. H., and Boyd, G. E. The exchange absorption of ions from aqueous solutions by organic zeolites. IV. The separation of yttrium-group rare earths. J. Am. Chem. Soc. 69, 2800-12, 1947. CA 42, 1782g, 1948. The studies presented had as their objective the production, identification, or characterization of the radio-isotopes of the Y-group rare earths by the ion-exchange method. Radioisotopes were used, and the separation was followed by means of a counting cell. Various theoretical factors involved in the studies were surveyed. Studies under various conditions of temperature and pH with Amberlite IR-1 or Dowex-50 as the ion-exchange resin and the citrate elution technique (Spedding, et al., CA 42, 1520d) Tompkins, et al., (CA 42 1834i), led to the following conclusions: With a 97-cm by 0.26-sq cm bed of 270/325 mesh Dowex-50 adsorbent maintained at 100°, the optimum pH of the 4.75% citric acid eluant was 3.2 for the separation of the Y earths and 3.4 for the Ce earths. A temperature of 100° permitted the use of elutriant flow rates as high as 2 ml/sq cm/min, which greatly reduced the time required for a separation. In a typical experiment, mg quantities of Lu, Yb, Tm, Er, Ho, and Y were separated in 30 hr. The fractionation of the heavy rare earths could be made so complete that the method was established as a promising procedure for the quantitative analysis of rare earths for cationic impurities. A sample of Er_2O_3 , previously exhaustively purified, in which all other rare earths were reported absent by spectrographic analysis, was shown to contain 10 p.p.m. of Tm by irradiation of the Er_2O_3 with neutrons and subsequent chromatographic separation. The sequence of relative adsorbability

among the rare earths is La>Ce>Pr>Nd>61>Sm>Eu>Gd>Tb>Dy>Y>Ho>Er>Tm>Yb>Lu. This progression is in the same order as that of the crystal ionic radii and the variation of basicity predicted by von Hevesy (CA 21, 2614). Thus, rare earths that form strong bases will replace those that form weaker bases from the absorbent. The relative position of Y, between Dy and Ho, is in excellent agreement with predictions based on ionic radius. The triad Dy, Y, and Ho constitutes what may be taken as the most difficultly separable of all the rare earths. Quantitative comparisons of the relative adsorbability within the Y-group earths were made possible by using the data from a large number of chromatograms. The ratios of the distribution coefficients of neighboring members are given in the following table.

Element	$S_{n+1}:S_n$
Lu }	1.21 = 0.01
Yb }	1.44 = .02
Tm }	1.55 = .02
Er }	1.57 = .02
Ho }	1.30 = .02
Y }	1.20
Dy }	

The average deviation found for these ratios from experiment to experiment, in spite of differing conditions of flow rate, pH, and temperature, is less than 2%; this emphasizes the highly reproducible character of adsorption-column performance.

61. Ketelle, B. H., and Boyd, G. E. The ion-exchange separation of the rare earths. J. Am. Chem. Soc. 73, 1862-3, 1951; cf CA 42, 1782h. CA 45, 7407f, 1951. Separation of the Y-group rare earths from Gd, Eu, and Sm was effected with a 0.26-sq cm by 97-cm 270/325-mesh Dowex-50 column at 100° with citrate buffer at 100° (pH 3.28) at -0.64 cm/min. Previous errors in interpretation are corrected.
62. Lister, B. A., and Smith, M. L. The fractionation of cerium (III) and neodymium mixtures on an ion-exchange column. J. Chem. Soc. p. 1272-5, 1948. CA 43, 6535e, 1949. Eleven 1.1 m columns in series, 1 cm in diameter, were packed with Zeokarb H.I.P., sulfonated

coal The columns were filled with water and 1M or 0.25 M Ce-Nd nitrate solution was started through the column at a rate of 1.4 ml/min. When the percolate contained Ce-Nd, the initial reservoir was changed back to water and the flow was continued as long as Ce-Nd washed out. The first and last fractions showed an increase in Nd concentration, the last due to dilution of the solution with the following water. The separation was better with the dilute solution. The resin retention of the larger Ce ion agrees with the results of Jenny (CA 21, 3785), but not with those of Russell and Pearse (CA 37, 3363.3).

63. Loriers, J , and Carminati, D. Utilization of nitrilotriacetic acid for the separation of ceric earths by ion exchange. Compt. rend. 237, 1328-30, 1953. Crerar Met. Abstr. 2, No. 6, 35, 1954. It was found that ceric earths can be separated very efficiently by the use of nitrilotriacetic acid as an eluant on an ion exchange column. The ion exchange column used was carried out at a pH of 4 with a solution of 14 g nitrilotriacetic acid per l. The separation of 10 g of ceric earths, containing 2% Sm, 48% Nd, 24.5% Pr, 0.5% Ce and 25% La is shown in a diagram. The greater part of neodymium and praseodymium and almost all of the lanthanum were obtained practically pure. The same principle was used successfully in the separation of larger quantities of 300 to 400 g of oxides on larger columns
64. Marinsky, J. A. , and Khym, J. X. Order of elution separation of rare earths from Amberlite resins with ammonium citrate. Natl. Nuclear Energy Ser. Div. IV, 9, Radiochem. Studies: The Fission Products, Book 3, 1747-51, 1951. CA 47, 12103f, 1953. The order of elution of the lighter rare earths from Amberlite resins was shown to be that of decreasing atomic number except that Y behaves like a rare earth in the Gd region.
65. Mayer, S. W , and Tompkins, E. R. Ion exchange as a separation method. IV. A theoretical analysis of the column separation process. J. Am Chem. Soc 69, 2866-74, 1947. CA 42, 3237g, 1948. A simple theoretical analysis of the ion-exchange column separation process based on the analogy of the ion-exchange separation column to the fractional-distillation or extraction column was developed for the case in which the distribution coefficient of the solute between the

solid and liquid phases remains constant throughout the column. Application of this theory to the rare-earth separations reported earlier by Harris and Tompkins (CA 42, 1835g), and for the prediction of separation in studies of the pairs Eu-61 and Ce-Pr demonstrated its usefulness. The elution curves derived from the theory fit the observed data within the limits of experimental error when near-equilibrium conditions prevail in the column. The theory was also applied to determination of the purities of the rare earths separated by this process, and the general applicability of the theory was discussed.

66. Mayer, S. W., and Schwartz, S. D. The association of cerous ion with sulfite, phosphate, and pyrophosphate ions. J. Am. Chem. Soc. 72, 5106-10, 1950. CA 45, 2286g, 1951. The distribution of Ce^{3+} between ion-exchange resin Dowex 50 and solutions of H_2SO_3 , H_3PO_4 , and $\text{H}_4\text{P}_2\text{O}_7$ was measured. The constants for the reaction between Ce^{3+} and these acids were calculated. The association constants for CeSO_3^+ , CePO_4 , and CeP_2O_7^- are 1.1×10^8 , 3.4×10^{18} , and 1.4×10^{17} , respectively. Bjerrum's theory (CA 22, 1263) for ion-pair formation does not predict these association constants. A correlation between the association of oxy-acid anions with H^+ and their association with Ce^{3+} was pointed out.
67. Mayer, S. W., and Freiling, E. C. Ion exchange as a separation method. VI. Column studies of the relative efficiencies of various complexing agents for the separation of lighter rare earths. J. Am. Chem. Soc. 75, 5647-9, 1953. Crerar Met. Abstr. 2, No. 5, 962, 1954. Am-Eu and Eu-Tb separation factors were determined for some complexing agents in the varying concentrations under dynamic conditions. A comparison of separation factors gives the order of selectivity as $\text{EDTA} > \text{lactate} = \text{glycolate} > \text{malate} > \text{citrate}$. EDTA has a low solubility in the pH range most useful for separation. Graphs and tables are given.
68. McLane, C. K., and Peterson, S. Separation of actinium from rare earths using ion-exchange resin. Natl. Nuclear Energy Ser., Div. IV, 14B, Transuranium Elements, Pt. II, 1385-7, 1949. CA 44, 3808h, 1950. Act^{228} was separated from La^{140} by using pretreated Amberlite IR-1 resin in a 35-cm column, from which La and Act

were eluted with a 0.25 M citrate solution containing 2.4 parts of citric acid to 1 part of di-NH₄ citrate.

69. Moeller, T., and Starr, D. D. Separation of rare earths by ion exchange. (Scientific Report), 1947. University of Illinois, Urbana. ATI- 86 664 UNCLASS. Research on the behavior of rare earth ions in exchange reactions is described. The materials and methods of analysis are discussed, and ion exchange studies in both static and dynamic systems are outlined. The equilibria of 0.1 M solutions of yttrium, lanthanum, and neodymium nitrates with Amberlite IR-100 H, Zeo-Karb Na, were found to be nearly alike. The order of the removal of several rare earth ions from an ion exchange column by selective elution with citric acid elutriants was found to be yttrium, neodymium, cerium, lanthanum, corresponding to the order of increasing crystal radii. It was found that rare earth oxalates could be dissolved by boiling a slightly acid aqueous suspension of the oxalate with ammonium peroxydisulfate.
70. Moeller, T., and Matheson, A. R. Observations on the rare earths ion exchange studies on thorium-rare earth mixtures. (Scientific Report) University of Illinois, Urbana. May 1948. ATI-86 690. UNCLASS. In connection with ion exchange studies on thorium-rare earth mixtures, a cation exchange resin, Amberlite IR-100 H, was used to determine if thorium and neodymium ions could be separated from each other by this means. The preparation of solutions and the analytical methods used are described, and the action of various eluting agents is discussed. Various substances were found to be capable of effecting a separation of thorium ions from neodymium ions, namely, 0.5% and 5% hydrochloric acid solutions, in the pH range 2.60-2.88; saturated ammonium carbonate solution, pH 8.56, saturated ammonium oxalate solutions, pH 5.15, 6.28, and 8.70. The pH of the solutions used as eluting agents is very important in effecting any elution and separation.
71. Myers, L. S., et al. The exchange adsorption of ions from aqueous solutions by organic zeolites - V. Equilibrium and rate measurements on the trivalent rare earths. U.S. AEC. ATI-55876. UNCLASS. An experimental determination of the exchange adsorption of trivalent

lanthanum, cerium and yttrium from 0.1 M hydrochloric acid solutions by Amberlite IR-1 gave the following sequence of adsorption affinity: $\text{La}^{+++} \text{Ce}^{+++} \text{Y}^{+++}$. Measurements of the rate of exchange of the trivalent rare earth cations showed that either a film or a particle diffusion rate process controlled depending upon the magnitude of the equilibrium distribution coefficient and on the adsorbent particle diameter. The transition from a film process to particle diffusion occurred in the concentration range: 0.2-0.5 M with ammonium perchlorate solutions. The same transition occurred around 0.01 M with hydrochloric acid solutions for the exchange of the univalent alkali metal cations. The rates of the exchange adsorption of La(III) , Ce(III) and Y(III) from 0.1 M hydrochloric acid solutions were approximately 1000 times smaller than those for the univalent alkali cations under the same circumstances.

72. Parker, G. W., and Lantz, P. M. The separation of milligram quantities of element 61 from fission. U. S. AEC ATI-56062. UNCLASS. Ion-exchange elution experiments have been performed to eliminate coinciding contaminants from rare earth separations. The work was directed principally toward the purification of milligram amounts of the ca. 4y element 61^{147} . At this time, there are only three well established isotopes of element 61 with respective masses 147, 148, and 149, although 151 is a probable 12 m activity. Others at masses 144, 145, 146 of varying characteristics have been proposed and will soon be clarified as to their radioactivity. Identification of the 5.3d 61^{148} radioisotopes, produced by radioactive neutron capture of 61^{147} in the Clinton pile, is described. The incidental purification of the little-known long-lived fission isotopes of Sm^{151} and Eu^{155} has permitted an observation of their radiation characteristics.
73. Pinta, M. Analysis of rare earths fractionated on an ion-exchange column. J. recherches centre natl. recherche sci., Labs. Bellevue (Paris), No. 22, 19-35, 1953. CA 47, 7936c, 1953. Mixtures of rare earths were dissolved in diluted HCl adsorbed on a column of Dowex 50 (120 cm high and 5 cm in diameter) and eluted with NH_4 citrate solution containing 5% citric acid at various pH values (adjusted with NH_4OH). The eluates were collected in 125, 250, and 500 ml

fractions, and the rare earth oxides were precipitated with base. Sufficient HCl to dissolve 0.1 g of precipitated oxide was added, the solution diluted to 10 ml, and the flame spectrum photographed (14 min exposure, 80 μ slit width). Standards were oxides of theoretical formula M_2O_3 , obtained by calcination of hydroxide or oxalates. By this method eluate fractions were examined for rare earth content in less than 1 hr. The error was not over 3%, and oxide concentrations up to 0.5% were detected. Greater sensitivity could not be had because of the complexity of the flame spectra of the rare earths. A solution of Ce earths was adsorbed on a column and eluted at pH 3.1. After elution of Tb, Y, Gd, and Sm, Nd and Pr were eluted separately, then La after the pH was raised to 3.4. A solution of Y earths was adsorbed and eluted at pH 2.85. Yb, Tb, Er-Ho, Ho-Dy, and Y-Tb fractions were separately eluted. A solution of Y earths, rich in Er and Y, was adsorbed and eluted at pH 2.80, giving a separation into Er and Y fractions, each containing small amounts of Ho.

74. Pressly, R. S., and Rupp, A. F. Purification of fission-product rare earths by ion exchange. U.S. AEC ORNL-1313, 29 pp. *Crerar Met. Abstr.* 1, No. 10, 49, 1953. Uranium slugs that were in reactors for thirty days to four years were processed to remove several fission products, resulting in a fraction enriched in rare earths. A solution of rare earth 0.1 N in HCl is fractionated on an ion-exchange column. Operating the column includes preparing the resin in the ammonium form, degassing of heated columns, and periodic sampling for purity analyses. The equipment is described. Small resin size tends to give better separations. Actinides separate out before lanthanides. A too low pH tends to remove the activities in spread out bands during elution of the exchanged activities. Many graphs, tables and diagrams are given.
75. Radhakrishna, B. P. The separation of scandium, lanthanum and yttrium. *Anal. Chim. Acta* 8, 140-45, 1953. *Crerar Met. Abstr.* 1, No. 10, 50, 1953. Experimental procedures are given for the study of scandium on a resin column. By varying the pH of citric acid from 2.8 to 3.2, the separation of scandium from lanthanum was successfully effected, using the Amberlite resin column. The same

method was successful in separating scandium and yttrium. There is a discussion of the role of hysteresis accompanying the adsorption of scandium; calculations are made taking this phenomena into account.

76. Radhakrishna, B. P. Separation of thorium and lanthanum by ionic exchange. *Anal. Chim. Acta* 6, 351-4, 1952. *CA* 46, 7453f, 1952. A simple and efficient method is described for the separation of Th and La by ion exchange, especially by Amberlite IR 100, with a radioactive indicator. La is eluted first with citric acid, and then the Th is separated with H_2SO_4 as eluant. The separation is complete, and the method can be applied to all of the rare earth elements.
77. Russell, R. G., and Pearce, D. W. Fractionation of the rare earths by zeolite action. *J. Am. Chem. Soc.* 65, 595-600, 1943. *CA* 37, 3363-4, 1943. The principal purpose was to study the use of base-exchange materials of high capacity in rare earth separations and to arrive at working hypotheses with regard to the mechanism of base exchange as it concerns the ions of these elements. Single-stage and multiple-stage fractionations were used; in the latter a 50 ft column (of Crystallite No. 20) was employed. It is concluded that the phenomenon of base exchange is more general than has often been supposed. In this preliminary study no cation was encountered the valence or the size of which was so large that it was unable to enter into base-exchange reactions. Fractional separations within the rare earth group are obtainable by means of zeolite action when concentrated solutions, containing sufficient ions to exceed the capacity of the exchange material, are used. The rare earth ions of decreasing (crystal) ionic radius are held more firmly in the zeolite lattice while the larger ions are held less firmly. By regeneration of the base-exchange material the rare earth ions can also be removed in a fractional manner, the largest, most loosely held ions being removed first.
78. Schubert, T. Applications of ion exchange to the separation of inorganic cations. Nachod, F. C. Ed., *Ion Exchange - Theory and Application*, Academic Press, Inc., New York, 1949. *CA* 44, 6f, 1950. This review describes the integrated efforts of various teams aimed at the separation of rare earths and the transuranic elements.

79. Seiler, J. A., Robinson, W., and Edwards, R. R. Cerous-ceric ion exchange. Natl. Nuclear Energy Ser., Div. IV 9, Radiochem. Studies: The Fission Products, Book 3, 1702-5, 1951. CA 46, 6014a, 1952. Carrier-free radioactive Ce as cerous or ceric ion was added to various mixtures of 6-60 mg of cerous and ceric Ce and the distribution of the radioactivity between the 2 states was determined Ce(IV) was separated from Ce(III) by precipitation in the hot from 4-5 M HNO_3 solution with 0.35 M H_3PO_4 . Under these conditions exchange between the 2 states seems to be complete within a few min. There was some indication that the presence of La inhibited the exchange.
80. Spedding, F. H., et al. A rapid separation of the rare earths employing ion exchange U.S. AEC., Oak Ridge, Tenn. ATI-24058. UNCLASS. A systematic investigation was conducted on the variables which control the separation of adjacent rare earths from a column of Amberlite IR-1 resin. The resin, acting as the adsorbent, was used with the eluant, citric acid-ammonium citrate, to obtain separations of neodymium and praseodymium in macro amounts. Spectrophotometric and spectrographic analysis were used to show the extent of separation which changed markedly with changing conditions. The variables studied were pH, flow rate, length and diameter of the column, and the weight and composition of the starting sample. A set of optimum conditions are presented to be used when 5% citric acid is employed. Under these conditions, one pass through the column yields approximately 22% of the Nd with spectroscopic purity when the starting mixture contains equal amounts of Nd and Pr.
81. Spedding, F. H., Fulmer, E. I., and Ayers, B. Improved ion exchange method for separating rare earths in macro quantities. U.S. AEC., Oak Ridge, Tenn. ATI-25410. UNCLASS. Studies have been made using 0.1% citric acid solution in the pH range 5.0 to 5.5 for the elution of the rare earths from Amberlite IR-100 columns. Marked improvements were observed over the separations obtained using higher concentrations of citric acid at lower pH values. The shapes of the elution bands under the new conditions are nearly rectangular, and one rare earth follows another with little overlapping.

82. Spedding, F. H., et al. The separation of rare earths by ion exchange. I. Cerium and yttrium. J. Am. Chem. Soc. 69, 2777-81, 1947. CA 42, 1520d, 1948. The separation of macro quantities of rare earths of spectrographic purity by adsorption on Amberlite-type resins and subsequent elution with such agents as citric acid-ammonium citrate solution at controlled pH depends on the fact that the rare earths form complexes with citrate ions. If the pH is suitably adjusted, competition is set up for the rare earth ions between the citrate complexes and the active centers of the resin. Therefore, as the citrate solution washes the rare earths down the column, each rare earth ion is adsorbed and desorbed many times. Since the equilibrium constants for the rare earth citrate complexes vary slightly among the different rare earths, their rates of travel down the column differ sufficiently to lead to their separation. The repeated cycles in the columns effectively replace the thousands of individual operations required by the older methods for separating the rare earths. Cerium and yttrium radioisotopes, 275-day Ce^{144} and 57-day Y^{91} , were used as tracers in following progress of the separation. The resin used was Amberlite IR-1. The effect of various factors including the concentration of the eluant, the pH of the element, the ratio Ce/Y in the starting sample, and the length of columns were established by which Ce and Y, of spectrographic purity, could be separated, in macro quantities.
83. Spedding, F. H., et al. The separation of rare earths by ion exchange. II. Neodymium and praseodymium. J. Am. Chem. Soc. 69, 2786-92, 1947. CA 42, 1520g, 1948. The use of Amberlite IR-1 resin as an ion exchanger for cerium and yttrium (see preceding abstract) is extended to separation of neodymium and praseodymium.
84. Spedding, F. H., et al. The separation of rare earths by ion exchange. III. Pilot plant separations. J. Am. Chem. Soc. 69, 2812-18, 1947. CA 42, 1521a, 1948. The citrate elution procedure was applied to large-scale separation of rare earth elements. Detailed procedures are outlined for the pilot-plant-scale separation of the rare earths using Amberlite IR-100 and 0.5% citric acid-ammonium citrate solutions as eluant. Twenty-four columns 4 in. in diameter and with resin bed 8 ft long were used. The pH of the eluant was 3.9, and 0.1%

phenol was used to prevent mold growth. Large samples of rare earths of high purity were obtained by these procedures. Examples of the quantity and quality of various fractions obtained by this process include: (1) Nd, 800 g 99.9% Nd_2O_3 , < 0.1% Pr_6O_{11} ; 770 g 98% Nd_2O_3 , 2% Pr_6O_{11} ; (2) Pr, 35 g 99% Pr_6O_{11} , 1% Nd_2O_3 ; 160 g 90% Pr_6O_{11} (Impurities Ce, La, and Ca); (3) Sm, 160 g > 99.9% Sm_2O_3 ; 600 g 99% Sm_2O_3 , 0.5% Eu_2O_3 , 0.5% Ca. In addition considerable quantities of slightly impure heavy rare earth salts and Y salts were obtained.

85. Spedding, F. H., et al. Improved ion exchange methods for separating rare earths in macro-quantities. J. Am. Chem. Soc. 70, 1671-72, 1948. CA 42, 6260d, 1948. Ion exchange methods for the separation of rare earths from one another in kg quantities, consisting essentially of adsorbing the mixed materials on the top of long columns of commercial Amberlite resin, have been improved by eluting with 0.1% citric acid solution of pH 5.0-5.5%.
86. Spedding, F. H. Progress report on the separation of the rare earths by ion-exchange for the period May 1, 1947 to 1949. U.S. AEC. ISC-61, 20 pp. UNCLASS. Ceram Met. Abstr. 2, No. 7, 42, 1954. Presented are abstracts of previous reports on the separation of cerium group metals and the variables involved in separating praseodymium, samarium, and neodymium with 0.1% citric acid-ammonium citrate solutions on Amberlite IR-100. Lowering the temperature changes the elution curves in the same way as increasing the pH. A faster flow rate delays rare earth breakthrough, flattens the peak concentration and spreads out the curve. Decreased resin particle size allows an approach to equilibrium. Separation was independent of column lengths over the minimum. Experiments on separation of yttrium group rare earths are reported for column runs, equilibrium and purification of NBS samples. Use of citrate systems for this group is less efficient than for the cerium group. Experiments on separations from gadolinite and Blomstrandine gave good results.
87. Spedding, F. H., et al. Separation of rare earths by ion exchange. IV. Variables involved in the separation of samarium, neodymium, and praseodymium. J. Am. Chem. Soc. 72, 2349-54, 1950; cf. CA 42, 1520a. CA 46, 6533i, 1952. With 0.5% citrate solutions as eluant,

the effects of pH, temperature, resin particle size, and flow rate on the elution of pure Sm^{+++} or Nd^{+++} were determined. From these results and from experiments on the elution of equimolar mixtures of Sm_2O_3 and Nd_2O_3 at varying pH and flow rate, the best of the conditions tested for separation were pH 3.80 at a linear flow rate of 0.5 cm/min. Under these conditions, the recoveries 99.5% pure oxides were 96 and 95% respectively. These were also the best of the conditions tested for separation of equimolar mixtures of Nd_2O_3 and Pr_6O_{11} with 84 and 82% recoveries, respectively, of 99.5% purity.

88. Spedding, F. H., et al. The separation of rare earths by ion exchange. V. Investigations with 0.1% citric acid-ammonium citrate solutions. J. Am. Chem. Soc. 72, 2354-61, 1950; cf. CA 42, 6260d. CA 46, 6996i, 1952. Variables involved in the separation of Sm, Nd, and Pr with 0.1% citric acid-ammonium citrate solution and Amberlite IR-100 resin were investigated. Both the degree of separation and the elution time increased as the pH of the eluant decreased. Optimum yields of pure rare earths for a given operating time were obtained at pH 6.0. The slower the flow rate and the smaller the size of the resin particles the less was the observed band overlap and the better the separation. For a fixed charge of rare earth, separation was independent of column length beyond a certain minimum length and became poorer at the longer lengths owing to increased channeling. Increasing column length and column load in the same ratio increased the separation. An upper limit on these increases was met owing to a slow-forming rare earth-citrate precipitate. VI. Conditions for effecting separations with Nalcite HCR and one-tenth per cent citric acid-ammonium citrate solutions. Ibid. 73, 4840-7, 1951. Procedures were developed for the successful separation of the rare earths by using a high-capacity resin, Nalcite HCR, and 0.1% citrate solution. The high-capacity resin proved to be superior to a low-capacity resin, Amberlite IR-100, for the separation of the heavy rare earths. Er, Ho, and Dy were obtained in purities greater than 99%. The process proved to be equally efficient when stepped up 50-fold to a pilot-plant-scale separation of the more abundant rare earths.

89. Spedding, F. H., and Dye, J. L. Efficient separation of dysprosium and yttrium. J. Am. Chem. Soc. 72, 5350, 1950. CA 45, 2805c, 1951. Two successive ion-exchange treatments yield pure Y and Dy from ore concentrates. A preliminary elution with 0.1% NH_4 citrate at pH 5.8-6.1 from Nalcite HCR resin separates Y and Dy from the other rare earths, and subsequent elution of the Y-Dy fractions with 5% citrate at pH 2.8 gives Y and Dy that are spectrophotometrically pure. The separation is based on a shift in the order of elution of Y with respect to the rare earths in going from 0.1 to 5% citrate solution.
90. Spedding, F. H., and Butler, T. A. Methods of preparing spectrographically pure praseodymium salts. June 1951. ISC-148. 58pp. UNCLASS. An ion-exchange process was developed for the separation of spectrographically pure praseodymium salts in kilogram amounts from commercially available concentrates. The application of either 0.5% or 0.1% citrate solutions as eluting agents was shown to result in excellent separations of praseodymium from samarium, neodymium and lanthanum when mixed rare earths were eluted from Amberlite IR-100 or Nalcite HCR cation-exchange resins.
91. Spedding, F. H., et al. The separation of rare earths by ion exchange. XI. Conditions for effecting separation with Nalcite HCR and one-tenth per cent citric acid-ammonia citrate solutions. J. Am. Chem. Soc. 73, 4840-47, 1951. CA 46, 6997b, 1952. Materials, apparatus and general procedures employed in the successful separation of rare earths, using a high-capacity resin (Nalcite HCR) and 0.1% citrate solution are described, and results are tabulated and illustrated. Nalcite HCR resin was definitely superior to low-capacity Amberlite IR-100 for such separation. Gram quantities of Er, Ho and Dy were obtained at >99% purity, and the process proved equally efficient in a 50-times-larger (pilot plant) scale separation of the more abundant rare earths.
92. Spedding, F. H., and Voigt, A. F. (to U.S. A.E.C.) Separation of rare earth elements by adsorption and desorption. U.S. 2,539,282, Jan. 23, 1951. CA 45, 4008f, 1951. This invention relates to the separation of rare earths by adsorbing a mixture of the rare earths from aqueous solution of their water-soluble inorganic salts, prefer-

ably chlorides, on a cation-exchange resin and passing a citric acid solution at a controlled pH through a column of the adsorbed resin with the collection of successive portions of the eluate. Separation of a simple mixture of adjacent rare earths has been effected in which fractions of pure rare earths were obtained. The amount of resin used is at least 5 times the amount required to adsorb the rare earths. The rare earth pairs used were neodymium-praseodymium and samarium-neodymium. Complex mixtures of rare earths were separated into simpler mixtures by the same techniques. The effect of pH of the eluant on the separation was studied and found to be dependent upon the specific rare earth mixture used. The effect of the concentration of citric acid in the eluant was studied. It was found that 0.1% citric acid is better than 0.5% citric acid for increasing the degree of separation of heavy rare-earth elements. Cf. CA 42, 1520dg.

93. Spedding, F. H., and Powell, J. E. Quantitative calculation of the behavior of elution bands in the separation of the rare earths on the ion-exchange columns. J. Am. Chem. Soc. 74, 856-7, 1952. CA 47, 3652e, 1953. A theory is given for the separation of rare earths on ion-exchange columns in the pH range 5.5-7.3 with 1% citric acid.
94. Spedding, F. H., and Powell, J. E. Quantitative theory of rare earth separations on ion exchange columns. J. Am. Chem. Soc. 74, 857, 1952. CA 47, 3652f, 1953. The method consists essentially in adsorbing a mixture of neutral rare earth chlorides on a high-capacity ion-exchange column and eluting them with 1% citric acid.
95. Spedding, F. H., and Powell, J. E. A practical separation of yttrium group rare earths from gadolinite by ion-exchange. U.S. AEC, ISC-349, 32 pp, May 27, 1953. Cramer Met. Abstr. 2, No. 4, 51, 1953. Starting with a rare earth concentrate from gadolinite, containing 0.6% Lu, 4% Yb, 0.6% Tm, 4% Er, 1% Ho, 6% Dy and a remainder of yttrium and of other rare earths, ion exchange using citrate ion as a complexing agent separated the elements. 82% of the erbium and 50% of the ytterbium were obtained 99.9% pure in a single operation. Similar purities of some of the dysprosium, holmium and thulium were also obtained. Lutecium was obtained as an enriched binary mixture with ytterbium and was completely separated from the other

rare earths. The mixture could be separated by a sodium amalgam extraction. The method is a continuous elution process in which low concentrations are enriched in the primary elution step and like fractions are combined by rerouting the eluant. Graphs are shown.

96. Spedding, F. H., and Powell, J. E. The separation of the rare earths by ion-exchange. VII. Quantitative data for the elution of neodymium. U.S. AEC. ISC-383, 28 pp. 1953. Crerar Met. Abstr. 2, No. 5, 36, 1954. The elution of neodymium from Nalcite HCR resin beds with 0.1% citric acid-ammonium citrate solution was studied and the distribution of constituents between the aqueous and resin phases was measured. Data obtained in the pH range 5-8 are tabulated and indicate that the total neodymium concentration in the eluate is related linearly with ammonium ion concentration of the eluant. The mechanism of formation for the neodymium band is described.
97. Spedding, F. H., and Powell, J. E. The separation of the rare earths by ion-exchange. VIII. Quantitative theory of the mechanism involved in elution by dilute citrate solutions. U.S. AEC. ISC-385, 26 pp., 1953. Crerar Met. Abstr. 2, No. 5, 26, 1954. Classical thermodynamics and the concepts of electrical neutrality and material balance are used to explain the elution of rare earths from cation-exchange resins with citrate solutions in the pH range 5.0-8.0. As the pH increases, the predominant ion species are H^+ , NH_4^+ , H_2Cit^- , $HCit^-$, Cit^{3-} , R^{+3} , $RCit_2^{-3}$, $RCit_2^{-2}$, and $RCitOH$, where R is a rare earth atom; minute quantities of H_3Cit , $RCit$ and H_2RCit_2 are also present. Constants of the Nd- $(NH_4)_2Cit$ system have been evaluated. The theoretical and experimental curves are shown. 8 references.
98. Spedding, F. H., and Powell, J. E. Methods of separating rare earth elements in quantity as developed at Iowa State College. ISC-444, Jan. 25, 1954. Nuclear Sci. Abstr. 8, 222, No. 1844, 1954. Three distinct processes involving ion-exchange resins have been developed which have been exceptionally efficient in producing quantities of individual rare earths in a high state of purity. The first method is the elution of an adsorbed band of mixed rare earths down a cation-exchange bed in the H or ammonium state by means of a 5% citric acid solution adjusted to a pH of 2.5 to 3.0 with NH_4OH . The second

method is the elution of an adsorbed band down a cation-exchange resin bed in the hydrogen state with a 0.1% citric acid solution adjusted to a pH of 5.0 to 8.0 with NH_4OH . The third method consists of the elution of an adsorbed band of rare earths through a cation-exchange bed in the Cu II cycle with an ammonium salt of ethylenediamine tetraacetic acid (EDTA). The three methods are compared, and it is concluded that the third method is more desirable and economical than the citrate methods for separating the more difficult groups of rare earths.

99. Spedding, F. H., Powell, J. E., and Wheelwright, E. J. The separation of adjacent rare earths with ethylenediamine tetraacetic acid by elution from an ion-exchange resin. *J. Am. Chem. Soc.* 76, 612-13, 1954; cf. *CA* 47, 3652f, 12092b; 48, 489i. *CA* 48, 4353i, 1954. Add enough EDTA (I) to complex only part of the rare earth mixture. I complexes more strongly with the rare earths whose stability constants are greater. Pass this mixture through an ion-exchange bed which is in the ammonium cycle; the exchanger acts only as a filter. The heavier rare earths which are more strongly complexed pass through the column, while the uncomplexed ions adsorb on the resin. With a single operation this method causes the separation of a complex rare earth mixture into fractions which contain only a few adjacent rare earths. Since the rare earth ions complex very strongly with I under almost all normal operating conditions for column elution, the complexed ions tend to pass directly through ion-exchange beds with cations whose I stability constants are smaller than those of the rare earths. This difficulty can be overcome by eluting the rare earth ions down an ion-exchange column in the Fe cycle. The stability constant of the I-Fe(III) complex is much larger than any of the rare earth constants, consequently, when the rare earth complex reaches the Fe phase resin, an exchange takes place and the rare earth is re-adsorbed. The method is very efficient in separating adjacent rare earths but optimum conditions have not yet been established.
100. Spedding, F. H., Powell, J. E., and Wheelwright, E. J. The separation of adjacent rare earths with ethylenediamine tetraacetic acid by elution from an ion-exchange resin. *ISC-362*, 6 pp., July 8, 1953.

Nuclear Sci. Abstr. 7, 613, 1953. Rare earth separation by citrate elution and EDTA fractionation involving ion exchange are described. Preliminary runs indicate the latter method to be very efficient in separating adjacent rare earths. In this method enough EDTA is added to complex only part of the rare earth mixture. The EDTA complexes more strongly with rare earth mixtures whose stability constants are greater. This mixture is passed through an ion-exchange bed which is in the ammonium cycle, the exchanger acting only as a filter. The heavier rare earths which are more strongly complexed pass through the column, while the uncomplexed ions, mostly lighter rare earths, adsorb on the resin. With a single operation this method allows the separation of a complex rare earth mixture into fractions which contain only a few adjacent rare earths.

101. Spedding, F. H., Powell, J. E., and Wheelwright, E. J. The use of copper as a retaining ion in the elution of rare earths with ammonium ethylenediamine tetraacetate solution. J. Am. Chem. Soc. 76, 2557-61, 1954. Crerar Met. Abstr. 2, No. 11, 40, 1954. Lanthanum mixtures may be rapidly separated into the pure components by eluting a band of mixed lanthanons on a cation-exchange resin through a second cation exchange bed in the Cu(II) state. The eluant is ammonia-buffered EDTA solution. Copper in the divalent state proved a more effective retaining ion than iron in the trivalent state. Other possibilities are nickel, and lead in the divalent state. While holmium and some lighter lanthanons are complexed less strongly than divalent copper by EDTA, the reverse is generally true. Gram quantities of heavy lanthanum can be obtained in a few days with little attention to column operations.
102. Spedding, F. H., Powell, J. E., and Wheelwright, E. J. The use of copper as the retaining ion in the elution of rare earths with ammonium ethylenediamine tetraacetate solutions. U.S. AEC. ISC-433, 12 pp., Dec. 8, 1953. Crerar Met. Abstr. 2, No. 9, 36, 1954. A fast method for lanthanum separations consists of eluting a band of mixed lanthanons adsorbed on a cation-exchange resin through a second bed in the Cu(II) state. The eluant is ammonia-buffered EDTA. Gram quantities of purified heavy lanthanons may be obtained in a few

days. Data are tabulated. 3 references

103. Taylor, A. E. Observations on the rare earths - studies in ion exchange. (Technical Rept.). February 1950. University of Illinois, Urbana. ATI-85 685. UNCLASS. Rare earth studies involving ion exchange phenomena are presented with particular reference to the separation of thorium and the rare earths by ion exchange procedures. An attempt is made to determine the effect which the variation of certain factors (pH, concentration of the complexing agent and total ionic strength of solution, type of resin and resin mesh size, mass of rare earth per unit area of cross section, flow rate, column length, and temperature) has upon the separation of the members of the cerium group of the rare earths. Apparatus and materials, preparation of reagents, analytical procedures, and exchange experiments are discussed in detail. Data from experiments with exchangers Amberlite IR 100-H, and Dowex-50 are furnished. The various conclusions are listed, and graphical data is provided.
104. Tevebaugh, A. D. Properties of citrate complexes of rare-earth ions and their adsorption on Amberlite resin. U.S. AEC. ATI-78 354, 1949 UNCLASS. The complexes for water-insoluble compounds of lanthanum, neodymium, and samarium with citric acid, the distribution of lanthanum between citrate solutions and Amberlite resins, and the rate of reaction of lanthanum chloride solutions with Amberlite IR-100 were investigated. Adsorption spectra of solutions containing neodymium chloride and citric acid at different pH values indicated the existence of four citrate complexes. The rate of reaction of a solution of lanthanum chloride with Amberlite IR-100 was dependent upon the pH of the solution and upon the degree of agitation. The concentrations, corrected and uncorrected, of the three citrate ions in a 5% citric acid solution at various pH values were calculated. Procedures for the further investigation of the problem were also suggested.
105. Tompkins, E. R., Khym, J. X., and Cohn, W. E. Ion exchange as a separation method. I. The separation of fission produced radioisotopes, including individual rare earths, by complexing elution from Amberlite resin. J. Am. Chem. Soc. 69, 2769-77, 1947. CA 42,

1834h, 1948 The ion-exchange technique was applied to the separation of major fission species. The ion-exchanger used was Amberlite IR-1, a phenol-formaldehyde polymer containing methylenesulfonic acid (free), carboxyl and phenolic groups, the anion being insoluble but holding ionizable (therefore exchangeable) cations. When an aqueous solution containing cation M^{+n} is brought into contact with the resin, M^{+n} in the solution exchanges with those cations originally held in the resin by its free acid groups: $nRH + M^{+n} = R_nM + nH^+$. The final equilibrium concentrations depend upon the activities of the two cations and upon the respective affinities of each for the resin. In general, the cation-resin bound strength increases with the charge on the cation and decreases with the ionic (hydrated) radius. A typical series from strong to weak is: $Th > La > Ce > \text{rare earths} > Y > Ba > Cs > Sr > K > NH_4 > Na > H$. The effective concentration of the ion may be lowered by complex formation and thus any cation may be effectively replaced from its resin compound by a relatively dilute solution of a second cation containing a compound which will complex the other cation. . . . Just as a packed column can be considered to contain a certain number of theoretical plates, so can an ion-exchange column be regarded as containing a certain number of theoretical batches of resin. . . .

106. Tompkins, E. R., and Mayer, S. W. Ion exchange as a separation method. III. Equilibrium studies of the reactions of rare earth complexes with synthetic ion-exchange resins. J. Am. Chem. Soc. 69, 2859-65, 1947. CA 42, 1835h, 1948. For any given composition of solution, the distribution coefficient of a rare earth between two phases does not change as the ratio of the weight of Dowex 50 resin to the solution volume is varied. The exchange reaction between a rare earth ion and the NH_4^+ resin compound follows the relation predicted by the mass law. The exchange constants for several rare earths, equilibrated with the NH_4^+ compound of Dowex 50 resin, vary. This shows that some separation of rare earths is possible without the use of complexing agents when this resin is employed. A study of the citrate complexes showed that the one in which three H_2Cit^- ions are combined with a rare earth ion is responsible for the relatively large

separation factors between these elements. A preliminary, comparative study of the effectiveness of several exchangers (Dowex 50, Dowex 30, Duolite C and Amberlite IR-1) and complexing agents (citric acid, tartaric acid, lactic acid, sulfosalicylic acid, ethyl acetoacetate, ethyl oxalic acid, citric acid in 50% EtOH) was made.....

107. Tompkins, E. R., and Mayer, S. W. Ion exchange as a separations method. III. Equilibrium studies of the reactions of rare earth complexes with synthetic ion exchange resins. U.S. AEC., Oak Ridge, Tenn. Aug. 1947. ATI 25285. UNCLASS. It was shown that the distribution coefficient of a rare earth does not change as the resin weight to solution volume is varied. The exchange reaction between a rare earth and the ammonium resin compound was shown to follow the relationship predicted by the mass law. Some separation of rare earths is possible without the use of complexing agents when Dowex-50 is employed. Citrate complexes in which three H_2Cit^- ions are combined with a rare earth ion are responsible for the relatively large separation factors between these elements. The results of studies on the effects of pH, citrate concentration, ammonium ion and rare earth concentrations on the relative distribution constants, give a reliable basis for choosing optimum conditions for column separation as far as these factors are concerned.
108. Tompkins, E. R., Harris, D. H., and Khym, J. X. The effect of a number of column variables. J. Am. Chem. Soc. 71, 2504-10, 1949; cf. Spedding, et al., CA 42, 1520g; Cohn, et al., CA 43, 4129c. CA 44, 4798e, 1950. The effect of column area, column length and flow rate on the efficiency of an ion-exchange column for applications of volume reduction and separation of fission products was studied for Y and Ce with Y^{91} and $\text{Ce}^{141, 144}$ tracers. For maximum volume reduction, the ion-exchange column should be in the H form initially and elution of the rare earths should be made with citrate solution at a pH of 3.3-3.5. For optimum separation, it is preferable to elute the mixture of rare earths from a column in the NH_4 form with citrate at a lower pH. Addition of a carrier, unnecessary for the ion-exchange fission-product separation, has a deleterious effect on the separation of the solutes.

109. Tompkins, E. R. Application of ion exchange to the separation of substances in low concentrations. Discussions Faraday Soc. No. 7, 232-7, 1949. CA 45, 18g, 1951. The factors that affect the separation of solutes, column efficiency and the shape of elution curves are enumerated and discussed. 11 references.
110. Tompkins, E. R. Ion-exchange separations. Anal. Chem. 22, 1352-9, 1950. CA 45, 912d, 1951. A review. Properties and uses of commercial ion exchangers are discussed. Some current laboratory procedures for equilibrium experiments and for column separations are described. Theories of column separation are evaluated. Rare earth purification is briefly reviewed. 92 references.
111. Trombe, F., and Loriers, J. Improved method of separation of rare earths by ion exchangers. Compt. rend. 236, 1567-69, 1953. Crerar Met. Abstr. 1, No. 11, 52, 1953. Notable improvements in the chromatographic separation of rare earths in an ammoniated citric acid solution were made possible by taking into account the fact that small changes in the pH of the solution reverse the effect, i.e. instead of an adsorption an elution will take place when a certain critical pH value has been reached. Since these critical values are different for various rare earths, a selective elution of single elements can be made from an adsorbed mixture, by successively using eluants of different pH. One of the main advantages of such a method is the comparatively high concentration of the fractions obtained, whereby the tedious volume reductions are avoided and, generally, larger quantities of rare earths can be handled in a single series of operations. Another advantage is the possibility of recovering the rather costly citric acid.
112. Trombe, F., and Loriers, J. A procedure for the separation of rare earths by adsorption on ion-exchange resins. Compt. rend. 236, 1670-72, 1953. Crerar Met. Abstr. 1, No. 11, 52, 1953. An arrangement is described which improves considerably the efficiency of other procedures using ammoniated citric-acid solutions as eluants. In place of one column, a battery of several resin-filled columns is used; connected in series during the process of elution, the tubes can be drained separately. Owing to the great total length of the adsorber,

the overlapping of the components is effectively reduced, while the separate emptying of columns permits an easy isolation of the fractions. An installation comprising six columns, each 1.5 m high and 11 cm in diameter, was capable of treating 1-2 kg of a mixture of ceric rare-earth oxides in an operation lasting about 8 days. The purity of the products was at least 95%, reaching the value 99.5% in many fractions.

113. Vickery, R. C. Ion-exchange elution series. *Nature* 170, 665-6, 1952. *CA* 47, 8459g, 1953. Although the elution sequence for ions of the same charge remains the same in systems of mixed bi- and trivalent ions of the lanthanons, the elution series of the mixed ions does not conform to the stability series for the mixed ions. It is postulated that the stability series varies because of a factor affected by the valency of the ions. A preponderance of trivalent ions induces an apparent increase in the stabilities of bivalent-ion complexes and vice versa. This is confirmed with EDTA solutions as the eluant as follows: With preponderance of bivalent ions: Yb, Er, Ni, Cu, Sm, Nd, Pr, Ce, La, Cd, Co, Fe, Mn. With preponderance of trivalent ions: Ni, Yb, Y, Cd, Eu, Zn, Sm, Nd, Mn, Pr, La. With equivalence of bi- and trivalent ions: Yb, Ni, Pb, Er, Sm, Nd, Pr, Cd, Co, La, Fe, Mn.
114. Vickery, R. C. Separation of lanthanons by ion exchange; a comparison of eluants. *J. Chem. Soc.*, p. 4357-63, 1952. *Cramer Met. Abstr.* 1, No. 6, 44, 1953. Eluant efficiency of nitrilotriacetic acid, EDTA, glycine and more common acids are compared in the separation of lanthanons by ion-exchange. Stability constant determinations can be used to predict the complexing agent's value. EDTA gave the best results in elution when pH's are high and the resin is in ammonium form. Use of manganous ion as a separation element used with EDTA gave excellent separations of Nd and Pr. Molar rather than weight concentration should be used in such comparisons.
115. Voigt, F. H., et al. A rapid separation of rare earths employing ion-exchange I. Cerium and yttrium. U.S. AEC, Oak Ridge, Tenn. ATI-24034. UNCLASS. A rapid means of separating the rare earths using the ion-exchange resin Amberlite IR-1 is described. Separations of

both tracer and macro amounts of Ce^{+++} and Y^{+++} from each other were obtained, with analysis being performed by using radioactive tracers. A column of the resin is prepared in the acid cycle and the rare earth ions are adsorbed. This requires only a small fraction of the total column. Desorption of the material is done by a citric acid-ammonium citrate solution. The separation is caused by the competition between two processes: the adsorption of the rare earth ions on the resin and the formation of the rare earth-citrate complex ions. The processes are continuously repeated as the material is eluted from the column. It is shown that the separation can be made very effective when such factors as pH of the citrate, column length, and composition of the starting material are considered.

116. Wheelwright, E. J., and Spedding, F. H. A rapid method for fractionating crude rare earth ores into mixtures greatly enriched with regard to particular rare earths. *J. Am. Chem. Soc.* 75, 2529-30, 1953. *Crerar Met. Abstr.* 1, No. 12, 49, 1953. Rare earth production efficiency is increased if the as-leached rare earth mixtures are first rapidly fractionated, the fractions being enriched in specific rare earths. The process consists of complexing part of the rare earths with EDTA and separating these by passing the mixed solution through an ion-exchange column, where the uncomplexed ions are absorbed. These are removed fractionally by pouring through four successively stronger EDTA solutions. The five fractions were spread into 20-30 secondary fractions, each with two to four rare earths, by running through small ion exchange columns. Such a preliminary separation permits five times as much heavy rare earths to be added to the ion-exchangers, resulting in increased production.
117. Wheelwright, E. J., et al. A rapid method for fractionating crude rare earth ores into mixtures greatly enriched with regard to particular rare earths. U.S. AEC ISC-332, 7 pp. *Crerar Met. Abstr.* 2, No. 3, 45, 1953. Efficiency in producing very pure rare earths may be increased if the crude, as-leached mixtures are first rapidly fractionated. The less desirable elements are thereby removed and the fractions enriched in desirable rare earths are purified by ion-exchange methods using EDTA as a complexing agent. Data are tabulated.

118. Wiklander, L. Studies on Ionic Exchange with Special Reference to the Conditions in Soils. Klg. Lantbruks Hogskol Ann. 14, 1-171, 1946. CA 41, 3561i, 1947. This monograph is divided into the following 7 parts in addition to an introduction, review (167 references), a summary and a bibliography: the relative pH-reducing power of the alkali and alkaline earth ions in electrodialyzed materials; general properties of a resin acidoid and basoid: the relationship between the replacing power of the H ion and the acidoid strength and the position of this ion in the lyotropic series; amphoteric reactions of an Al phosphate complex; the effect of dilution on exchange equilibria; the influence of heating on the exchangeability of the adsorbed ions; the influence of the degree of saturation of the exchanger and of the nature of the complementary ions on the exchangeability of the adsorbed ions. Each section has its own conclusions which are then summarized in part 10. Tables and graphs are presented to show the comparison of the power of different ions in solutions of varying concentrations to displace a selected ion on the exchange material. Exchange materials studied in one section included: humus, litter of beech leaves, AlPO_4 , FePO_4 , Al silicates, ferric silicates, zeolite, bentonite, kaolinite, bleaching earths, and 4 mineral soils. The exchange resins studied were Wolfatit K and M. In another section Vardsberg clay and ordinary bath sponge were included. The various exchange materials were similar in behavior and the comparison of displacing powers yielded series that closely followed the type $\text{Li} < \text{Na} < \text{K} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba} < \text{La}$. The H ion appeared between La and Na or farther down the series depending on the nature (acidoid strength) of the various exchange materials.

III. EXTRACTIONS

119. Appleton, D. B., and Selwood, P. W. Fractional partition of the rare earths. J. Am. Chem. Soc. 63, 2029, 1941. CA 35, 5817.1, 1941. Preliminary results are given of the fractionation of La and Nd thiocyanates in H₂O with BuOH; the ratio of Nd/La in the BuOH layer to Nd/La in the aqueous layer is 1.06. The process lends itself to continuous operation and may lead to comparatively rapid separation of these elements.
120. Asselin, G. Separation of rare earths by liquid extraction. May 1947. University of Illinois, Urbana. ATI-13090. UNCLASS. Normal butanol cannot be used for extracting rare earth chlorides from their aqueous solutions. Rare earth and thorium nitrates are extractable to a reasonable extent in n-butanol from aqueous solutions. Neodymium and erbium chlorides are extracted to a very great extent in n-butanol from aqueous solutions containing ammonium thiocyanate. Rare earth nitrates are extracted to a reasonable extent in n-pentanol from water solutions containing ammonium thiocyanate. Thorium is more extractable than any of the rare earths.
121. Asselin, G. F., Audrieth, L. F., and Commings, E. W. The separation of thorium and rare earth salts by solvent extraction. J. Phys. and Colloid Chem. 54, 640-8, 1950. CA 44, 8202d, 1950. Th was separated from aqueous solutions of Th and Nd nitrates by extraction with 1-pentanol containing NH₄SCN. The degree of separation depended on the NH₄SCN and Nd(NO₃)₃ concentrations. The extraction of rare earth nitrates and chlorides with 1-butanol was investigated. The solubility of the chlorides in 1-butanol was too low to permit feasible separation of the rare earths, but the separation by extraction of the nitrate solutions was considered feasible.
122. Asselin, G., and Audrieth, L. F. (to U.S. Secy. of Navy) Concentration of thorium. U.S. 2,578,623, Dec. 11, 1951. CA 46, 3718b, 1952. The process of extraction of Th from an aqueous solution of a monazite ore with amyl or butyl alcohol is used to separate Th from the rare earths. The equilibrium distribution ratios (concentration

in amyl alcohol to concentration in H_2O) for Th increased from 0.32 to 1.2 as the Th concentration in the aqueous phase was decreased from 48.2 to 2.41 g./l. Similarly the ratio for Nd increased from 0.10 to 0.14 as the Nd concentration in the aqueous phase decreased from 30.7 to 7.04 g./l. The ratios were smaller when BuOH was used for the extraction.

123. Audrieth, L. F., Commings, E. W., and Asselin, G. F. Rare earths by liquid extraction. H 347-8. University of Illinois, Aug. 12, 1947. 57 pp. Rare earths and $Th(NO_3)_4$ were extracted with n-BuOH for their aqueous solutions. $NdCl_3$ and $ErCl_3$ were extracted to a very great extent with n-BuOH from solutions containing NH_4CNS . The separation of Th and the rare earths was effected by selective extraction of Th in n-pentanol from aqueous solutions containing rare earth nitrates and NH_4CNS . Bibliography is included.
124. Bochinski, J., Smutz, M., and Spedding, F. H. Separation of individual rare earths by liquid-liquid extraction from multicomponent monazite rare earth nitrates. U.S. AEC. ISC-348, 31 pp., May 27, 1953. Crerar Met. Abstr. 2, No. 4, 51, 1953. Rare earths may be separated individually by extracting the aqueous nitrate solutions with undiluted tributyl phosphate without using nitric acid or salting-out agents. Separation factors increase with increasing concentration and are almost independent of the composition of the mixture. If the concentration in the extractor is kept high by refluxing solutes in the product streams, significant separations can be made in a few stages. Total concentrations in adjacent stages are constant and the optimum conditions can be calculated. Graphs and mathematical treatment are given. 10 references.
125. Bock, R., and Bock, E. Distribution of rare earth nitrates between aqueous solutions and organic solvents. *Naturwissenschaften* 36, 344, 1949; cf. CA 37, 5325.9. CA 44, 5749a, 1950. Ce(IV) can be extracted by Et_2O from 4.5 N HNO_3 to the extent of more than 90%; from 8 N HNO_3 , to the extent of more than 95%. The extraction of $Th(NO_3)_4$ from aqueous HNO_3 solution by Et_2O is much increased by saturation of the aqueous phase with other nitrates (e.g., $LiNO_3$, $NaNO_3$, $Sr(NO_3)_2$, $Al(NO_3)_3$). Extraction with esters, ketones, and

alcohols is more effective than with ether. Sc nitrate also can be extracted with ether.

126. Dyrssen, D. , and Dahlberg, V. Studies on the extraction of metal complexes VIII. The extraction of La, Sm, Th, and U(VI) with oxine and cupferron. *Acta Chem Scand.* 7, 1186-96, 1953. *Crerar Met. Abstr.* 2, No. 4, 53, 1953. Extraction data on the oxinates and cupferrates of La(III), Sm(III) and Hf(IV) are tabulated. Chloroform and hexone were the organic solvents used. A mathematical interpretation of the data is presented. It is noted that the pH of precipitation of the metal oxinates is related to the pH of extraction. Curves show the partition of metals between the aqueous and organic phase as a function of the oxinate or cupferrate ion concentration. Extraction methods can evidently be used to separate these metals.
127. Hagiwara, Z. Separation of the rare earths and their accompanying elements VI. Fundamental studies of the extraction. *J. Chem. Soc Japan, Ind. Chem. Sect.* 56, 659-61, 1953. *Crerar Met. Abstr.* 2, No. 7, 45, 1954. Optimum conditions for colorimetric analysis of nitrosophenyl hydroxylamine were sought using a photoelectric colorimeter. The distribution ratio of nitrosophenyl hydroxylamine in "solvent-water" was measured. The distribution ratio in $N-CH_3COO-C_6H_5-H_2O$ and CCl_4-H_2O is extremely great, and it was determined that the distribution into the $C_6H_5N(NO)OH-H_2O$ solution phase is sufficiently small to disregard.
128. Moeller, T. , and Kremers, H. E. The rare earths. LIV. Extraction of ytterbium from rare earth mixtures with sodium amalgam. *Ind Eng. Chem., Anal. Ed.* 17, 798-800, 1945. *CA* 40, 805.4, 1946. The method of Marsh (cf. *CA* 37, 4025.2) for the extraction of Yb from rare earth mixtures was investigated in perchlorate, chloride, formate, acetate, and alkaline citrate solutions. Extraction was best with the first three anions; with acetate solutions it was somewhat inferior, and with alkaline citrate definitely poor. With acetate solutions separation of the aqueous and amalgam layers is easier, and for this reason they were used in extractions from mixtures. Extraction at 50° was slightly better than at room temperature. Optimum acidity was at a pH of 5.0 to 5.5. Five successive extractions

from a rare earth mixture removed 97% of the Yb initially present. For detection of Yb, add to 5 ml of nearly neutral rare earth chloride solution 5 ml to 0.1% Na amalgam. Shake and add immediately 10 drops of concentrated HCl. Shake again; when evolution of H diminishes, an apple-green color appears if 2 mg or more of Yb_2O_3 is present. Recovery of Na-free rare earth salts is best effected by an oxalate precipitation, followed by two successive precipitations with NH_4 succinate. cf. CA 39, 883.5.

129. Moeller, T., and Jackson, D. E. The rare earths. Separative extraction of certain rare earth elements as 5,7-dichloro-8-quinolinol chelates. Anal. Chem. 22, 1393-7, 1950. CA 45, 1463a, 1951. The 5,7-dichloro-8-quinolinol chelates of the tripositive rare earth elements are completely extracted into CHCl_3 in controlled pH ranges. Extraction of Nd and Er at pH values exceeding 9.4 and 8.3, respectively, indicates that extraction is favored by decreasing basicity in the rare earth metal ion; the separation of Nd and Er is fractional, not complete. The CHCl_3 solutions show broad chelate absorption of radiant energy centering around 4000 Å. with sharp characteristic rare earth absorptions at longer wave lengths. Nd absorption at 5818 Å. and Er at 5208 Å. follow Beer's law and are more intense than corresponding absorptions in aqueous solution. Spectrophotometric determination of Nd as the chelate in CHCl_3 solution makes feasible the determination of lower concentrations of Nd in the presence of neighboring rare earth elements.
130. Peppard, D. F., et al. Studies of the solvent extraction behavior of the transition elements; order and degree of fractionation of the trivalent rare earths. J. Phys. Chem. 57, 294-301, 1953. Crerar Met. Abstr. 1, No. 9, 43, 1953. Extractability of the lanthanides into $(\text{C}_4\text{H}_9)_3\text{PO}_4$ from aqueous HCl and from 8-15.6M HNO_3 increases with increasing atomic number and decreasing basicity. This order is inverted for the system TBP and 0.3M HNO_3 . Logarithms of the distribution ratios of a given pair diverge with increasing acidity in relatively concentrated HNO_3 , so maximum separation requires use of concentrated HNO_3 . An inert diluent of TBP decreases extractability more than theory predicts. The lanthanides may be arbitrarily

split into two groups at a predetermined point, by control of variables in counter-current fractionation. Thus, a valuable Tm-Lu fraction has been obtained from a mixed rare earth source. Graphs and tables are given.

131. Peppard, D. F., Gray, P. R., Markus, M. M. Actinide-lanthanide analogy as exemplified by solvent extraction behavior. J. Am. Chem. Soc. 75, 6063-4, 1953. Nuclear Sci Abstr. 8, 125, 1954. A comparison of the solvent extraction behavior of the lanthanides and actinides was made for the purpose of pointing out similarities between the two series in the trivalent state. The experiments show that $\log K$ is a linear function of atomic number for both lanthanides (III) and actinides (III). The Am behavior parallels that of Pm in the nitric acid dependency of K and in the third power dependence of K on TBP concentration.
132. Scadden, E. M., and Ballou, W. E. Solvent extraction separations of zirconium and niobium. Anal. Chem. 25, 1602-04, 1953. Anal. Abstr. 1, No. 4, 673, 1954. Application of the solvent system to other separations is indicated. Conditions for simply separating Y-group rare earths from those of the La-group with 0.6M di-n-butyl hydrogen phosphate in n-butyl ether have been found.
133. Topp, A. C. Liquid-liquid extraction of neodymium and samarium nitrates. Sept. 26, 1952. Oak Ridge National Lab., Tenn. (Index No. ORNL-1409). ATI-173 804. UNCLASS. No abstract.
134. Warf, J. C. Extraction process for cerium. U.S. 2,523,892, Sept. 26, 1950. CA 45, 1314a, 1951. Quadrivalent Ce salts can be extracted from aqueous solutions (0.2-2 M for Ce salt, 3-12 M for the nitrate, 1-6 M for HNO_3) by nitromethane. The Ce(IV) salt in the nitromethane phase after separation is reduced to Ce(III) salt and extracted with H_2O from which it is recovered.
135. Weaver, B., Kappelmann, F. A., and Topp, A. C. Quantity separation of rare earths by liquid-liquid extraction. I. The first kilogram of gadolinium oxide. J. Am. Chem. Soc. 75, 3943-5, 1953. CA 47, 11062f, 1953. Countercurrent liquid-liquid extraction techniques using a York-Schneibel extraction column have separated large quantities of rare earths, specifically for the purification of Gd. More

than a kg of better than 95% Gd_2O_3 has been produced. The solutions used were: feed, 13N HNO_3 containing 20 g rare earths per l.; aqueous, 10 N HNO_3 ; and an organic solvent, a 60:40 mixture of Bu_3PO_4 and Varsol, equilibrated with HNO_3 . Increases in temperature decreased extraction into the organic phase. Distribution coefficients of rare earths between freshly prepared Bu_3PO_4 and HNO_3 are nearly independent of rare earth concentration within the practical operating range.

136. Wylie, A. W. Extraction of ceric nitrate by solvents. J. Chem. Soc. 1474-80, 1951. CA 45, 10134h, 1951. $\text{Ce}(\text{NO}_3)_4$ (I) is extracted from 5-6 N HNO_3 into peroxide-free Et_2O and other solvents which extract HNO_3 from H_2O . The complex extracted is a mixture of $\text{H}_2\text{Ce}(\text{NO}_3)_6$ and $\text{HCe}(\text{NO}_3)_5(\text{H}_2\text{O})$. Nd and Pr as nitrates have a salting-out effect. The nitrate is extracted from 7N HNO_3 with iso- Pr_2O and PhMeCo and from 5 N HNO_3 with tert- BuMeCo . HNO_3 is extracted by many ethers and ketones from 5N solution. Reduction of I prevents many extractions.

IV. PRECIPITATIONS

137. Ballard, A. E., and Martinson, L. W. Purification of lanthanum compounds. Brit. 583,961, Jan. 3, 1947. CA 41, 2864e, 1947. La compounds, suitable for making color-free optical glasses, are prepared free from Fe and Ce salts by treating a 25% solution of water-soluble La salts by either one of two methods. To the La salt solution is added H_2O_2 in an amount in excess of that necessary to oxidize all the oxidizable ions present. Add sufficient $(\text{NH}_4)_2\text{CO}_3$ to neutralize any free acid ions present and just start precipitation of La. Bring solution to boil and filter. An alternative method is to add to the La salts solution sufficient $(\text{NH}_4)_2\text{CO}_3$ to neutralize any free acid ions present and just start precipitation of La. Heat almost to boiling. Add $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in excess to oxidize any Fe and Ce. Heat to boiling and filter. Evaporate the filtrate to dryness and ignite, or treat the filtrate with $\text{H}_2\text{C}_2\text{O}_4$, filter off La oxalate, and ignite to La_2O_3 . Cf. CA 39, 3638.3; 40, 2276.3.
138. Ballou, N. E. Determination of rare earth activities in fission. Natl. Nuclear Energy Ser. Div. IV, 9, Radiochem. Studies: The Fission Products, Book 3, 1673-9, 1951. CA 47, 12025b, 1953. The rare earth elements were separated from other elements by the precipitation of the fluorides with HF from acid solution and redissolved by the formation of the solution complex ion BF_4^- by treatment with HNO_3 and H_3BO_3 . Ce was separated by oxidation with KClO_3 and HNO_3 and precipitated as the iodate. The La group was separated from the Y group by the precipitation of $\text{KLa}(\text{CO}_3)_2$. The determinations of chemical yield were made by weighing the hydrated oxalates dried under controlled conditions.
139. Ballou, N. E. Rapid separation of lanthanum and yttrium groups of rare earths. Natl. Nuclear Energy Ser. Div. IV, 9 Radiochem. Studies: The Fission Products, Book 3, 1706-9, 1951. CA 47, 12025b, 1953. A rapid separation of the La group from the Y group was accomplished by boiling with 6% K_2CO_3 solution until the precipitate $\text{K}_5\text{La}_3(\text{CO}_3)_7$ was formed which removed 97% of the La and about 80% of the carrier-free Pr from the solution, leaving 90-95% of the

Y in solution as a complex carbonate. The $K_5PR_3(CO_3)_7$ precipitate removed about 95% of the Pr and about the same fraction of carrier-free La from the solution.

140. Beck, G. A new principle for the fractionation of rare earths with nitrilotriacetate. The separation of lanthanum and cerium. *Helv. Chim. Acta* 29, 357-60, 1946. *CA* 40, 4308.5, 1946. Oxalates and fluorides of the rare earths dissolve in weakly alkaline nitrilotriacetate solutions with complex formation. When the pH is raised to 9-10 with NaOH, the rare earth hydroxides or basic salts precipitate. The most stable complex is $Na_3[La\{N(CH_2CO_2)_3\}_2]$, which gives a very insoluble precipitate of $[Co(NH_3)_6][La\{N-(CH_2CO_2)_3\}_2]$. A similar precipitate is given by most of the rare earths and by Ce(IV), Be, and Tl (III), but not by Th, Zr, Al, Fe, and Bi. Hence it is a good qualitative test for rare earths. The rare earth complexes with $N(CH_2CO_2H)_3$ in the presence of oxalates precipitate the oxalates as the solution is acidified. Precipitate occurs at about the following pH values: La 6.0, Pr and Nd 5.5, Sm 5.0, Gd 4.5, Er 4.0. Thus, nearly pure La can be obtained by careful acidification of the solution of its complex with AcOH. Ce(IV) also dissolves under these conditions, but when the alkaline solution is treated with H_2O_2 , the orange peroxide hydrate precipitates. During this reaction the pH falls, but the weak alkalinity must be maintained when Ce and La are being separated. The reaction permits detection of 8% Ce per cc. Ti, Zr, and Th oxalates behave like Ce, but do not dissolve in alkaline solutions.
141. Beck, G. New fractionating principle for the rare earths with nitriloacetate; a displacement method. *Mikrochemie ver. Mikrochim. Acta* 33, 344-7, 1948. *CA* 42, 6264g, 1948. In a previous paper (*CA* 40, 4308.5) B. has shown that $N(CH_2CO_2H)_3$ in slightly basic solution forms anionic complexes which can prevent the precipitation of oxalates. In the acidic region, however, the rare earths can be precipitated successively beginning at pH 6.5-7 for La and ending at about pH 3.5-4 for the Er earths. Ce, for its part, can be precipitated as the only constituent of its group from ammoniacal solution of the nitriloacetate by means of H_2O_2 and La can easily be obtained pure by fractionating. If to a neutral or slightly acidic solution the

rare earths in nitriloacetate, some CuSO_4 is added, the Cu^{+2} will displace the more positive rare earths in the complex. But the rare earths themselves can act similarly. Thus if a solution of rare earth nitrates is divided into 4 parts, the first part can be treated with NH_4OH and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and then with just enough nitriloacetate to dissolve the oxalate precipitate. If now the second portion of the solution is added, some rare earth oxalate will be precipitated. This can be filtered off and boiled after the addition of a third portion of the original solution which will cause further precipitation. Then in the filtrate, treatment with the fourth portion will cause more precipitation. This fractionation method has been used successfully for separating mixtures of the rare earths.

142. Beydon, J. A study with the aid of radioactive indicators of a rapid procedure for the separation of yttrium and lanthanum. *Compt. rend.* 224, 1715-16, 1947. *CA* 41, 7304g, 1947. The sulfate precipitation of the Y group from the Ce group was studied with $_{39}\text{La}^{140}$, $t_{1/2} = 40$ hrs., and $_{39}\text{Y}^{90}$, $t_{1/2} = 60$ hrs. To a concentrated neutral solution of the Y and La sulfates (50:50 mixture) containing the appropriate isotope of known specific activity an excess of a saturated solution of K_2SO_4 was added. The mixture was cooled on ice for 15 min., and the precipitate of the double sulfates was filtered, washed with a saturated solution of K_2SO_4 , and dissolved in H_2O slightly acidified with HNO_3 . The hydrated oxide or oxalate was precipitated from this solution, calcined to the oxide, weighed, and assayed for activity. In successive fractions, the quantity of Y precipitated with the La represented 16, 4.5, 1.5, and 0.8% of the initial Y concentration. However, the filtrate from the initial precipitation contained only 3% of the initial La concentration. By precipitating the double sulfates of Tl under the same conditions, only 2% of the Y concentration was found with the La in the initial precipitate, although 20% of the La was found in the filtrate.
143. Berg, R., and Becker, E. Determination of cerium and separation of thorium and cerium by means of 8-hydroxyquinoline (oxine). *Z. anal. Chem.* 119, 1-4, 1940. *CA* 34, 4012.6, 1940. Cerous solutions containing NH_3 and tartarate give a greenish-gray precipitate of

$\text{Ce}(\text{C}_9\text{H}_6\text{ON})_3$ when treated with oxine. The precipitate can be weighed after drying at 110° , or it can be titrated with bromate. The method is satisfactory for determining 50 mg of Ce^{III} . Any Ce^{IV} is first reduced by heating with NH_4OH . HCl is added until the solution is colorless. When Th^{IV} and Ce^{III} are both present, the Th^{IV} can be precipitated by oxine in the presence of AcOH as $[\text{Th}(\text{C}_9\text{H}_6\text{ON})_4 \cdot \text{C}_9\text{H}_7\text{ON}]$. After washing this yellowish red precipitate with hot water the Ce^{III} can be precipitated in the filtrate by adding 10 ml. of concentrated Na tartarate solution heating to 60° , making distinctly ammoniacal and adding more oxine solution.

144. Boldridge, W. F., and Hume, D. N. Improved determination of cerium and other rare earth activities in fission. Natl. Nuclear Energy Ser., Div. IV, 9, Radiochem. Studies: The Fission Products, Book 3, 1693-1701, 1951. CA 46, 6544e, 1952. Oxidation in the cold by BrO_3^- in dilute HNO_3 and precipitation with HIO_3 has been found to be the most satisfactory method of separating Ce from trivalent rare earths. The precipitation of Ce is quantitative. After 2 reprecipitations, trivalent rare earth contamination is less than 0.1%. The results are applied to the determination of Ce and rare earth activities in fission mixtures.
145. Buyers, A. G., and Audrieth, L. F. The phosphates and polyphosphates of the rare earths and thorium (Technical Rept.) March 1950. University of Illinois, Urbana. ATI-86 911. UNCLASS. A study has been made of the phosphates and polyphosphates of the rare earths and thorium to characterize their chemical composition and properties. These studies have disclosed that the normal orthophosphates of the rare earths and thorium are precipitated when the respective ions are allowed to react in aqueous solution. It has also been shown that normal pyro and triphosphates of the rare earths precipitate when solutions of rare earths and the respective polyphosphate ions are adjusted to a pH of 4.5. Most significant are the findings which have to do with the formation of polyphosphate complexes of the rare earths and of thorium. It is indicated that it should be possible to effect separation of thorium from the rare earths by precipitation of the thorium at a pH of 1, using either aqueous triphosphate or pyrophos-

phate as precipitants or by formation of soluble complexes of thorium at a pH above 5.

146. Clifford, A. F., and Beachell, H. C. The chemical isolation of samarium from lanthanide mixtures. *J. Am. Chem. Soc.* 70, 2730-1, 1948. *CA* 42, 8687g, 1948. Samarium has been separated from the other rare earth elements (except europium and ytterbium) by reduction of ethanolic solutions of rare earth trichlorides with Mg and HCl (aqueous or anhydrous), and has yielded red SmCl_2 . With aqueous HCl and dilution largely with dioxane, even from very low Sm concentrations green samarous hydroxide is produced directly instead. This reaction may be of significance for detection of Sm. By metathesis of the dichloride, the sulfate (previously prepared), the hydroxide, citrate, carbonate and fluoride (new compounds), all water-insoluble, were prepared. The poisoning effect of Fe and particularly Pt on the reduction has been noted. In neutral ethanolic solution, samarous chloride was precipitated by Mg amalgam. The reaction, however, was complicated by hydroxide precipitates. In neutral aqueous sulfate solution, samarous sulfate was likewise precipitated by Mg amalgam, with the same complications. Addition of a little MeOH in the last case aided the reaction. The potential for the samarous-samaric couple in ethanolic chloride solutions has been placed in the region of 1.9-2.3 volts.
147. Dodonov, Ya. and Protyanova, K. F. The α -bromo-d-camphor- π -sulfonates of the rare earths. *Doklady Akad. Nauk S. S. S. R.* 68, 861-4, 1949. *CA* 44, 968a, 1950. NH_4 bromocamphorsulfonate was converted to the Ag salt by exchange with AgNO_3 ; the Ag salt treated with the corresponding metal chlorides in aqueous medium, filtered, and evaporated, gave on cooling the following rare earth salts, which were dried over H_2SO_4 to constant weight; the hydration was determined by vacuum drying. All are soluble in H_2O , decompose on heating, and are insoluble in organic solvents. $\text{La}(\text{C}_{10}\text{H}_{14}\text{O}_4\text{BrS})_3 \cdot 8\text{H}_2\text{O}$, $[\alpha]_D$ 76.36°; $\text{Ce}(\text{C}_{10}\text{H}_{14}\text{O}_4\text{BrS})_3 \cdot 8\text{H}_2\text{O}$, $[\alpha]_D$ 76.22°; $(\text{NdC}_{10}\text{H}_{14}\text{O}_4\text{BrS}) \cdot 9\text{H}_2\text{O}$, $[\alpha]_D$ 75.97°. The rotation increases with decrease of atomic weight of the metal, and the atomic weights can be calculated from the optical data with good agreement except for Nd, which gave too

- low a value, probably because of some contamination with Ce and La.
148. Erametsa, O. Quinaldic acid as a reagent for thorium. Suomen Kemi-
stilehti 17B, 30, 1944. CA 40, 7047.5, 1946. Quinaldic acid (I) pre-
cipitates Th quantitatively in the cold. The precipitate is partially
soluble in hot water, completely soluble in an excess of Th salts, but
difficultly soluble in an excess of I. It is soluble in mineral acids,
but is stable to AcOH. Since La, Ce, Pr, Nd, Y, and mixtures of
the Y metals are not precipitated by I, the method can be used for
the separation of Th from these elements. Zr is not precipitated in
the cold I, but is precipitated hot; the precipitate is readily soluble
in dilute AcOH. Al, Be, and Cr are precipitated by I (cf. Ray and
Bose. CA 28, 1626.2). U salts are also precipitated, but not quanti-
tatively, either from hot or cold solutions.
149. Gher, R., Bushey, G. L., and Audrieth, L. F. Oxides and hydroxides
of praseodymium (Technical Rept.) University of Illinois, Urbana.
June 1950. ATI-87 415. UNCLASS. The possible use of hydrazine
dihydrochloride as a standard reducing agent for the determinations
of active oxygen in higher valent praseodymium oxide has been in-
vestigated. Results for the percentage active oxygen obtained by
this method are low in comparison with other analytical procedures,
but are consistent within themselves. It has been shown that black
praseodymium oxide, when heated in a 5% solution of hydrazine, is
reduced to the yellow-green hydroxide. The material formed by this
method, and that formed by precipitation from praseodymium chlor-
ide solution with ammonium hydroxide, are identical in color and in
x-ray diffraction patterns. The hydroxide prepared by the hydrazine
reduction method possesses better physical characteristics in that it
is granular instead of gelatinous and therefore easier to filter, wash
and dry.
150. Gordon, L., Vanselow, C. H., and Willard, H. H. Precipitation of
thorium from homogeneous solution. Separation from rare earths of
monazite sand with tetrachlorophthalic acid. Anal. Chem. 21, 1323-
5, 1949. CA 44, 2409g, 1950. When Th^{4+} is treated with a dicar-
boxylic acid, preferably tetrachlorophthalic acid, precipitation is
extremely slow at room temperature, but a gelatinous precipitate

forms promptly if the solution is near the boiling point. A double precipitation at pH 1.0 effects quantitative separation of Th from the large quantities of rare earths usually found in monazite sand. For the attack of the sand with HClO_4 , the urea method (CA 42, 2543c) prescribes a 50-g sample and the use of an aliquot for the analysis. A 1-g sample can be treated as follows: treat with 5 ml concentrated HNO_3 + 30 ml of 70% HClO_4 . Boil the contents of the open flask very gently for 1.5 hours after dense fumes of HClO_4 are evolved. Cool, add 15 ml of water and 5 ml of 3% H_2O_2 . Heat gently and, if the gelatinous residue does not dissolve, add 5-10 ml of concentrated HCl . Cool, filter and wash with 4.75 N HNO_3 . Evaporate to fumes again, cool, add 100 ml of water + 5 ml dilute H_2O_2 , heat until clear and then add 100 ml of water. Add NH_4OH dropwise and when stirring fails to keep the solution clear, quickly add 10 ml of concentrated HCl . After 5 minutes, add 6 g of MeHC_2O_4 . Heat to 70-85° and stir mechanically for 30 minutes. Add a hot solution of 8 g oxalic acid in 200 ml of water. After 30 minutes more, cool to room temperature and make the pH about 0.9 by adding NH_4OH . Wash with 2% oxalic acid, and then precipitate Th and the rare earth as described in the previous paper and make a reprecipitation with MeHC_2O_4 . Dissolve in HClO_4 , and 200 ml of water + 1 g of NaI , adjust the pH to 1.5-1.6 and add 200 ml of a 0.3% solution of tetrachlorophthalic acid. Adjust the pH to 1.0-1.1, stir and heat to 70-80°, filter, wash with cool 0.1% solution of the reagent at pH 1.5. Treat the precipitate with NaOH to form hydrated ZrO_2 , dissolve this in hot 2 N HCl , reprecipitate with tetrachlorophthalic acid, wash, ignite, and weigh as ZrO_2 .

151. Helger, B., and Rynninger, R. Analytical group-separation of small amounts of rare earths from uranium, (in English). Svensk Kem. Tid. 64, 224-33, 1952. cf. CA 43, 1281a, CA 43, 1684a. CA 47, 443.h, 1953. A method is given for separating as little as 0.5 γ of rare earths from U products, in a form ready for the determination of the individual rare earths by physical methods. The rare earths are precipitated with HF on CeF_3 as a carrier, the Ce is precipitated as the iodate, and the rare earths are collected by precipitation with NH_3 on Fe as the carrier. If the separation is carried out on a micro

- scale, the Fe can be removed as FeCl_3 by extraction with Et_2O .
152. Hilal, O. M. Preparation of pure erbium salts. *Z. Anorgan. and Allgem. Chem.* 273, 241-246, 1953. *Crerar Met. Abstr.* 2, No. 3, 47, 1953. A comparison was made of the following methods of separation of erbium from mixtures of oxides containing yttrium and ytterbium: fractional crystallization of oxalates from HCl solutions, partial decomposition of nitrates, removal of ytterbium through reduction with sodium amalgam, and fractional precipitation with NH_3 diluted with air (from HCl solutions). The latter method was found to be the most convenient when handling small quantities of substances.
 153. Hirt, R. C., and Nachtrieb, N. H. Determination of rare earth elements in uranium compounds. U.S. AEC. June 1944. ATI-53004. UNCLASS The separation of the rare earth elements from uranium and its compounds may be obtained by means of an ether extraction, precipitation as fluorides, and purification by way of the hydroxides. The final determination is carried out spectrographically, using a Jarrell-Ash Wadsworth Spectrograph and an A.R.L. Dietert Multisource. Dysprosium, gadolinium, samarium, neodymium, praseodymium, lanthanum, and cerium were investigated, and their limits of sensitivity and their recoveries from U_3O_8 determined. The method may be applied to other rare earth elements as well. In these determinations, greater sensitivities were obtained by use of a condensed discharge from the Multisource instead of a DC arc, and by the use of a Dietert Projection-Comparator Densitometer for measuring the relative transmissions of the lines from samples and those of a standard plate.
 154. Krishnamurty, K. V. S., and Raghava Rao, Bh. S. V. Analytical chemistry of thorium. VII. Separation from cerite earths. Use of anisic acid. *J. Indian Chem. Soc.* 28, 261-4, 1951. *CA* 46, 5950c, 1952. Anisic acid, in neutral or slightly acidic solutions, reacts with thorium and a filtrable precipitate is obtained from boiling solutions containing NH_4Cl . Most bivalent cations do not interfere. There is some coprecipitation with Cr^{+++} , Zr^{4+} , Ce^{4+} , V, and Ti interfere as does UO_2^{++} in high concentrations. The precipitate is the normal salt and ThO_2 is obtained on ignition. VIII. Aliphatic dicarboxylic

- acids. Suryanarayana, T. V. S., and Raghava Rao, Bh. S. V. Ibid. 511-14. Succinic acid forms a fairly insoluble precipitate with Th^{4+} but at the optimum pH cerite earths are also thrown down. Adipic acid, however, gives quantitative precipitation and by a double precipitation at pH 4.2-4.4 it can be freed from cerite earths. Th can be determined in monazite by a procedure like that previously given (CA 45, 7914i).
155. Krury, J. W. Problems in the aqueous chemistry of cerium (III) fluoride and lanthanum (III) fluoride. U.S. AEC. UCRL-2271, 64pp., 1953. Crerar Met Abstr. 2, No. 5, 39, 1953. Trivalent rare earth ions form insoluble gelatinous fluorides in aqueous HF. The solubilities of such fluorides of Ce(III) and La(III) have been studied. Data were also obtained on the heat of precipitation and the extent of complexing. Similar data were obtained for the complexing and solubility of La(III). The solubility of these ions is about the same, but that of Gd(III) fluoride is 50 times as large. Thermodynamic data are treated mathematically and values are tabulated.
 156. Kurlifay, S. M. The separation of the rare earths neodymium and praseodymium by precipitation as chloride. 1947. University of Missouri, Rolla, Mo. ATI-12201. UNCLASS. Hydrochloric acid method is utilized for the purification of praseodymium and neodymium compounds when the products to be purified already exist in a state of approximate purity. The complete crystallizations were performed on each chloride and the elapsed time was less than 20 minutes per crystallization. The recovery was 53.2% of the neodymium oxide and 61.2% of the praseodymium oxide, while the purity progressed from 97% in each case to 99.71% in the case of neodymium oxide and 99.27% in the case of praseodymium oxide.
 157. Lakshmana Rao, B. R., and Raghava Rao, Bh. S. V. Analytical chemistry of thorium. I. Separation from cerite earths with o-chlorobenzoic acid. J. Indian Chem. Soc. 27, 457-8, 1950. CA 45, 2365hi, 1951. An aqueous solution of o-chlorobenzoic acid (I) cause incomplete precipitation of Th^{4+} if the pH is below 2.8 and at pH 3.8 other rare earths begin to precipitate. To the solution containing not over 150 mg of dissolved ThO_2 , add a few drops of Congo red indicator

solution and just enough NH_4OH dropwise until the neutral point is reached. Dilute to 100 ml, boil, and while stirring add a 1% solution of I. Boil 3 minutes, let stand 0.5 hours, filter, wash with a 0.05% solution of I, and finally with hot water. Ignite and weigh as ThO_2 . The precipitate contains about 3 moles of I to 1 mole of Th and 3 moles of water. II. Separation from cerite earths by o- and p-amino-benzoic acids. Murthy, D.S.N., and Raghava Rao, Bh. S. V. Ibid. 459-61. Th is precipitated by both the acids at pH 4.2. Precipitation of other rare earths starts at pH 4.8. Make the solution just acidic to Congo red and dilute to 10 ml, add 5 ml of 5% NH_4OAc solution and, with stirring, 75 ml of a boiling 1% aqueous solution of the reagent. Filter, wash with a 1% solution of the reagent, then with hot water, dry, ignite, and weigh. If the ratio of rare earth to Th is greater than 4:1, dissolve the precipitate in hot, dilute HNO_3 and repeat the precipitation after neutralizing and adding NH_4OAc . Ignition tests indicate that Th anthranilate is anhydrous, 2 moles of acid are associated with 1 of Th and there are 2 OH groups. Th p-amino-benzoate appears to contain 1 mole of acid, 1 of Th and $4\text{H}_2\text{O}$: it is probably $\text{O}=\text{T}-\text{OH}.\text{OAc}.4\text{H}_2\text{O}$.

158. Marsh, J. K. The place of yttrium and the application of ferricyanide precipitation in the rare-earth group. The purification of erbium. J. Chem. Soc. p.118-22, 1947. CA 41, 4056e, 1947. Y lies between Ho and Dy in ionic radius and between Nd and Sm in atomic radius. Y can be collected first in one position, then in a second in the rare-earth series, and to be readily separated and purified. Ferricyanide precipitation is effective for the separation of Y from Ho and Er. Y in Er was decreased from 7 to 0.32 atom % by six precipitations, with 50% yield.
159. Marsh, J. K. Lanthanon (rare-earth) sodium sulfate precipitations. Nature 163, 998-9, 1949. CA 43, 7855i, 1949. The use of double sulfates to effect a more rapid separation of the lanthanons is described.
160. Marsh, J. K. Separation of the lanthanons with the aid of ethylenediamine tetraacetic acid. J. Chem. Soc. pp., 1819-23, 1950. CA 45, 2358e, 1951. The lanthanons can be separated by fractional precipi-

- tation of oxalates or other insoluble salts on breaking their complexes with NH_4 or alkali salts of EDTA. By this mode of fractionation, yttrium comes close to dysprosium in the lanthanon series, and is separated very rapidly from erbium and the ytterbium earths. A rapid separation of all the heaviest earths, which form the firmest complexes, is also indicated. The method is recommended as being superior to double alkali-sulfate precipitation for an initial separation
161. Marsh, J. K. Separation of yttrium and erbium with the aid of ethylenediamine tetraacetic acid ("Enta Acid"). J. Chem. Soc. pp. 1461-63, 1951 CA 45, 10112i, 1951 Rapid concentration of Y occurs in the precipitate when Y-Er oxalates are dissolved in diammonium dihydrogen ethylenediamine tetraacetate and fractionally precipitated by acidification. Er is not obtained free from Y without difficulty. Ho and Y are not separated efficiently
162. Marsh, J. K. Separation of the lanthanons with the aid of ethylenediamine tetraacetic acid. III. The salt $\text{H}_4\text{Na}_4\text{Ln}_4\text{enta}_5 \cdot 24\text{H}_2\text{O}$ and its use in (a) fractional crystallization and (b) double-sulfate precipitation. J. Chem Soc pp. 3057-60, 1951; cf. CA 45, 2358e, 10112i. CA 46, 3446c, 1952. $\text{H}_4\text{Na}_4\text{Ln}_2\text{EDTA}_5 \cdot 24\text{H}_2\text{O}$ (I) prepared from lanthanon oxide, NaOH, and EDTA gives a rapid separation of the lanthanons by fractional crystallization. An equilibrium such as $4\text{Na} [\text{Ln EDTA}] \cdot \text{H}_4\text{EDTA} \rightleftharpoons 3\text{HLnEDTA} + \text{Na} [\text{LnEDTA}] + \text{Na}_3\text{H EDTA}$, with solid solution occurring, is believed to be the reason, HLn EDTA collecting in head crystals and Na $[\text{Ln EDTA}]$ at the tail. Stability of I falls with decreasing basicity in the Ln series. Separation is most effective for middle earths but gives a rapid, rough concentration of the ytterbium earths. The K salt is amorphous, but its use is not advantageous. Small amounts of Nd have been eliminated from $\text{H}_4\text{Na}_4\text{Gd}_4\text{EDTA}_5$ solution much more rapidly by double-sulfate precipitation than from GdCl_3 solution.
163. Misumi, S. Studies on the chemical analysis of the rare earth elements IV. Possibility of the separation of lanthanum from cerium by 8-hydroxyguinoline. J. Chem Soc. Japan, Pure Chemistry Sect. 73, 931-34, 1952. Crerar Met. Abstr. 1, No. 10, 50, 1953. It was found that cerium and lanthanum of valence III precipitate quantita-

tively in ammonium solutions of certain organic acids at a given pH when in the presence of oxine, while cerium of valence IV does not precipitate an oxime salt. Experimental results showed that cerium and lanthanum can be quantitatively precipitated in an ammonium solution of succinic acid and tartaric acid. Minimum pH at which salts of each element precipitate differ: In particular, when ammonium solution of succinic acid is used, the minimum pH value for the two elements differs considerably, so that separation of the two elements is facilitated.

164. Misumi, S. Determination of rare earth elements. VI. J. Chem. Soc., Japan, Pure Chem. Sect. 74, 453-6, 1953; cf. CA 47, 7937d. CA 48, 2508c, 1954. La is precipitated by an alcohol solution of 8-quinolinol in the range of pH 9.4-11.5, with Na citrate-NH₄OH buffer. The precipitate (La 0.1-1 mg) is dissolved in 30 ml of 15-20% H₂SO₄ and a known volume of 0.1-0.01 N KMnO₄. After exactly 20 minutes 0.5 g KI is added and the I liberated by the excess KMnO₄ is titrated with 0.1-0.01N thiosulfate to determine La. This oxidation of the quinolinol complex with KMnO₄ gives more accurate results than the usual bromate titration. VII. Ibid. 681-5. Separation of Ce(III) from La is made by a homogeneous precipitation method. The pH where basic salicylate and formate of Ce(III) and La began to precipitate are 5.17, 5.14, 5.87 and 5.65, respectively, when the pH of the solution is increased slowly by the hydrolysis of urea at 90° (cf. Willard, CA 45, 1459a). By applying this precipitation method 6 times to a mixture of La and Ce(III), the per cent CeO₂ increased from the original 50.47 to 95.14%.
165. Moeller, T., and Kremers, H. E. Rare Earths. L. The separation of Er from Yt by fractional precipitation of the ferrocyanides. J. Am. Chem. Soc. 66, 307, 1944. CA 38, 1441.2, 1944. The method of Prandtl (CA 25, 4191) for the separation of Er and Yt by use of ferrocyanides has been modified; its success depends upon the complete removal of Fe. Er Yt chloride solutions were prepared in 3 N HCl to contain 2% rare earth oxide and 10% NH₄Cl; sufficient 20% K₄Fe(CN)₆ was added to precipitate about 50% of the rare earths; about 20 ml precipitated the equivalent of 1 g of oxide from material

analyzing 85-100% Er_2O_3 and 20 ml for lower Er concentrations. Details of 2 fractionations are given. cf. CA 33, 6749.7.

166. Moeller, T., and Kremers, H. E. Rare earths. LI Electrometric study of the precipitation of trivalent hydrous rare earth oxides or hydroxides. J. Phys. Chem. 48, 395-406, 1944. CA 39, 1111.9, 1945. Data obtained by the electrometric method are given for Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Er, Tm, Yb and Lu as nitrate, sulfate and acetate solutions. These data serve for checking the effects of anions, determining the precipitation pH values and the solubility-product constants and indicating the basicity order and relative basicities of the hydrous oxides or hydroxides. Decrease in pH either at incidence of precipitation or at mol ratio $\text{OH}^-/\text{R}^{+++}=0.4$ closely parallels decrease in ionic radius. Precipitation generally occurred at a higher pH value with an acetate than with the corresponding nitrate or sulfate. In all instances, the titration curves rise steeply before the theoretical 3OH^- to 1R^{+++} mol ratio is attained; this suggests the formation of basic salts during the precipitation processes. The solubility-product constants were calculated (on the assumption that the precipitates formed during the titrations were hydrous hydroxides) from pH values and ion concentrations at $\text{OH}^-/\text{R}^{+++}$ mol ratios of 0.6, 1.2 and 1.5; the average of the solubilities ($\times 10^6$) of the hydroxides are: La 7.8, Ce 4.8, Pr 5.4, Nd 2.7, Sm 2.0, Eu and Gd 1.4, Y 1.2, Er 0.8, Tm 0.6, Yb and Lu 0.5. Basicity in the hydrous hydroxides of the trivalent rare earth elements decreases with decrease in ionic size of the constituent metal; the relative basicities were calculated from the ratio of the solubility products; if Y is 1, the ratios are: La 1235, Ce 185, Pr 333, Nd 23.5, Sm 8.4, Eu 4.2, Gd 2.6, Er 0.16, Tm 0.041, Yb 0.036, Lu 0.031.
167. Moeller, T., and Kremers, H. E. Rare earths. Double Na_2SO_4 precipitation for separation of Tb and Y earths. Ind. Eng. Chem. Anal. Ed. 17, 44-5, 1945. CA 39, 883.5, 1945. The rare earths can be divided roughly into 3 groups: (1) La, Ce, Pr, Nd and Sm which form relatively insoluble double salts with alkali sulfate; (2) Eu, Gd, and Tb whose double sulfates are somewhat more soluble; (3) Dy, Y, Ho, Er, Tm, Yb and Lu whose double sulfates are fairly soluble.

Because many earlier experiments were made before the complete identification of some of the members were possible, additional experiments were made to test the value of the separation. Systematic fractional precipitation of the soluble fractions from a preliminary separation of the crude earths effects rapid separation of the Tb and Y groups and a rapid concentration of Y. Precipitation with Na_2SO_4 does not serve to separate satisfactorily any individual rare-earth element but it works very nicely for preparing concentrates for further systematic separations. cf. CA 38, 1441.

168. Murty, D. S. N., and Raghava Rao, Bh. S. V. Analytical chemistry of thorium. VI. Separation from rare earths by camphoric acid. J. Indian Chem. Soc. 28, 218-20, 1952; cf. CA 46, 60f, 4950f. CA 46, 9465i, 1952. Camphoric acid precipitates Th^{4+} completely in an NH_4OAc -buffered solution at pH 4.2 or higher. Cerite earths are precipitated at pH 6.2 or higher. By precipitating at pH 4.4, dissolving the $\text{Th}(\text{O}_2\text{C})_2\text{C}_8\text{H}_{14} \cdot 3\text{H}_2\text{O}$ precipitate in hot 3 N HNO_3 , and reprecipitating at pH 4.4, a good separation of Th^{4+} from cerite earth can be effected. Wash the precipitate with a hot 1% solution of camphoric acid, and dry at 105° to constant weight or ignite to ThO_2 . The latter procedure is preferred.
169. Osborn, G. H. Some analytical applications of m-nitrobenzoic acid with particular reference to the separation of quadrivalent elements from the rare earths (lanthanides). Analyst 73, 381-4, 1948. CA 42, 7656d, 1948. A solution of 4g m-nitrobenzoic acid in 1 l. of water proved an excellent reagent for precipitating and determining under carefully controlled conditions, Th, Zr, Ce^{+4} , Hf and Hg. Harvey, et al. (CA 42, 821a) have shown that it reacts similarly with Pu. It does not react with the trivalent rare earths of the lanthanide series. Aside from possible interference by hydrolysis of certain Sn salts and the presence of Hg, the reagent appears to be a specific precipitating agent for all quadrivalent ions except Ti^{+4} . Precise directions are given for separating most of the elements that are precipitated.
170. Ostroumov, E. A. Separation of cerium from rare earths by the bromate-pyridine method. Zhur. Anal. Khim. 2, 111-17, 1947. CA 43,

5697c, 1949. Ce can be separated quantitatively from other rare earths as a basic bromate in a solution buffered with pyridine and pyridine-HCl. Evaporate the solution containing the rare earths to dryness. Dissolve the residue in 2.5 ml of HCl, add approximately 100 ml of hot H₂O, and 0.3 g of NaBrO₃ (to oxidize Ce³⁺), stir, cover with a watch glass, and boil carefully on a hot plate, adding hot H₂O from time to time as it evaporates. Boil for 30-35 minutes, until the odor of Br vanishes. Remove from the hot plate, add 5 g of NaBrO₃, mix, and repeat the slow boiling for approximately 1 hour. Remove from the hot plate, and after 3-4 minutes, add dropwise with stirring, 10 ml of buffer solution (20 ml of 6 N HCl + 20 ml water + 25 ml of pyridine + 35 ml of water). Let stand overnight, filter, and wash the precipitate with cold H₂O; basic Ce bromate is precipitated quantitatively. Treat the precipitate with 50 ml of a hot, 10% oxalic acid solution, add 0.5-1.0 g more of oxalic acid, and boil for 40-45 minutes to complete the conversion of bromate to oxalate. Dilute the mixture to its original volume and keep overnight. Filter, wash with dilute oxalic acid solution, ignite, and weigh as Ce₂O₃. Excellent results were obtained.

171. Ostroumov, E. A. Separation of scandium with the aid of pyridine. Zhur. Anal. Khim. 3, 153-61, 1948. CA 42, 7655e, 1948. A method for separating Sc from other rare earths is based on the difference in pH at which their hydroxides precipitate.
172. Pilkington, E. S., and Wylie, A. W. Rare earth and thorium compounds from monazite. J. Soc. Chem. Ind. (London) 66, 387-94, 1947. CA 42, 2884h, 1948. The rare earth elements in monazite (I) are separated into (a) Ce-group hydroxides containing Th(OH)₄ and (b) crude Th oxalate, both suitable for the production of most rare earth compounds used in industry, by (1) digesting I with concentrated H₂SO₄, (2) dissolving the pasty mixture of sulfates in ice H₂O and filtering off the insoluble material, (3) treating the filtrate with Na₂SO₄ to precipitate the double sulfates of Na and the Ce group, filtering, and washing, (4) decomposing the double sulfates by boiling with NaOH, and filtering, washing, and drying the precipitated hydroxides at 120°, and (5) adding (COOH)₂ to the filtrate from (3)

at 90° to precipitate crude Th oxalate, which is filtered off, washed, and dried at 120°. A flow sheet is given. The yields obtained are: mixed Ce-group hydroxides 99%, and ThO₂ (from (a) and (b)) 97%. The effect of the different variables on the yields is discussed. Several features of the process are similar to that of Powell (Brit. 510, 198, CA 34, 4530.3). 22 References.

173. Poleuektov, N. S., and Nikonova, M. P. Quantitative approximate semimicro determination of cerium and total rare earths in ores and minerals. Zhur. Anal. Khim. 3, 354-61, 1948. CA 43, 8950f, 1949. A greater sensitivity is obtained by a modification of the accepted method. This modification consists of determining Ce in a solution containing Na citrate, H₂O₂, and K₂CO₃. In the presence of elements interfering with the colorimetric determination, Ce is precipitated as oxalate and the precipitate dissolved in Al(NO₃)₃. Experiments with quantities of Ce of 50-1000 γ showed that the precipitation of Ce with oxalate is not complete. The less Ce in solution the greater is the percentage left unprecipitated. Considerable losses of Ce were also experienced if precipitation was done in the presence of Mo or V. For the analysis of minerals this is not serious since these elements are not likely to be encountered frequently. Also, the presence of other rare earths will induce better precipitation of Ce by virtue of coprecipitation. In a sample of 10-25 mg Ce was estimated by this method with an accuracy of $\pm 10-20\%$. The refinement in the determination of the total rare earths consists of the use of a torsional micro-balance equipped with a Pt weighing pan. The decomposition of the sample depends on the nature of other elements present.
174. Popov, A. I., and Weylandt, W. W. Cupferron complexes of the rare earth elements. Anal. Chem. 26, 883-86, 1954. Crerar Met. Abstr 2, 43, 1954. Cupferron and neocupferron seem excellent precipitants for lanthanon ions if there are no interferences but can not compete with the oxalate method for separation from impurities. Optimum results are obtained with small amounts of lanthanons in solution.....

175. Quill, L. L., and Salutsky, M. L. Separation of praseodymium from lanthanum by fractional carbonate precipitation in trichloroacetate solution. *Anal. Chem.* 24, 1453-6, 1952. *CA* 47, 5291, 1953. Mixed La and Pr oxides were dissolved in hot 25% $\text{CCl}_3\text{CO}_2\text{H}$, and the solutions were diluted to a rare earth oxide content of 10-25 g/l. These solutions were heated at 90° for periods up to 2 hours, and the carbonate precipitates formed were studied. By decomposing one-third to one-fourth the trichloroacetate in a sample, filtering, and continuing the decomposition on the filtrate, the Pr_6O_{11} was increased from 36 to 72%. This procedure was preferred for initial samples less than 80% Pr. When the original trichloroacetate solution was heated longer and 75-80% of the rare earth was precipitated, the precipitate redissolved in $\text{CCl}_3\text{CO}_2\text{H}$, 75-80% precipitated again, etc., to a total of 7-8 decompositions, the final sample was $\geq 99\%$ Pr. This method was best for samples $> 80\%$ Pr. Varying the temperature of decomposition from 60 to 90° had no effect on the separations. The separation was best from more dilute solutions. The same technique was used for Y earth separations. The average atomic weight of the earths in a mixture was changed in one separation from 152.2 to 162.5 in the carbonate precipitate and 145.7 in the filtrate.
176. Ryabehikov, D. I., and Volkova, V. Ya. Rare earth thiosulfates. *Compt. rend. acad. sci. U.R.S.S.* 55, 501-03, 1947. *CA* 41, 6832a, 1947. Soluble rare earth salts react with $\text{Na}_2\text{S}_2\text{O}_3$ solution by metathesis to yield rare earth thiosulfates. Addition of 3 volumes MeOH to 1 volume of the solution yields a quantitative recovery of the anhydrous salt as a white or characteristically colored powder, slightly soluble in water but easily soluble in acids with the evolution of S and formation of the sulfite. Free S corresponding to 1/2 the total S in the compounds is formed on long standing in the mother liquor after alcohol precipitation. On heating to $800-1000^\circ$, $\text{Th}(\text{S}_2\text{O}_3)_2$ and $\text{Ce}_2(\text{S}_2\text{O}_3)_3$ yield, respectively, ThO_2 and CeO_2 , almost completely insoluble in HCl, while La, Nd, and Pr thiosulfates give compounds of the general formula $\text{M}_2\text{S}_2\text{O}_7$, soluble in warm 1:4 HCl. By use of this solubility difference after calcination, $\text{Ce}_2(\text{S}_2\text{O}_3)_3$ was separated

from mixtures of La and Pr thiosulfates and La and Nd thiosulfates. Addition of $\text{Na}_2\text{S}_2\text{O}_3$ to $\text{Ce}(\text{SO}_4)_2$ in neutral or nearly neutral solution yields a $\text{Ce}_2(\text{SO}_4)_3$ and $\text{Na}_2\text{S}_4\text{O}_6$. The reaction is quantitative, showing a color change and a marked change in potential at the equivalence point.

177. Schirmer, F. B., Jr., Fluoroalkyls of the rare earth elements Status Rept Dec. 1, 1947 - Mar. 31, 1948. Apr. 1, 1948, 3 p. Clemson Agricultural Coll. U1553. UNCLASS. The purpose of this investigation is to prepare fluoroalkyls of the rare earth elements and to develop a method of separating these elements. The reaction of HgO with CCl_3COOH in ether yielded a clear homogeneous solution from which a fine crystalline white solid was separated. This solid was analyzed analytically for Hg and Cl content. Results indicate that a method can be found for the preparation of mercuric trichloroacetate provided hydrolysis of the salt can be prevented.
178. Schlyter, K., and Sillen, L. G. Coprecipitation of tetrapositive ions with lanthanum fluoride. Acta Chem. Scand. 4, 1323-5, 1950. (In English) CA 46, 6964i, 1952. Precipitates obtained by adding NaF to acidic solutions of La^{3+} and a metal ion (M) were examined by x-ray powder photography. For M of radii close to La^{3+} (Ce^{3+} , Pr^{3+} , Nd^{3+}) mixed crystals of LaF_3 and isomorphous MF_3 precipitated. With shorter ionic radii, MF_3 and LaF_3 were not isomorphous, and a range of solid solutions was observed. Ce^{4+} and U^{4+} gave precipitates with the LaF_3 structure but of smaller lattice dimensions. It is suggested that these solid solutions occur by replacement in the lattice of 4 La^{3+} by $3\text{M}^{4+} + 1$ "hole" and that similar phenomena explain the coprecipitation of Pu^{4+} with LaF_3 .
179. Scott, T. R. Preparation of core ingredients for searchlight carbons. Australia, Council Sci. Ind. Research, Bull. No. 200, 27 pp., 1946. CA 41, 7062g, 1947. Methods for the preparation of rare earth fluorides of the Ce group of metals (exemplified by CeF_3) are critically reviewed, and 3 methods described in detail. Although CeF_3 has been used for many years in the manufacture of anodes for the high-intensity arc, no detailed account of a simple method of preparation adaptable to large-scale production has previously been

published. The 3 methods described were selected as most suitable for large-scale production and were investigated in detail. They were (a) treatment of rare earth oxides with H_2F_2 , giving oxides and fluorides; (b) treatment of aqueous suspensions of rare earth hydroxides with H_2F_2 , giving crystalline fluorides; (c) reaction of dilute H_2SiF_6 with rare earth oxides and hydroxides, by which fluorides are precipitated, and separation of the product from the bulk of associated SiO_2 ; only the trivalent hydroxides are suitable for this reaction. The methods are critically compared regarding the nature of the rare earth compound and acid used, purity of product, and proportion of F lost. Procedures used in analysis and testing of CeF_3 samples are given in detail.

180. Seiler, J. A. Separation of lanthanum, praseodymium and neodymium by potassium carbonate. Natl. Nuclear Energy Ser. Div. IV, 9, Radiochem. Studies: The Fission Products, Book 3, 1713-15, 1951. CA 47, 12111c, 1953. The procedure presented for the separation of La, Pr, and Nd made use of the increasing solubility of the rare earth in K_2CO_3 with increasing atomic number.
181. Serebrennikov, V. V. Precipitation of rare earths with ammonia and oxalic acid in the complete quantitative analysis of minerals. Uchenye Zapiski Tomsk. Gosudarst. Univ. im. N. V. Kuibysheva No. 8, 111-23, 1948. CA 44, 5762a, 1950. In the presence of NH_4 salts there may occur incomplete precipitation of rare earths by NH_4OH along with Fe and Al during the separation from Ca and Mg. The rare earth analysis should be done by the fluoride method if much Fe and Al are present since the oxalate method gives low results. A recommended alternative is: Precipitate the test solution with 10% NH_4OH with 2-5 ml in excess, heat to coagulation, filter, wash with ammoniacal 2% NH_4NO_3 . Ash in Pt vessel and evaporate with HF; after treatment with H_2O containing a little HF filter the solution, ash the precipitate and decompose with H_2SO_4 to SO_3 fumes; dissolve the residue, dilute with HCl, then add NH_4OH to precipitate the hydroxides and boil with 40-50 ml of saturated oxalic acid solution until clear of the hydroxide precipitate. Filter off the rare earth oxalates and wash with H_2O containing oxalic acid. Dissolve and re-

precipitate from HNO_3 solution.

182. Short, H. G., and Dutton, W. L. Determination of rare earth elements and yttrium in uranium compounds. Anal. Chem. 20, 1073-6, 1948. CA 43, 1281a, 1949. Most of the U is removed by extracting $\text{UO}_2(\text{NO}_3)_2$ with ether. The rare earths are then precipitated as fluorides and purified as hydroxides. The final determination is then made with the spectrograph. With a 50-g sample, 0.2 parts of Th can be determined in the presence of 10^6 parts of Gd. Treat 10 g of the original material with 50% HNO_3 . If necessary, filter off any residue, fuse it with $\text{K}_2\text{S}_2\text{O}_7$ in a Pt crucible, dissolve the cold melt in HCl , and evaporate the excess acid on the steam bath. Precipitate the rare earths in this solution as described below. Evaporate the main solution until crystallization of $\text{UO}_2(\text{NO}_3)_2$ begins, then cool and break up lumps with a glass rod. Dissolve as much as possible with 70 ml of Et_2O . Transfer to a separating funnel, leaving as much as possible of the residue in the beaker. Wash this with 10 ml more of Et_2O . Add sufficient water to give 1 ml of aqueous layer, shake, allow the layers to form, and drain off the aqueous solution into the original beaker. Repeat the extraction after adding 1 ml more of water. Reject the Et_2O solution containing the U. Evaporate off the ether carefully from the aqueous fraction, add a little water and 2 drops of HNO_3 . Evaporate nearly to dryness, transfer to a Pt dish and dilute to 50 ml with water, add 15 ml of 40% HF and allow to stand overnight. Filter through paper on a waxed funnel and into a waxed beaker. Wash once with water and ignite in a Pt crucible. Wash out the Pt dish with 1-2 ml of hot concentrated H_2SO_4 and add the solution to the Pt crucible. Evaporate to fumes of H_2SO_4 to remove F. Dissolve the residue in 10% HCl and transfer the 5-10 ml of solution to a beaker. Add 0.1 g of salicylic acid and a slight excess of NH_4OH . After 30 minutes, filter off the insoluble hydroxides and wash with 4% NH_3 solution. Ignite, dissolve in a little concentrated HCl , and evaporate in a depression of a 5-mm. Cu rod. Examine in a large Hilger automatic Littrow spectrograph and estimate the quantities of the rare earth elements.

183. Soddy, F. Separation of thorium and the rare earths from minerals. Brit. 572,411, October 8, 1945. CA 42, 731c, 1948. In the process in which Th and the rare earth minerals are separated as solid sulfates from the acid liquors, the H_3PO_4 content of the system is substantially increased instead of being eliminated as in certain processes. Before proceeding to the separation, H_3PO_4 is added to the H_2SO_4 employed to treat the mineral material. Cf. CA 41, 7688c.
184. Soddy, F. Separation of thorium and the rare earths from minerals. U.S. 2,425,573 August 12, 1947. CA 41, 7688b, 1947. Sulfates of rare earths, Th and meso-Th are produced from monazite or other rare earth minerals by the following process: Monazite is heated with H_2SO_4 in the ratio of 1:2. H_2O is added until the Th and rare earths are brought into solution, the resulting solution has a volume of about 9 l per kg of monazite. The ratio of H_3PO_4 to free H_2SO_4 in the solution will be about 1:5. A mixture of concentrated H_3PO_4 and H_2SO_4 in the same ratio is added to the monazite solution to precipitate the rare earth sulfates free from Th. The rare earth sulfate precipitate is then washed with 9 N H_2SO_4 , and the liquor from the precipitation and washing is concentrated to precipitate the Th concentrates. The concentrated acid liquor remaining after removal of the Th may be used to solubilize the monazite until the H_3PO_4 - H_2SO_4 ratio is at least 1:2 or to separate the rare earth sulfates.
185. Trombe, F. New method of basic precipitation applied to the separation of the rare earth elements. Compt. rend 215, 539-41, 1942. CA 38, 3211.9, 1944. To effect successive precipitations of hydroxide without greatly increasing the volume of solution, T. bubbles air through weak NH_3 solution, and then through the rare earth solutions. The pH can be controlled carefully, and excellent results obtained, particularly in the separation of the Ce and Y groups, and for the elimination of Y from its group.
186. Trombe, F. The pH corresponding to the threshold of precipitation of the rare earth elements. Compt. rend. 216, 818-90, 1943. CA 38, 4525.3, 1944. Gaseous NH_3 greatly diluted with air was slowly introduced into the agitated solution of the nitrate of the metal to be precipitated. This procedure is better than that of Britton (cf. CA

20, 26), because a more uniform pH exists throughout the solution than when a solution of NH_3 is used for the precipitation. The pH values for the threshold of precipitation obtained by T. at identical concentrations are slightly higher than those of Britton. Curves showing the variation of pH and concentration were obtained which make possible the selection of the optimum conditions for the separation of the mixed salts.

187. Trombe, F. Rapid extraction of pure lanthanum oxide from rare earths. *Compt. rend.* 225, 1156-8, 1947. *CA* 42, 2201g, 1948. A current of NH_3 mixed with air is passed into a solution of the nitrates of the rare earths from which Ce has been eliminated. Four successive precipitates were filtered off, and the last fractions contained practically all the La, comparatively pure because of the difference in the pH corresponding to the precipitation threshold (more than 0.7) from that of the other rare earths. cf. *CA* 38, 3211.9; 4225.5.
188. Venkataramaniah, M., and Raghavarao, Bh. S. V. Separation of quadrivalent cerium from thorium and trivalent rare earths - use of potassium periodate. *Current Sci. (India)* 18, 248-9, 1949. *CA* 44, 1351i, 1950. Under controlled conditions of acidity and KIO_4 concentration, Ce^{IV} can be precipitated as $\text{CeHIO}_6 \cdot \text{H}_2\text{O}$ from Th, rare earths, and Ce^{III} . Ten cc of the ceric solution containing not more than 0.5 g of ceric oxide and other elements is mixed with 120 cc of dilute (1:5) HNO_3 and 70 cc of the periodate reagent in the cold (the periodate reagent is prepared by saturating 1:5 dilute HNO_3 with the salt). The mixture is heated for 10 to 15 minutes on a vigorously boiling water bath and left to settle. On cooling, it is filtered through a sintered-glass crucible No. 4, and partially washed with 1:10 HNO_3 . The precipitate is returned to the original beaker, dissolved in the minimum of concentrated HNO_3 and diluted so that the acid concentration is approximately 2 N, when the CeHIO_6 is reprecipitated. The precipitate is filtered and washed, first with about 200 cc of dilute HNO_3 (1:10) and finally with 100 cc of cold water. It is then dried for 3-4 hours at 100 to 110° and weighed as $\text{CeHIO}_6 \cdot \text{H}_2\text{O}$. For Th, the filtrate is made ammoniacal and the periodates of Th and the rare earths are filtered off and recovered as

oxalates after appropriate treatment. These are taken up with HNO_3 and Th is separated by any of the known methods, preferably by double precipitation. The rare earths including Ce^{III} are again recovered as oxalates, ignited and weighed as R_2O_3 . In the precipitation of Ce^{IV} , HNO_3 dilution must not vary from the ratio 1:5.

189. Venkataramanah, M., Satyanarayanamurthy, T. K., and Raghava Rao, B. S. V. Thorium; its separation from cerite earths and estimation. *J. Indian Chem. Soc.* 27, 81-6, 1950. *CA* 45, 1909f, 1951. Analytical methods for Th were tested on pure Th solution, synthetic Th-cerite earths mixtures, and Travancore monazite. Trimethylgallic acid in faintly acid solution precipitates Th. Coprecipitation of cerite earths was slight and removed by reprecipitation. Double precipitation by phenoxyacetic acid from solutions, neutral to Congo red gave good results. Double precipitation by veratric acid gave slightly high results. Benzoic acid, ammonium benzoate, and tannic acid also were satisfactory reagents. Th was always weighed as ThO_2 . Zr and Ce^{4+} interfered in all cases.
190. Vickery, R. C. Rare earth tungstates. *J. Chem. Soc.* 2501-5, 1949. *CA* 44, 2881i, 1950. Tungstates of La, Ce, Pr, Nd, and Sm were prepared by addition of solutions of Na_2WO_4 and the corresponding lanthanon nitrate. Compounds of the composition $\text{R}_2\text{O}_3 \cdot 3\text{H}_2\text{WO}_4$ were obtained regardless of the method of preparation. No evidence was found for hydrates other than the trihydrate as determined from dehydration and vapor-pressure curves. The solubility of the tungstates at 20° varied from 0.14 g/l for La to 0.25 g/l for Sm. On ignition the tungstates showed previously undescribed color changes; these are attributed to partial reduction to tungstites of varying composition, which are finally reoxidized to stable crystalline tungstates. The separation and purification of lanthanum. I. Hydroxide precipitation. *Ibid.* 2506-11. La was separated from the other Ce earths by fractionally precipitating the hydrated oxides with air-borne NH_3 (cf. *CA* 38, 4525.3). The degree of separation and the ease of filtration of the precipitate were greater with decreasing concentration of NH_3 vapor. The operative concentration of NH_3 vapor was adjusted to 20% of its concentration above the parent NH_3 solution. Constant

volume was maintained by a reflux condenser. Stepwise fractionation was effected by precipitating and filtering off 10% of the oxides at each step, the filtrate being regassed. From a solution containing 36.5% La_2O_3 in 100 g of mixed Ce earth oxides as nitrates in 4.5 N NH_4NO_3 and without $\text{Cd}(\text{NO}_3)_2$ (CA 16, 3599), 98% La_2O_3 was obtained in 8 fractionations in a 77% yield. II. Solubility of rare earth hydroxides in fused ammonium nitrate. Ibid. 2508-11. The approximate solubilities of individual rare earth hydroxides in molten NH_4NO_3 were determined by mixing 5 g of the appropriate hydroxide with 10 g of NH_4NO_3 , fusing at 130° for 10 minutes, digesting the melt with a minimum of H_2O , and removing the soluble portion by filtration. The insoluble hydroxide remaining was ignited to the oxide. The rare earth in the soluble portion was determined by the oxalate method. The g of $\text{R}(\text{OH})_3$ soluble in 10 g NH_4NO_3 were: La 2.39, Pr 1.65, Nd 1.58, Sm 1.42, Y 1.62, and Ce(IV) 0.50. A Ce oxide mixture of 25 g, containing 36.5% La_2O_3 , was converted to the hydroxides and dried. By pyramidal fractionation with a $\text{R}(\text{OH})_3:\text{NH}_4\text{NO}_3$ ratio of 1:7 and at temperature of 130° for 5 minutes, in 5 fractionations an 82% yield of >98% La_2O_3 was obtained. No enhanced separation was obtained upon the addition of $\text{Cd}(\text{NO}_3)_2$ to the fusion mixture. The addition of Ce to the fusion mixture had a scavenging effect (cf. CA 40, 3355.1, 7).

191. Vickery, R. C. Some reactions of cerium and other rare earths with chlorine and hypochlorite. J. Soc. Chem. Ind. (London) 69, 122-5, 1950; cf. CA 43, 4168e. CA 44, 9287i, 1950. The nature of the products formed in the "basic chloride" process for the separation of Ce from other rare earths was studied. In a gas-solid reaction system, Cl and HOCl vapor, obtained by low-temperature distillation of chlorine water in a stream of N, was passed through a manifold attached to reaction tubes carrying La, Pr, Nd, Ce(III), and Ce(IV) hydroxides. The analyses of the solids for total Cl and active Cl after 4 hours of reaction time corresponded to the values for the compound $\text{R}(\text{OCl})_3 \cdot \text{RCl}_3$ in all cases except Ce(IV), which did not react. The La, Nd, and Pr products dissolved completely in H_2O and gave tests for Cl^- and ClO^- . The Ce(III) compound reacted in H_2O to give

Cl, HOCl, and $\text{Ce}(\text{OH})_4$. In solution, the action of $\text{Ca}(\text{OCl})_2$ with trivalent rare earth ions was followed by electrometric titrations of 10 ml aliquots of a rare earth stock solution (containing 15 g CeO_2 as Ce(III) and 30 g of other rare earths/l), with 1 ml aliquots of a freshly prepared 0.1 M aqueous slurry of $\text{Ca}(\text{OCl})_2$. Two breaks in the curve were observed, the first at a pH of 6.1-6.15 and the second at 5.95. The first point was associated, with the formation, from the precipitated hydroxides, of the hypochlorites, which dissolved leaving the precipitate enriched in $\text{Ce}(\text{OH})_4$. The solution process continued with further addition of $\text{Ca}(\text{OCl})_2$ until at the second break the RCl_3 , $\text{R}(\text{OCl})_3$ decomposed to the hydrated oxides. Oxidation of cerium by potassium chlorate in chloride solution. Ibid. 125-6. To 250 ml of a chloride solution of monazite residues containing 5.15 g CeO_2 and 6.25 g of other rare earth oxides, 10 g KClO_3 was added. The solution was boiled in the presence of marble chips and the precipitates were filtered off every 10 minutes. Fe and Th along with some Ce appeared in the first 8 fractions, but the ninth was a pure Ce compound (99.95%). This purity was maintained until the 21st fraction, when Pr and Nd appeared. In all, 27 precipitations were necessary to free the solution completely from Ce. This is not to be preferred to the bromate method.

192. Waring, C. L., and Mela, H., Jr. Method for determination of small amounts of rare earths and thorium in phosphate rocks. Anal. Chem. 25, 432-5, 1953. CA 47, 5302, 1953. The work was suggested by the possibility of rare earths occurring in the phosphate minerals from Florida and western U.S.A. After removal of Fe as FeCl_3 by extracting the HCl solution with ether, the rare earths and Th are concentrated by a double oxalate precipitation with Ca^{++} as carrier. The rare earths are separated from Ca^{++} by NH_4OH precipitation with a definite quantity of Al^{3+} as carrier. The Al also serves as an internal standard in the final spectrographic analysis. The method will determine 0.02-2 mg of each rare earth and Th within 10% of the truth. Detailed directions are given.
193. Weaver, B. Fractional separation of rare earths by oxalate precipitation from homogeneous solution. Abstr. of Papers, 124th Meeting

Am. Chem. Soc., Chicago, p. 7B, 1953. Crerar Met. Abstr. 2, No. 2, 68, 1953. Fractional precipitation of oxalates was studied and semiquantitative relationships among the rare earths were established. Separation factors for pairs throughout the series were calculated. Sm precipitates preferentially to others, with lighter elements precipitating in order of decreasing atomic number and the heavier ones in order of increasing atomic number. The effect of the rate of precipitation on separation was studied.

194. Weaver, B. Fractional separation of rare earths by precipitation with mandelic acid. Abstr. of Papers, 123rd Meeting, Am. Chem. Soc. p. 4B-5B, Chicago, 1953. Crerar Met. Abstr. 1, No. 9, 43, 1953. Most rare earths form precipitates with mandelic acid. The very selective process is like precipitation from homogeneous solution. Minimum pH for precipitation varies markedly among the elements. Variables in rapidity and completeness are pH, mandelic acid concentration, rare earth concentration and temperature. Dry samarium mandelate is stable at 110°C and appears to be a dihydrate. Erbium mandelate is a trihydrate. Separation factors were found for neodymium and samarium in synthetic mixtures and for other pairs in complex concentrates. Application of the process to 100 g quantities gives fractions rich in samarium and gadolinium and might be successful in purifying the heaviest rare earths.
195. Weaver, B. Fractional separation of rare earths by precipitation with mandelic acid. Anal. Chem. 26, 476-78, 1954. Crerar Met. Abstr. 2, No. 6, 35, 1954. Most rare earths are precipitated from mandelic acid solutions. Minimum pH varies markedly among the elements in selective precipitation. Rapidity and completeness of precipitation depend on the pH, temperature and concentrations of acid and rare earths. Fractionation of mixtures may be continued through a long series by a single addition of acid; the pH changes are affected by NH_4OH and HCl additions. The filtrates are converted to oxalates and then to the oxides for weighing since mandelates burn with a sooty flame. Mandelic acid does not interfere with oxalate precipitation. The process is useful for purifying the heavier rare earths. Elements precipitate in the reverse order of

increasing basicity and ionic radii. Yttrium falls between gadolinium and dysprosium rather than between holmium and erbium, as is usual. Data are tabulated. 16 references.

196. Weaver, B. Fractional separation of rare earths by oxalate precipitation from homogeneous solution. *Anal. Chem.* 26, 479-80, 1954. *Crerar Met. Abstr.* 2, No. 6, 35, 1954. By fractionation from homogeneous solution of pairs of rare earth oxalates and multi-component mixtures, separation factors for the pairs were determined. . .
197. Wenger, P., Duckert, R., and Rusconi, Y. Critical study of reagents for cations. XIII. Reagents for the cations of the rare earths and yttrium. *Helva. Chim. Acta* 28, 274-8, 1945. *CA* 40, 529.6, 1946. As general reagent for the groups a saturated solution of oxalic acid in water is satisfactory. It precipitates equally well Y, Th, Ba, Sr, and Ca and does not precipitate Cb, Ta, Al, Fe, U, Ti, Zr, Hf, and Sc. The ions of La, Ce, Nd, Sm, and Pr give characteristic crystals when studied under the microscope when NH_4 succinate is added to a drop of solution. Ta does not react, Zr gives an amorphous precipitate and Fe^{+++} a reddish brown precipitate. Precipitates of different characters are obtained with Cb, U, Eu, Be, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Th, Sc, and Ca. For the yttric group containing Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y, lactic acid is recommended, which gives characteristic crystals under the microscope; Cb, Ta, Fe, U, Ce, La, Nd, Zr, Th, and Ca do not react. For La, a specific reagent is I_2 which gives a flocculent blue precipitate. All other reagents are eliminated. Tests for Ce were discussed previously (*CA* 37, 5335.6, 8). For Eu^{++} , $\text{Zn} + \text{HCl} + \text{cacotheline}$ give a violet coloration which is a specific test in this group. No specific reagent can be given for Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, although NH_4 succinate is useful for characterizing Pr^{+++} , Nd^{+++} and Sm^{+++} , and quinalizarine is useful for Pr^{+++} and Nd^{+++} . Y can be identified only by fractional precipitation.
198. Willard, H. H., and Yu, S. T. Separation of cerium from the rare earths by precipitation as iodate from homogeneous solution. *Anal. Chem.* 25, 1754-6, 1953. *Anal. Abstr.* 1, No. 4, 660, 1954. The

sample as (CeO_2) containing 25-100 mg of Ce^{IV} is dissolved in warm dilute H_2SO_4 (2:1) diluted to about 300 ml with water and made 0.4 to 0.5 M with respect to HNO_3 and a few drops of 3% H_2O_2 solution are added to reduce all Ce^{IV} . The excess H_2O_2 is destroyed by boiling and the solution is cooled to about 50°C . Three grams of NH_4IO_3 are added then 1 g of ammonium persulfate and the solution is stirred and heated $70-80^\circ\text{C}$. After 1 1/2 - 2 hours, 2 g of the persulfate are added and the solution is allowed to stand overnight. The precipitate is filtered and washed with 1% HIO_3 solution, ignited and weighed as CeO_2 . If the sample contains elements other than rare earths, the rare earths are separated as the oxalates ignited to oxides and the procedure is carried out on a solution of the oxides in warm dilute H_2SO_4 .

V. AMALGAMATIONS

199. Beck, G. Detection of ytterbium in rare earth mixtures. *Helv. Chim. Acta* 29, 506-7, 1946. *CA* 40, 5357.3, 1946. By means of Mg or, better still, Na amalgam, it is possible to reduce Yb^{+++} to Yb^{++} and the bivalent Yb reacts with oxalic acid to form glyoxylic acid, which can be recognized by the red color that it gives with naphthorescorcinol. To 1-2 ml of a solution of the sulfate of the unknown in dilute H_2SO_4 add a piece of ice and about 0.5 ml of Na amalgam. After the reduction is complete, add 3-4 drops of saturated oxalic acid solution. Transfer the mixture from the separatory funnel recommended for the reduction to a test tube, add a little naphthorescorcinol and an equal volume of concentrated HCl. Boil about a minute; cool, dilute with water, and extract with ether. A rose color indicates Yb. Other rare earths, Ti^{++} , Cr^{++} , Mo^{+++} , Zr, and Ta do not interfere, but V^{++} , U^{+++} , Cb^{+++} , and Re^{+++} must be absent. Under favorable conditions 3% of Yb will give the test, although Yb^{++} is easily oxidized and is, therefore, unstable.
200. Marsh, J. K. Rare earth metal amalgams. II. Separation neodymium, samarium and gadolinium. *J. Chem. Soc.* p. 523-6, 1942. *CA* 37, 321.9, 1943. The reaction between Na amalgam and rare earth acetates described previously is applied to Nd-Sm and Gd-Sm separations. Sm forms an amalgam more readily than Nd or Gd and this amalgam is much less stable than that of Nd or Gd; thus fractional decomposition is useful for further purification. In 1 operation the Nd content in Sm is reduced from 70% to 0.01%. Eu if present accompanies Sm in the separation, but it can readily be removed by other methods. The conditions most applicable to the extraction of Sm from neighboring elements depend on the relative amounts present. Cf. *CA* 36, 6429.7
201. Marsh, J. K. Rare earth metal amalgams. III. Separation of ytterbium from its neighbors. *J. Chem. Soc.* p. 8-10, 1943. *CA* 37, 4025.2, 1943. Lu and Tm acetate solutions have no amalgam-forming power when treated with Na amalgam, while Yb acetate forms an amalgam readily. This makes it possible to eliminate Yb from its

neighbors. To remove Yb most completely Sm acetate is added and removed as amalgam taking the last part of the Yb with it. Lu with an Yb content of 0.001% can be prepared in this way. Yb separated from a mixture in which Lu and Tm predominate is spectroscopically free from them. Cf. CA 37, 321.9

202. Marsh, J. K. Rare-earth-metal amalgams. IV. Isolation of Eu. J. Chem. Soc. 531-5, 1943. CA 38, 1441.4, 1944. A method of concentration and purification of Eu is described which makes use of Eu amalgam. Sm and Eu are removed together from the crude material by treatment with Na amalgam. The resulting amalgam is decomposed by mixed AcOH and H₂SO₄ to give pure Sm(III) acetate and impure Eu(II) sulfate containing Sm(II). Cold concentrated HNO₃ selectively oxidizes the Sm(II) leaving solid Eu(II) sulfate. This is converted to the acetate and then to the amalgam, which is then treated with concentrated HCl to yield pure EuCl₂·2H₂O crystals. Eu amalgam remains mirror-bright in air for 10 minutes; this stability is an excellent indication of purity. Various methods of separating Sm and Eu on decomposition of the mixed amalgam are discussed. Cf. CA 37, 4025.2.
203. McCoy, H. N., and Hammond, R. P. Separation of ytterbium from accompanying rare earths by means of its amalgam. J. Am. Chem. Soc. 64, 1009, 1942. CA 36, 3113.1, 1942. Repetition of the preparation of Yb amalgam by the electrolytic method shows that only Yb and Eu of the rare earths form amalgams; separation as chlorides gives a fraction from the amalgams containing only Yb and Eu (the latter can be easily removed); the residual electrolytes give a small amount of chloride fraction containing some Yb and Eu, together with other rare earths. This affords a method of isolating Yb.
204. McCoy, H. N. The electrolysis of rare earth acetates and the separation of europium as amalgam from other rare earths. J. Am. Chem. Soc. 63, 3432-3, 1941; cf. CA 35, 5049.2. CA 36, 971.6, 1942. The method used for the preparation of Eu and Yb amalgams by the electrolysis of their acetates dissolved in aqueous tertiary K citrate is extended to aqueous solutions of Eu, Yb or Sm acetates and K citrate, the yield decreasing in the order given. The same elements in like solutions give amalgams when stirred with K amalgam. None of the

other rare earths similarly treated gave amalgams. Eu and probably Yb can be separated from accompanying rare earths by means of their amalgams.

VI. CHROMATOGRAPHY

205. Burstall, F. H., et al. Inorganic chromatography on cellulose. Nature 163, 64, 1949. CA 43, 4595g, 1949. Supplemental information is given on the chromatography of a number of metals. Au, Pt, and Pd were separated, from each other and from Ir or Rh by paper chromatography by using methyl propyl ketone containing 30% (volume/volume) of concentrated HCl. Metals of the Cu and Sn groups were also separated, with solutions of the chlorides and ethyl isopropyl ketone, containing 10% (volume/volume) of concentrated HCl, for group IIa, and dry EtOAc previously shaken with 2% HCl, for group IIb. Columns of cellulose pulp have been used to separate and estimate Ni and Co in minerals and steels and to separate Sc from a large number of metals, including the rare earths.
206. Burstall, F. H., et al. Inorganic chromatography on cellulose. II. The separation and detection of metals and acid radicals on strips of absorbant paper. J. Chem. Soc. 516-28, 1950, cf. CA 43, 4595g. CA 44, 7182h, 1950. Successful separations of the following were achieved by chromatography on paper strips by using the indicated solvents: Pb^{2+} , Cu^{2+} , Bi^{3+} , Cd^{2+} , Hg^{2+} - BuOH saturated with 3 N HCl; As^{3+} , Sb^{3+} , Sn^{2+} - acetylacetone saturated with H_2O , containing 0.5% HCl (d. = 1.18) and 25% acetone; Fe^{3+} , Al^{3+} , Cr^{3+} - glacial AcOH containing 25% CH_3OH ; Ni^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+} - acetone containing 5% H_2O and 8% HCl; Ca, Sr, Ba - pyridine containing 20% H_2O and 1% KCNS; Li, Na, K - CH_3OH ; Pt, Pd, Rh, Ir, Ru, Os, Au chlorides, or chloro salts - Me Et ketone containing 30% HCl; Au from Pt metals - Et_2O containing 2% dry HCl and 7.5% dry Me(OH); Hg from Pb, Cu, Bi, Cd, As, Sb, Fe, Al, Cr, Ni, Co, Mn, Zn - CH_3OAc containing 3% MeOH and 10% H_2O ; Se, and Te in dilute HNO_3 solution - dry BuOH containing 40% dry MeOH; Th, Sc, rare earth nitrates - tetrahydrosilvan containing 5% H_2O and 10% HNO_3 ; F^- , Cl^- , Br^- , I^- - pyridine containing 10% H_2O ; Ni, Mn, Co, Cu, Fe - acetone, Me Et ketone, or mixtures of these with HCl; U, V, Ti - acetone, Me Et ketone, or mixtures of these with HCl. After separations spot tests were used for identification. The ratio of the distances moved

by the ion to that moved by the solvent (R_F value) was studied and its significance noted.

207. Croatto, U. Chromatographic separation of the rare earths. *Ricerca sci.* 12, 157, 1941; *Chem. Zentr.* I, 1537, 1942. CA 37, 2680.4, 1943. Chromatographic analysis was used to identify rare earths. This method possesses a number of advantages. In particular the possibility of the chromatographic separation of La^{+++} and Ce^{+++} with Al_2O_3 as adsorbent is mentioned. Ce^{+++} is more strongly adsorbed than La^{+++} .
208. Croatto, U. Chromatographic separation of rare earths. *Atti reale ist. veneto sci.* 102, 103-17, 1943; cf. CA 37, 2680.4. CA 43, 6941e, 1949. The separation of Ce^{4+} and La^{3+} , Ce^{4+} and Sm^{3+} , Ce^{4+} and Pr^{3+} , Ce^{4+} and Nd^{3+} nitrates by means of Al_2O_3 (which, if precipitated from $\text{Al}_2(\text{SO}_4)_3$ with NH_4OH was found to be the best adsorbent) is described. Ce^{4+} was made visible on the adsorption columns by treating the chromatograms with NH_4OH and H_2O_2 . For the Ce^{4+} - La^{3+} mixture it was found that the addition of Fe^{3+} and Ca^{++} ions realizes a more distinct chromatographic separation of Ce and La, which enables a purification of the mixture up to 95%.
209. Erametsa, O. Chromatography of rare earths. *Bull. comm. geol. Finlande* 14, 36-49, 1941. CA 37, 3316.5, 1943. A mixture of rare earths that had been examined by an x-ray spectrograph was dissolved and passed through a tube filled with Al_2O_3 and the resulting chromatogram examined spectroscopically and sometimes with x-rays. The adsorptive ability of Y appeared to be less than that of the real lanthanides. The addition of Rochelle salt to the solution had a remarkable effect on the adsorption.
210. Erametsa, O., Sahama, Th. G., and Kanula, V. Chromatographic separation of the rare earths. I. *Ann. Acad. Sci. Fennicae* A57, No. 3, 5-20, 1941. CA 38, 4490.5, 1944. A technical Y-Er nitrate of known composition (determined with an x-ray spectrograph) was passed through an Al_2O_3 -filled tube at various pH values and the rare-earth content of the various fractions was determined with both optical and x-ray spectrographs. The Y group was in general more strongly adsorbed than the Ce group and the adsorption was independent

of the pH. Addition of citric acid reversed the adsorption series in the La group. Purification of the rare earths is possible to a small degree by repeated fractional chromatography in combination with other known methods. Cf. CA 37, 3316.5.

211. Lederer, M. Paper chromatography of some metals. Australian J. Sci. 12, 78, 1949. CA 44, 6332h, 1950. R_f values for butanol saturated with N HCl, and color tests are given for the following ions: Tl^+ (0.0), Tl^{3+} (1.11), Zn^{2+} (0.77), Be^{2+} (0.33), In^{3+} (0.30), V^{4+} (0.17), Mg^{2+} (0.11), Ti^{4+} , Al^{3+} (0.07), Er^{3+} (0.05), Ce^{3+} , Y^{3+} , Th^{4+} , and Dy (0.03). Tl^{3+} can be separated from all metal ions except Au and Hg.
212. Lederer, M. Paper electrochromatography of lanthanides and homologues of lanthanum. Comptes rend. 236, 200-201, 1953. Crerar Met. Abstr. 1, No. 7, 41, 1953. A drop of a solution of rare-earth hydroxides in an aqueous solution of citric acid is placed on a paper strip and, with 1% citric acid as an electrolyte, submitted to a 300 V potential. The separation is revealed on the dried strip by spraying with an alcohol solution of 8-hydroxyquinoline and ammonia. In white light the blots are yellow and brown, while in ultra-violet light they are green or black. Ac and radioactive Sc, added to the rare-earth mixture, can also be separated by the procedure and revealed by measuring the activity. For the whole group of elements considered, the distance of chromatographic migration increases with the atomic number; however, within the lanthanide group, the reverse rule seems to hold, with the exception of Ce.
213. Lederer, M. Chromatographic separation of rare earths. Compt. rend. 236, 1557-59, 1953. Crerar Met. Abstr. 1, No. 11, 52, 1953. A satisfactory separation of rare earths by paper chromatography was obtained using acetylacetone as a complex-forming agent in an eluant of the following composition: acetylacetone, 30 cc; acetic acid, 5 cc; butanol, 100 cc; water 65 cc. At 60°C the solvent rises 20 cm in two hours and the R_f are: La, 0.31; Ce, 0.38; Pr, 0.38; Nd, 0.22; Sm, 0.47; Eu, 0.49; Gd, 0.43; Dy, 0.62; Ho, 0.56; Er, 0.60; Yb, 0.59; and Y, 0.59. The working solutions, which contained about 5 mg of an oxide in 1 cc, were prepared by dissolving freshly

- precipitated hydroxides in 1 N acetic acid. After complete drying, the chromatographic spots are revealed with the aid of alizarin S.
214. Lindner, R., and Peter, O. Separation of radioactive yttrium earths in an adsorption of column (radiometric adsorption analysis). Z. Naturforsch. 1, 67-70, 1946. CA 41, 2349b, 1947. A solution of the yttrium earths was neutron-irradiated and adsorbed in an Al_2O_3 column. The chromatographic analysis was made by measuring the radioactivity throughout the column.
 215. Lindner, R. Separation by adsorption of the cerium group of rare earths; in particular their isotopes formed in uranium fission. Z. Naturforsch. 2a, 329-32, 1947. CA 42, 2865c, 1948. Partial separation of rare earths from neutral solution was obtained by an Al_2O_3 chromatographic column. A rare-earth activity of 13-d. half-life, from U fission, was separated, from activities obtained by irradiation of rare earths and known to be assignable to La, Ce, Sm, and element 61, but could not be separated from 19-hour Pr. Hence the 13-d. activity was assigned to Pr.
 216. Pollard, F. H., McOmie, J. F. W., and Stevens, H. M. Analysis of inorganic compounds by paper chromatography; the separation and detection of certain lanthanons. J. Chem. Soc., p. 4730-4, 1952. Crerar Met. Abstr. 1, No. 7, 40, 1953. A preliminary account is given of the application of complex-forming mobile phases to the separation on paper and cellulose columns of mixtures of (1) La, Ce, Pr or Nd, and Yb; (2) Y, La and Ce; (3) Y and La; (4) Y, La and Yb; (5) Y and Er from Ce; and (6) Y and Er from La. Their detection on paper is described. Data are tabulated.
 217. Sato, T. R., et al. Electrochromatographic separations of rare elements. J. Am. Chem. Soc. 74, 6154-55, 1952. Crerar Met. Abstr. 1, No. 6, 44, 1953. Differential electrical migration in moist filter paper has been applied to the separation of the rare earths; complex formation principles used in ion-exchange separations are incorporated. The resolved ions are yielded in detectable and recoverable form. In 0.1 M lactic acid, Sc and Y and Nd were separated from Ce, Pr, Pm, and Eu, while, in $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_5$, Ce(III) migrates as a cation. Binary and ternary mixtures are completely separated.

218. Weil, H. Industrial chromatography. I. Column chromatography and radial chromatography. *Can. Chem. Process Inds.* 33, 956-9, 1949. CA 44, 1357g, 1950. New developments in radial and column chromatography are noted. A new mechanical isolation equipment and a new separator in radial chromatography are discussed. Fractions can be isolated by elution or by sectioning the adsorbent bed. The disadvantages of centrifuging are pointed out and future developments in chromatography indicated. II. Industrial chromatography of the rare earths. *Ibid.* 1036-42. The evolution of chromatographic technique from analytical methods to unit operation in industry is traced. The importance and properties of the rare earths and their separation by chromatography are pointed out, also some applications of recently designed equipment. Equations for the densities at 25° as a function of concentration are given for the 6 salts. The activity coefficients determined by experiment obey the Debye-Huckel law within experimental error. CA 47, 1471b.

VII. IONIC MIGRATION

219. Clusius, K., and Ramirez, E. R. Separation of rare earth metals in aqueous solution by the ion-migration method. *Helv. Chim. Acta* 36, 1160-5, 1953. *CA* 47, 12047a, 1953. The method of concentration isotopes by counter-current electromigration (cf. Brewer, et al., *CA* 41, 3692c) has been adapted to the separation of rare earths in aqueous solution. It was possible to separate quantitatively La from Nd and Sm and Pr from Nd and Sm. A description of the apparatus with automatic control of the countercurrent is given. The analysis were carried out by absorption spectra.
220. Clusius, K., and Ramirez, E. Electrolytic separation of rare earths. *Chimia* 7, p. 90, 1953. *Crerar Met Abstr* 1, No. 10, 49, 1953. Diffusion and convection prevent a successful separation of ions by any method based on differences of ion velocities. The authors introduced high potential gradients to combat diffusion, while a series of strips of dialysis paper placed perpendicularly to the field prevented convection along the field. In this way very successful separations were obtained. Using 40-100 cm long tubes and fields of 20-30 V/cm, it was possible to obtain in the cathode space a mixture of 99% La^{+++} and 1% Nd^{+++} from an original mixture of 48% La^{+++} and 52% Nd^{+++} . Similar results were obtained with other mixtures.
221. Dye, J. L., and Spedding, F. H. The application of Onsager's theory of conductance to the conductances and transference numbers of unsymmetrical electrolytes. *J. Am. Chem. Soc.* 76, 888-92, 1954. *CA* 48, 6789f, 1954. Consideration of the transference-number behavior of unsymmetrical electrolytes in aqueous solutions led to an examination of the mathematical development of Onsager's theory (*CA* 21, 2412) of conductance. A mathematical treatment of the theory is described which uses graphic methods to evaluate integrals that were only approximately evaluated by Onsager. The approximate methods, although satisfactory for 1-1 electrolytes, are unable to explain the transference-number behavior of unsymmetrical electrolytes. The new treatment of the theory was applied to the conductivities and transference numbers of CaCl_2 , NdCl_3 , and ErCl_3 . The

agreement between theory and experiment was greatly improved for both transference numbers and conductivities of these unsymmetrical electrolytes. These results show that the underlying assumptions made by Onsager are valid at higher concentrations than was previously thought to be the case.

222. Edwards, R. E., Ayers, A. S. and Banks, C. V. (Ames Lab.) Spectrophotometric determination of cerium. Aug. 31, 1951. 7 p. (ISC-165). An ultraviolet spectrophotometric method for the determination of Ce utilizes the reaction of a Ce solution with H_2O_2 in ammoniacal solution with citric acid as the complexing agent. The method is rapid and accurate, but suffers from many interferences, which may be eliminated by the use of a preliminary separation with oxalic acid. Apparatus and reagents are described and the recommended procedure is presented in detail. Results obtained on samples to which varying amounts of interfering ions were added are tabulated. Nuclear Sci. Abstr. 5, No. 23, Abstr. No. 7012, 15 Dec. 1951.
223. Hopkins, B. S. Electrochemistry of the rare-earth group. Trans. Electrochem. Soc. 89, 6 pp., 1946. CA 40, 1739.9, 1946. Electrochemical methods have been useful in the study of the rare earth group metals in several ways: (1) Cathodic reduction has produced europous ion and ytterbous ion, both of which form insoluble sulfates. This has made possible the separation of these scarce elements from the others in the group. (2) The electrolysis of rare earth solutions with use of a Hg cathode, has made possible the production of rare earth amalgams from which the rare earth metals can be obtained in a high state of purity. (3) Electrolysis of fused rare earth chlorides has been the most commonly used method of producing the metals. Those members of the group with smaller atomic weights have been produced and some of their individual properties have been determined. Misch metal, an alloy of rare earth metals with Fe, is the most important metallic product.
224. Spedding, F. H., and Dye, J. L. Conductances, transference numbers and activity coefficients of aqueous solutions of some rare earth chlorides at 25°C. J. Am. Chem. Soc. 76, 879-81, 1954. CA 48, 6789c, 1954. The equivalent conductances, cation transference numbers,

and activity coefficients at 25° of aqueous solutions of DyCl_3 , HoCl_3 , and TmCl_3 were determined for concentrations up to 0.1N by previously described methods. Since rare earth elements hydrolyze slightly, measurements were made on solutions at the equivalence pH as determined by acid titration. Onsager's law is obeyed up to about 0.008N for these chlorides. To determine whether the hydrolysis has a measurable effect on these properties the measurements were repeated for solutions of NdCl_3 , and YbCl_3 at the equivalence pH in order to compare with previously determined results. Hydrolysis has a negligible effect on properties of solutions of light rare earth chlorides but exceeds experimental error by a slight amount for the heavier rare earth chlorides. A linear dependence of the transference numbers with $N^{1/2}$ was obtained for all salts. The slopes differ from those predicted by the Onsager theory by about 20% but agree reasonably well with predictions of the new treatment of Onsager's equation.

VIII. COLORIMETRIC AND VOLUMETRIC METHODS

225. Bamann, E., and Heumuller, E. Determination of La, Ce and other rare earths by a colorimetric method. Ber 75B, 1514-17, 1942. CA 38, 1446.5, 1944. The method depends upon the precipitation of the rare earth as the orthophosphate and the colorimetric determination of the PO_4 ion by the molybdenum blue test. The solution (5 cc containing 50 mg $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or 50.15 mg $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and 3 cc N AcONa diluted with 17 cc H_2O in a 50 cc centrifuge tube is treated dropwise (not too slowly) with 5 cc primary or secondary alkali phosphate (concentration $\text{PO}_4\text{:La}$ about 2:1). After 0.5-1 hour the material is centrifuged, the liquid decanted, the precipitate washed 3 times with 0.02 N AcONa, dissolved in a few drops of 25% HCl and washed into a 200 cc flask; after making up to volume, an aliquot is tested colorimetrically.
226. Charlot, G. Determination of cerium by means of oxidation-reduction indicators. Anal. Chim. Acta 1, 309-13, 1947. CA 42, 7193c, 1948. Several oxidation-reduction indicators were considered for the detection of Ce^{+4} (o-phenanthroline-ferrous complex, N-phenylanthranilic acid, Ba diphenylaminesulfonate, o-tolidine, benzidine, anthranilic acid, p-phenetidine), and N-phenylanthranilic acid is recommended as the most suitable. The o-phenanthroline-ferrous complex is also useful for work with the rare earths. Other energetic oxidants give the same reaction. As little as $10^{-4.5}$ g ions of Ce per l can be detected, and the limit of dilution is $10^{-5.3}$.
227. Deshmukh, G. S. Volumetric estimation of cerium with potassium permanganate J. Sci. Research Benares Hindu Univ. 1, 121-4, 1950-51. CA 46, 3449f, 1952. Precipitate $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ in faintly acidic solution. If necessary make repeated precipitations from less than 0.5 N acid, to remove other rare earths. Dissolve the precipitate in hot dilute H_2SO_4 and titrate the $\text{C}_2\text{O}_4^{--}$ with KMnO_4 .
228. Edwards, R. E., and Ayers, A. S. Spectrophotometric determination of cerium. U. S. AEC., ATI 118-085, Aug. 31, 1951. UNCLASS. No abstract.
229. Foster, D. C., and Kremers, H. E. Europium determination in rare

earth mixtures. Anal. Chem. 25, 1921-2, 1953. Crerar Met. Abstr. 2, No. 6, 38, 1954. Europium concentrates cannot easily be analyzed spectrophotometrically due to interference of other rare earth bands. A method for determining europium at nearly any concentration consists of passing EuCl_2 (from a Jones reductor) into an excess of FeCl_3 . The FeCl_3 and FeCl_2 mixture resulting is titrated against a standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Ytterbium and samarium do not interfere since they are not reduced by zinc. The method is designed as a control in europium purification techniques. Precision is within 1%. Data are tabulated. 4 references.

230. Hagiwara, Z., and Banno, A. Separation of the rare earths and their accompanying elements VIII. New colorimetric determination of cerium. J. Chem. Soc. Japan, Ind. Chem. Sect. 57 No. 1, 26-28, 1954. Crerar Met. Abstr. 2, No. 9, 39, 1954. The complex salt formed by reaction of cerium IV and cupferron can be extracted with amyl acetate or N-butyl acetate, giving a sensitive reddish-brown coloration. A method of determination applying the finding is described, by which the cerium content of 5 to 35/ml in water solution can be determined with an error margin of only several percent. Coexistence of other rare earths posed no hindrance problem.
231. Kimura, K., and Ikeda, N. The color reaction between iodine and the basic acetates of some rare earth elements. Bull. Chem. Soc. Japan 21, 19-24, 1948. (In English). CA 43, 8948g, 1949. When I reacts with basic acetates, the following colors are observed at room temperature and at 100°: Y, colorless, colorless; Er, colorless, colorless. The effects of time, concentration of reagents, and of the presence of other ions were investigated. The absorption maximum of I-basic acetate shifts to shorter wave lengths with the decrease in basicity of the rare earth elements.
232. Malaguti, A., and Labianca, T. Volumetric determination of cerium and manganese with oxides of silver. Ann. chim. (Rome) 41, 385-90, 1951. CA 46, 6991c, 1952. A volumetric determination of Ce(I) and Mn(II) is proposed. Oxidizing agents are Ag_2O and AgO which in HNO_3 solution oxidize I to Ce^{4+} and II to MnO_4^- .

233. Misumi, S. Chemical analysis of rare earth elements. I. A new color for trivalent cerium. J. Chem. Soc. Japan, Pure Chem. Sect. 73, 171-3, 1952. CA 46, 11024a, 1952. The aqueous solution of Sunchromine Pure Blue B Extra (Na 2',6'-dichlorohydroxydimethyl-fuchsonedicarboxylate) gives a violet color with Ce(III). Amounts as small as 0.4 γ /0.05 ml can be detected. As Ce(IV) gives a yellow color with this reagent, it should be reduced to the trivalent state before testing. Fe(II) and La interfere. II. Colorimetric determination. Ibid. 173-5. To 5 cc of the slightly acidic solution whose Ce(III) content is 8-30 γ /cc, add 0.5 - 1.0 cc of glycerol and 0.5 cc of N NH₄OAc and dilute to 10 cc. Add 0.4 cc of 0.1% dye solution and adjust the pH to 7.5 with 1% with NH₄OH. After 15 minutes compare the violet color with standards. III. Colorimetric determination. Ibid. 249-52. The absorption maximum of the violet color produced by Ce³⁺ and the dye is 550 m μ and the filter S₅₇ is recommended for the colorimetric determination with the Pulfrich photometer. With this dye La, Pr, and Nd show pale violet, violet, and violet, respectively. In determining Ce by 8-quinolinol (CA 42, 6265d) tartaric acid is preferred to citric acid.
234. Misumi, S. Studies on the chemical analysis of the rare earth elements. V. Colorimetric determination of microgram quantities of cerium by 8-hydroxyquinoline. J. Chem. Soc., Japan, Pure Chem. Sect. 74, 67-70, 1953. Crerar Met. Abstr. 2, No. 3, 51, 1953. Research results on extraction solvents for oxime salts of cerium are given in a follow-up report of the author's search for accurate methods of colorimetric determination of cerium. Details on pH and influence of added substances are discussed, with the conclusion that the use of an amyl acetate solution of 8-hydroxyquinoline as extraction solvent to obtain oxime salts from a tartaric acid-ammonia solution gives sensitive results when colorimetric examination of the salts is conducted for detection or determination of microgram quantities of cerium. Optimum conditions for the process are discussed, as well as the application of the method to other rare earth elements.
235. Moeller, T, and Quinty, G. H. The rare earths. LVI. Spectrophotometric studies on colloidal "lanthanum blue". J. Phys. and Colloid Chem. 54, 315-21, 1950, cf. CA 41, 3007b. CA 44, 5241c, 1950.

The optimum conditions for the formation of La blue were determined. Stable sols were obtained from 2.5 ml of 0.1 M $\text{La}(\text{NO}_3)_3$ solution, 0.4-0.5 ml of 0.001 M I solution, 0.5-3.5 ml of 0.1 M HOAc, and twice the volume of 0.1 M aqueous NH_3 as of HOAc. In the propionate system only sols prepared from 2.5 ml of the La solution, 0.1-1.0 ml of the I solution, 2.5 ml of 0.1 M propionic acid, and 5.0 ml of the NH_3 solution were stable with respect to flocculation. No blue sols were obtained in any combination containing HCO_2H , CH_2ClCOOH , CCl_3COOH , or butyric acid. The acetate-containing sols are characterized by a single broad absorption band centered at approximately 580 $\text{m}\mu$; the band for the propionate sols was centered at approximately 600 $\text{m}\mu$. The intensity of absorption at the band center is a maximum for 0.025 M acetate solution; the decrease for higher concentrations probably results from sol flocculation. Absorption increases regularly with La-ion concentration up to 3.7 ml of 0.1 M solution per 25 ml; Beer's law is not followed well at low concentrations of La. For I concentration Beer's law is followed up to 5×10^{-5} M. Y and Sm gave no blue sols. Nd gave blue sols with both acetate (absorption maximum 580 $\text{m}\mu$) and propionate systems. The La sols can be used for the colorimetric estimation of small amounts of I.

236. Moeller, T., and Moss, F. A. J. Observations on the rare earths. LX. The ultraviolet-absorption spectrum of the gadolinium ion in aqueous solutions. J. Am. Chem. Soc. 73, 3149-51, 1951; cf. CA 44, 5241c, 5757a; 45, 3275g. CA 45, 8885c, 1951. The ultraviolet absorption spectrum of the Gd ion was reinvestigated for both aqueous Cl^- and ClO_4^- solutions, under conditions of high resolution. The spectrum is characterized by 18 absorption peaks and 2 definite inflections in the wave-length region 2400-3150 Å. The major and most complex absorption bands lie in the range 2720-2765 Å, were greater resolution than previously reported was obtained. Absorption is essentially the same for both Cl^- and ClO_4^- solutions. For both, absorptions at 2729, 2741-2, and 2756 Å are in accord with Beer's law to concentrations above 0.25 M.

237. Murthy, T. K. S., and Raghava Rao, Bh. S. V. Colorimetric detection and estimation of cerium. *J. Indian Chem. Soc.* 27, 383-4, 1950. *CA* 45, 2816f, 1951. Benzidine in the presence of HCl gives a bright yellow color with quadrivalent Ce. As little as 0.03% can be recognized on the spot plate. Trivalent Ce, other trivalent rare earth elements, and alkaline earths in moderate amounts do not interfere, but vanadate and chromate do, even in small quantities. The method can be used for exact determinations in range of 0.02 to 0.25 mg in 50 ml, but the measurement must be rapid as the color gradually fades.
238. Plank, J. Colorimetric determination of cerium. *Magyar Chem. Folyoirat* 50, 141-6, 1944. (Pub. 1948). *CA* 43, 8950b, 1949. The colorimetric method of *CA* 33, 5767.8, is modified to avoid interference by other elements. Pr, Nd, and Er do not interfere. Ferric ions must be removed by hydrolysis, Au and Pd by reduction to the metals. Trivalent Cr and vanadyl ions must be oxidized; then Cr is precipitated, and V becomes colorless. For the determination of Ce in pyrophoric alloy dissolve 0.1 g of the sample in HCl containing some Br, evaporate excess acid, dissolve the residue in water, and add excess K_2CO_3 solution until precipitate is dissolved. Dilute with an equal volume of water, warm on a water bath for 10 minutes, filter off the precipitated Fe, and wash the precipitate. Heat the solution on the water bath with some Devarda alloy, cool, shake with O_2 and determine Ce colorimetrically.
239. Rasin-Streden, R. Plant procedures for determining neodymium and praseodymium in cerite earths by an optical method. *Z. Anal. Chem.* 127, 97-112, 1944. *CA* 40, 5356.6, 1946. Of the rare earths, Pr, Nd, Sm, Eu, Er, Ho, Dy, and Tm show characteristic absorption spectra in the visible field. The possibility of making use of this fact in determining Pr and Nd is discussed, and 3 procedures are offered by which the plant chemist can quickly determine the approximate quantities of these elements in a short time. The first 2 procedures are based on spectroscopic comparisons, which can be made with a small or large spectroscope, but the third is based on the use of the Pulfrich photometer and suitable filters.

240. Ryabchikov, D. I., and Strelkova, Z. G. Colorimetric determination of cerium. Zhur. Anal. Khim. 3, 226-31, 1948. CA 43, 8950d, 1949. Ce^{3+} in the presence of excess citrate and sufficient NaOH to make the pH = 8-9 gives with H_2O_2 a reddish brown solution which is thought to contain $[\text{Ce}(\text{C}_6\text{H}_5\text{O}_7)]^{5-}$. For the colorimetric determination of Ce in a mineral, treat the sample with hot concentrated H_2SO_4 and evaporate until all acid fumes are expelled. Dissolve the residual sulfates in cold water, filter, and precipitate the oxalates of the rare earths in the usual manner. Dissolve the precipitate in a little saturated K citrate solution, dilute to a definite volume, and mix. Take 1 ml portions of solution in a series of test tubes and add 1 drop, 2 drops, etc., of 0.1 N NaOH and then some 10% H_2O_2 to see how the maximum color is best obtained. Finally compare the maximum color with that of standards similarly treated.

IX. POLAROGRAPHY

241. Estee, C. R., and Glockler, G. Reduction of neodymium at the dropping mercury electrode. *J. Am. Chem. Soc.* 70, 1344-7, 1948. *CA* 42, 4469i, 1948. A single wave is obtained from water solutions of $(\text{Nd})_2(\text{SO}_4)_3$; this is in contradiction to the results of earlier investigators. Similar single waves are obtained when LiCl , $(\text{CH}_3)_4\text{NI}$, or KCl is used as supporting electrolyte. By means of the Ilkovic equation it was shown that the reduction corresponds in all cases to $\text{Nd}^{+3} \rightarrow \text{Nd}^0$. The half-wave potentials are found to be dependent upon the concentration and acidity of the solution. From solutions of the above-mentioned electrolytes containing 2 millimoles of $\text{H}_2\text{SO}_4/\text{l}$ (with 0.01% gel added) diffusion currents proportional to the concentration of Nd^{+3} ion were obtained. The half-wave potentials remained constant in the range studied (0.01 M and below) at -1.83 ± 0.1 v versus the saturated calomel electrode in all cases.
242. Holleck, L. Polarographic determination of ytterbium in rare earth mixtures. *Z. anal. Chem.* 126, 1-8, 1943. *CA* 37, 6587.8, 1943. In the rare earth series, Eu, Yb and Sm can form bivalent and trivalent compounds. Optical and x-ray methods have been used mostly for identifying individual rare earths in mixtures of their hydroxides or oxalates but Holleck (*CA* 33, 4901.7) has shown that Eu can be determined with the polarograph; the half-wave potential for $\text{Eu}^{++}/\text{Eu}^{+++}$, referred to the N calomel electrode, lies at -0.77 v. It is here shown that Yb can be determined similarly at a potential of -1.48 v. All the remaining rare earths with the exception of Sm, form compounds containing only trivalent ions which deposit at more negative potentials so that they do not interfere. Sm cannot be determined with the polarograph, as the reduction potential lies in the region of the deposition of some of the trivalent cations. Full details are given for making the determination of Yb in solutions containing only sufficient acid to prevent hydrolysis. With the polarograph as little as 0.1% Yb can be detected and determined in rare-earth mixtures.
243. Holleck, L. Complex chemistry of rare earths. Polarographic current-potential curves of europium as indication of complex linkage. *Z. Naturforsch.* 2b, 81-9, 1947. *CA* 42, 4084i, 1948. Complex combina-

tion of rare earth ions in solution can be followed with polarograms; $\text{Eu}^{3+} + e = \text{Eu}^{2+}$ is most suitable for this purpose. Chloride and acetate curves are shown. Addition of the following anions gives in decreasing order complex linkage of trivalent ions: citric, tartaric, lactic, mandelic, and salicylic. The complexity constant of the citrate formation is of the order of 10^{15} . No complex formation was detected with amino acids. Complex formation affinity of the carbonate complex obtainable in alkaline carbonate solution corresponds approximately to that of the citrate complex in acid solution. The polarographic arrangement is illustrated

244. Holleck, L. Rare earths and polarography. Sbornik mezinarod polarograf, Praze, 1st Congr. Pt. I, 85-91, 1951. CA 46, 6980i, 1952. A review with 29 references
245. Laitinen, H. A., and Taebel, W. A. Europium and ytterbium in rare earth mixtures. Polarographic determination. Ind. Eng. Chem., Anal. Ed. 13, 825-9, 1941. CA 36, 364-7, 1942. The polarographic half-wave oxidation potentials of Eu and Yb in 0.1 N NH_4Cl solution are -0.671 and -1.415 v referred to the saturated calomel electrode. In a mixture of Eu and Yb oxides the polarographic determination of Eu agrees within 3% with the volumetric determination. If great care is taken to neutralize the excess acid used in dissolving Yb ore samples (containing about 5% Yb), polarographic and spectroscopic determinations check within $\pm 15\%$, the limit of accuracy of the latter. The polarographic method yields low results if the ores contain much Ce or are low in Yb. The wide separation of their half wave potentials permits a simultaneous determination of Eu and Yb, but necessitates a correction for the effect of decreasing negative potential
246. Onstott, E. I. Polarography of ethylenediamine tetraacetate complexes of europium. J. Am. Chem. Soc. 74, 3773-6, 1952. CA 46, 10959f, 1952. In the presence of a large excess of anions of ethylenediamine tetraacetic acid (symbolized as H_4Y) Eu(III) is reversibly reduced to Eu(II) at the dropping-Hg electrode in the pH range 6-13.6. Complex ions identified from half-wave potential and diffusion-current data are: $[\text{EuHY}]^-$, pH 6-8; $[\text{EuY}]^{2-}$, pH 11-13.6; $[\text{Eu}(\text{HY})_2]^{3-}$, pH 6-8; $[\text{EuY}_2]^{5-}$, pH 11-12; $[\text{EuY}(\text{OH})]^{2-}$, pH 13-13.6. Evidence is given for

the existence of $[\text{EuHY}]^-$ and $[\text{EuY}(\text{HY})]^{4-}$ in the pH range 8.5-10.3. The ratios of dissociation constants for several of the complex ions are calculated. The equilibrium constant for the reaction $[\text{EuY}_2]^{3-} + \text{OH}^- \rightleftharpoons [\text{EuY}(\text{OH})]^{2-} + \text{Y}^{4-}$ is calculated to be approximately 2.

247. Rabideau, W., and Glocker, G. The polarographic reduction of gadolinium. *J. Am. Chem. Soc.* 70, 1342-4, 1948. *CA* 42, 4469g, 1948. The results of Noddack and Brukl (*CA* 31, 5659-1) were not confirmed with regard to the polarographic reduction of $(\text{Gd})_2(\text{SO}_4)_3$. An increasing acid concentration shifts the half-wave potential of Gd to more negative potentials. A value of 4.0×10^{-6} sq cm/sec was calculated for the diffusion coefficients of Gd^{+3} at 25° . The results indicate that the reduction of Gd at the dropping Hg electrode involves 3 electrons. The average value of the diffusion current constant for Gd^{+3} was found to be 3.7 at 25° in a supporting electrolyte of 0.1 N LiCl or 0.1 N KCl. The half-wave potential for 4.0 millimolar Gd^{+3} was found to be -1.77 versus the saturated calomel electrode with 0.1 N LiCl and with 0.1 N KCl as the supporting electrolytes.
248. Stross, W. Polarographic analysis of light metals and alloys: a survey. *Analyst* 74, 285-92, 1949. *CA* 43, 7369e, 1949. The determination of alkali metals, alkaline earth metals, rare earth metals, Mg, Al, and Be in alloys of density 3.5 or less is reviewed. 40 references.
249. Swenson, A. W., and Glocker, G. The polarographic reduction of praseodymium. *J. Am. Chem. Soc.* 71, 1641-44, 1949. *CA* 43, 6524b, 1949. Half-wave potentials for the reduction of Pr^{+++} are given for solutions with no suppressor or supporting electrolyte, with gelatin and LiCl present, and with gelatin and $(\text{CH}_3)_4\text{NI}$ present. The half-wave potential becomes more negative with increase in concentration of either Pr^{+++} or H^+ . Only a single reduction step corresponding to a 3-electron change is observed. The pH of solutions of $\text{Pr}_2(\text{SO}_4)_3$ and PrCl_3 is independent of age, indicating no progressive hydrolysis.
250. Timnick, A., and Glocker, G. The half-wave potential of samarium. *J. Am. Chem. Soc.* 70, 1347-50, 1948. *CA* 42, 4470b, 1948. Solutions of Sm chloride and sulfate were studied polarographically without supporting electrolyte and in the presence of LiCl, KCl, and $(\text{CH}_3)_4\text{NI}$. Addition of H_2SO_4 to the sulfate solutions stabilized the half-

wave potential. With one millimolar Sm ion, in 0.001 NH_2SO_4 , 0.1 molar $(\text{CH}_3)_4\text{NI}$, and 0.01% gelatin medium a two-step polarogram was obtained. The half-wave potentials were -1.80 and -1.96 v against the saturated calomel electrode. The diffusion currents were, respectively, 6.0 and 13.0 microampere, corresponding to $\text{Sm}^{+++} \rightarrow \text{Sm}^{++} \rightarrow \text{Sm}^0$. However, in 4 millimolar solution the behavior is anomalous.

251. Zarinskii, V. A. Reduction of samarium, neodymium, and praseodymium ions on a mercury-drop electrode. *Zhur. Fiz. Khim.* 24, 662-9, 1950. *CA* 44, 10552d, 1950. Polarograms of 0.01 M solutions of Sm, Nd, and Pr sulfates in the absence of inert electrolytes did not disclose a 2-step reduction. With the chlorides of these metals in 0.1 N LiCl, the polarograms at 1.8-1.82 v (against a saturated HgCl electrode) indicated a bivalent intermediate in the reduction. The formation of a complex between Sm, Nd, and Pr and K citrate was studied polarographically. It was found from the polarograms of the sulfates of Sm, Nd, and Pr (against a 0.1 N LiCl background) that maxima of the 1st order resulted.

X. ELECTROMETRIC AND CONDUCTOMETRIC STUDIES

252. Moeller, T., and Fogel, N. The rare earths. LXI. J. Am. Chem. Soc. 73, 4481, 1951; cf. CA 45, 8885c. CA 46, 6907c, 1952. Electrometric titration data for perchlorate solutions of rare earths are, respectively, pH at precipitation incidence, pH at $\text{OH}^-/\text{R}^{+++} = 0.4$, average solubility product, average water solubility ($\times 10^6$) mole/l: La, 8.10, 8.18, 1.7×10^{-19} , 8.8; Pr, 7.40, 7.43, 6.7×10^{-22} , 2.2; Nd, 7.30, 7.34, 3.2×10^{-22} , 1.9; Sm, 7.13, 7.17, 8.4×10^{-23} , 1.3; Eu, 6.91, 6.99, 0.9×10^{-23} , 0.8; Gd, 6.84, 6.90, 1.8×10^{-23} , 0.9; Y, 6.81, 6.88, 1.6×10^{-23} , 0.9; Er, 6.61, 6.68, 4.1×10^{-24} , 0.6; Yb, 6.45, 6.55, 2.5×10^{-24} , 0.5; Lu, 6.45, 6.55, 1.9×10^{-24} , 0.5. The data support the theoretical basicity order for these cations and place Y in its logical place between Gd and Er. That precipitation was complete in all cases at OH:R mole ratios of 2.60-2.75 suggests basic salt formation to be at a minimum in perchlorate solutions. The differences in basicity between ions of adjacent elements are somewhat better defined, and the excessively high basicity of La is somewhat more apparent for perchlorate solutions.
253. Spacu, G., and Spacu, P. III. Potentiometric determination of lanthanum. Z. anal. Chem. 128, 229-31, 1948. CA 42, 5796a, 1948. La, like Th, can be determined by adding a known volume of KIO_3 and determining the excess reagent. To obtain complete precipitation of the La as iodate, it is necessary that the solution should contain about 35% EtOH. Of 2 results reported, one is excellent and the other is about 0.5% too high.
254. Spedding, F. H., and Jaffe, S. Conductances, solubilities and ionization constants of some rare earth sulfates in solution at 25°C. J. Am. Chem. Soc. 76, 882-4, 1954. CA 48, 6789i, 1954. The equivalent conductances and solubilities of sulfates of La, Ce, Pr, Nd, Sm, Gd, Ho, Er, Yb, and Y were measured in aqueous solutions at 25°. The solubilities in g/100 g H_2O are, respectively, 2.142, 5.063, 10.88, 5.591, 1.488, 3.299, 6.705, 15.19, 36.01, 9.673. The conductances are very much lower than is expected for strong

electrolytes. The deficiency in conductivity is attributed to the formation of complexes of the type MSO_4^+ in dilute solutions. The ionization constants for the dissociation of the complexes are calculated from the conductivity data and the Onsager equation for equivalent conductivity. For the equation $\text{MSO}_4^+ \rightleftharpoons \text{M}^{++} + \text{SO}_4^{--}$ the values of the ionization constants $\times 10^4$ for the elements in the order listed above are 2.4, 2.6, 2.4, 2.3, 2.2, 2.2, 2.6, 2.6, 3.4, all ± 0.25 .

255. Spedding, F. H., and Jaffe, S. Conductances, transference numbers and activity coefficients of some rare earth perchlorates and nitrates at 25°C. J. Am. Chem. Soc. 76, 884-8, 1954. CA 48, 6789h, 1954. The equivalent conductances and cation transference numbers at 25° of aqueous solutions of La, Pr, Nd, Sm, Gd, Ho, Er, and Yb perchlorates and La, Nd, and Gd nitrates were determined up to 0.1 N. The perchlorates obey the Onsager limiting law up to 0.003N and the nitrates up to 0.001N. The agreement with theory can be extended to almost 0.01N by application of a graphic integration of the electrophoretic term of the Onsager equation (cf. preceding abstract). Equations are given that express the densities of aqueous solutions of the above salts at 25° as a function of concentration.

XI COMPLEX FORMATIONS

256. Anonymous (Author not given) Investigation of rare earth problems. Quarterly progress rept. no. 12, March 1 - June 1, 1949. 39 p. incl. tables. H U7725. Illinois University. (N6011-71). Task Order 7. UNCLASS Comparison titration curves for neodymium and lanthanum have been determined indicating definite complex formation with stability increasing with increase of pH. The possibility of there being more than one species in solution, depending on the pH, is discussed. Solid complexes have been prepared in an attempt to find a possible mechanism for the complex formation. Two methods of preparation were carried out, analysis of the products indicating a 2:1 and 3:2 sequestrene to neodymium ratio for the solid complexes. Further investigations with the eluant EDTA were conducted. It was found that the ammonium salts of this acid readily removed thorium and cerium from Dowex 50 resin in the ammonium form. This reagent could not be used conveniently with the acid form of the resin because of the slight solubility of EDTA. Studies were carried out on the eluants ammonium oxalate and ammonium carbonate. Initial experiments with the latter gave good results. An investigation of the action of fused or solid reagents on rare earth minerals is in progress. Initial studies with monazite utilizing fused NaOH, fused KCNS, and fused NaCl have been performed. NaOH gives a definite reaction, as indicated by the presence of water soluble phosphate, and acid soluble rare earth material in the cooled reaction mixture. The highest yield of rare earth material (approximately 50 per cent) was obtained not by fusion but by treatment of the mineral with excess NaOH and H₂O on the steam bath for 72 hours. KCNS showed no visible reaction, but NaCl appeared to react, since the color of the ore was completely changed. The possibility of extracting the rare earth elements from yttrifluorite $x\text{CaF}_2 \cdot y\text{YF}_3$ by fusing with sodium polymetaphosphate is also being examined. This is based on the assumption that the rare earth monofluorophosphates, which are water-soluble, are formed in such a reaction. Several metallic fluorides, including neodymium fluoride, are readily soluble in

sodium polymetaphosphate glass. The solubilities of the rare earth and thorium monofluorophosphates are being studied as well. Praseodymium hydroxide has been examined at varying temperatures to study its dehydration characteristics. Gravimetric and x-ray diffraction studies of the materials obtained upon heating the hydroxides in vacuum show that a monohydroxide, $\text{PrO}(\text{OH})$, is formed at 300-350°C and Pr_2O_3 at 400°C and above. Praseodymium sesquioxide contaminated with a trace of other rare earths may be converted readily to the high temperature hexagonal structure; however, the pure sesquioxide with similar treatment does not appear to undergo this change. A new method for the preparation of radioactive disodium hypophosphate was developed based on the reaction of red phosphorous (radioactive phosphorous diluted with inactive phosphorous when an active product is desired) with sodium chlorite, the products being hypophosphorous, phosphorous, and hypophosphoric and pyrophosphoric acids. A brief outline is included for the quantitative analysis of thorium hypophosphate. A one to one ratio of thorium to hypophosphate is indicated, but several refinements are necessary before conclusive results can be obtained. Several lanthanum oximates have been precipitated from dilute solution and shown by ignition analysis to have the formula $\text{La}(\text{C}_9\text{H}_6\text{ON})_3$. An attempt to demonstrate the effect of temperature on the composition of yttrium oximate was partially successful.

257. Anonymous. Complexones in analytical chemistry. Chem. Age 69, 15-22, 1953. Crerar Met. Abstr. 2, No. 2, 69, 1953. The use of *complexones can be extended to the quantitative separation of various cations, and a study of the lanthanums has been made. Y comes close to Dy in the lanthanum series and is separated from the yttrium earths. La and Sm have been separated as have Pr and Nd to a certain degree. *Complexones are substances of a polydentate nature and are capable of forming inner complex compounds with a wide variety of cations.
258. Beck, G., and Gasser, A. Analytical chemistry of the rare earths. Anal. Chim. Acta 3, 41-52, 1949. CA 43, 8300i, 1949. In making a fractional separation of the rare earths by means of the nitrilo-

acetic complexes in the presence of oxalate, the light metals (Cb to Dy) are transformed into insoluble oxalates, while the heavy ones remain in solution as complexes. The stability of the nitriloacetic complexes as a function of the pH was studied and the ammoniacates of Sm, Gd, Dy, Er, and Y chlorides have been prepared and submitted to thermal decomposition. Sm can be separated rapidly and completely from the other rare earths by means of Na amalgam.

259. Biedermann, T. W., and Schwarzenbach, G. The "complexometric" titration of alkaline earths and some other metals with Eriochromschwarz. *Chimica (Switz)* 2, 56-9, 1948. *CA* 42, 3694f, 1948. The "complexometric" methods are those in which the ion to be determined from a complex ion with the anion of an aminopolycarboxylic acid such as ethylenediaminetetraacetic acid, which can be called H_4Y and the reaction becomes $Me^{+n} + Y^{-4} = MeY^{n-4}$. The conditions can be chosen such that at the end point there will be an abrupt change in pH which can be recognized by a color change in an acid-base indicator or potentiometrically. Such titrations have been proposed for Al, Ca, Cd, Co, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Zn, and some rare earths. The end point can also be recognized by means of an organic reagent that gives a colored compound with the ion titrated, so that the color changes as soon as all of the simple ions have formed a complex. Procedures are described for determining Mg, Ca, Sr, Zn, Cd, Pb, Mn, and Hg. Eriochromschwarz T is used as indicator. The procedures are simple and very accurate. Thus the total hardness of water can be determined in a few minutes within 0.2°. Besides doubly distilled water for the solutions, 3 reagents are necessary: (1) For the titrant dissolve 37.21 g $Na_2H_2Y \cdot 2H_2O$ in one l. of water. Standardize against the chloride or nitrate of Mg. (2) A buffer solution of N NH_4Cl + N NH_3 of pH = 10. It is best to prepare it by passing NH_3 into a N solution of NH_4Cl . (3) Indicator solution: Dissolve 0.2 g of the dye in a little of the buffer solution and dilute to 100 ml. This solution should be made up freshly. In the titrations about 30-70 mg per l of the dyestuff should be present. To determine Mg, add enough buffer solution so that the NH_3 content is about 20 times that of the Mg^{+2} . Add the indicator and titrate.

At the end point a wine-red color becomes violet. To determine Zn and Gd proceed similarly. To determine Ca it is best to add a little Mg^{+2} to sharpen the end point. The complex with Ca^{+2} is formed first but the end point comes a little early without the Mg^{+2} . About 5% as much Mg as Ca should be present. To determine Sr, the relations are the same and the end point is even less satisfactory without Mg^{+2} . To determine Pb, Mn, and Hg a different procedure is necessary, because the buffer solution causes precipitation. It is best to add an excess of the titrant, then add the buffer, and titrate the excess reagent with a standard solution of Mg^{+2} or, better still, of Zn^{+2} .

260. Boulanger, F. Determination of complexes formed by trilon with the rare earths. *Chim. anal.* 35, 253-4, 1953. *Anal. Abstr.* 1, No. 1, 42, 1954. Trilon A (nitrilotriacetic acid) and trilon B (EDTA) give stable complexes with most metals. Simple experiments indicate that the complex ions formed with Pr are $[Pr(A)_2]^-$ and $[Pr(B)]^-$. Progressive acidification from pH 6 of a solution containing the complexed rare earths and an oxalate leads to the precipitation of the oxalates of La at about pH 6, then Nd and Pr; at about pH 5, Sa; pH 4.5, Gd; and pH 4, Er. At $pH < 4$, the Yt group of earths are precipitated. Cu^{II} in acid solution displaces the rare metals from their complexes.
261. Bronaugh, H. J., and Suttle, J. F. Chelation of the rare earth elements as a function of pH using thenoyltrifluoroacetone. LA-1561, 33 pp., 1953. AD-15 432. *Nuclear Sci Abstr.* 7, 673, 1953. UNCLASS. Data presented here deal with the chelation of the rare earth elements by use of thenoyltrifluoroacetone (TTA). Data were obtained for Sc, Y, and all the rare earths except Er. A method is described for the separation of the lighter rare earths from each other by using chelation with TTA. A liquid continuous extraction apparatus has been designed and used to make fractional separations of Ce from La and Y from Ce. (AEC abstract).
262. Cornish, F. W. The equilibrium constant for the dysprosium T.T.A. - benzene system. Ministry of Supply, Harwell, Berks, Eng., Atomic Energy Res. Estab. C/R 891, 3 pp., 1952. UNCLASS.

CA 46, 11001b, 1952. The reaction, $\text{Dy}^{+++} + 3\text{HT} \rightarrow \text{DyT}_3 + 3\text{H}^+$, is carried out in a 2-layer system consisting of H_2O and C_6H_6 . The pseudo-formula, HT, signifies 1 molecule of thenoyltrifluoroacetone. K for the reaction as written is 3.6×10^{-8} .

263. Crouthamel, C. E., and Martin, D. S., Jr. Solubility of the rare earth oxalates and complex ion formation in oxalate solution. II Neodymium and cerium (III). July 1950. Iowa State College, Ames. ATI-89 041. UNCLASS. Radiochemical assays were used to measure the solubilities of cerium and neodymium in buffered oxalate solutions. The data have permitted the calculation of equilibrium constants, which satisfactorily describe the systems. These have been compared with those from earlier work on ytterbium. Neodymium was found to form the complex ion $\text{Nd}(\text{C}_2\text{O}_4)^+$ and $\text{Nd}(\text{C}_2\text{O}_4)_2^-$ with very nearly the same stability constants as ytterbium, but it had a minimum solubility of about 1.5×10^{-6} mols/l. compared to 3×10^{-5} mols/l. for ytterbium. Evidence was found for the formation of $\text{Ce}(\text{C}_2\text{O}_4)^+$, $\text{Ce}(\text{C}_2\text{O}_4)_3^{3-}$ and cerium had a minimum solubility of about 1.7×10^{-6} mols/l.
264. Crouthamel, C. E., and Martin, D. S., Jr. Solubility of rare-earth oxalates and complex ion formation in oxalate solution. II Neodymium and cerium (III). Nov. 1950. Iowa State College, Ames Lab. ATI-89 743. UNCLASS. Radiochemical assays to measure the solubilities of neodymium and cerium in buffered oxalate solutions are described. The data have permitted the calculations of equilibrium constants which satisfactorily describe the systems. These have been compared with those from earlier work on ytterbium. Neodymium was found to form the complex ion $\text{Nd}(\text{C}_2\text{O}_4)^+$ and $\text{Nd}(\text{C}_2\text{O}_4)_2^-$ with very nearly the same stability constants as ytterbium, but it had a minimum solubility of about 1.5×10^{-6} moles per liter compared to 3×10^{-5} moles per liter for ytterbium. Evidence was found for the formation of $\text{Ce}(\text{C}_2\text{O}_4)^+$, $\text{Ce}(\text{C}_2\text{O}_4)_2^-$, and $\text{Ce}(\text{C}_2\text{O}_4)_3^{3-}$ and cerium had a minimum solubility of about 1.7×10^{-6} moles per liter.
265. Dutt, N. K., and Mukherjee, H. G. Chemistry of the rare earths. X. Urotropin and antipyrine complexes of thiocyanates and dithiocyan-

ates of rare earths. J. Indian Chem. Soc. 30, 272-74, 1953. Crerar Met. Abstr. 2, No. 2, 71, 1953. Simple rare earth thiocyanates and dithiocyanates of La, Ce and Pr are known to be soluble and hygroscopic salts. Complexes of these salts with urotropin and antipyrine are only moderately soluble and have been obtained as crystals . . .

- 266 Dutt, N. K., and Goswami, N. Rare earths. XI. Urotropin and antipyrine complexes of tetrathionates of rare earths. J. Indian Chem. Soc. 30, 275-6, 1953. CA 48, 1194a, 1954. The following complexes of urotropine, $C_6H_{12}N_4$, and antipyrine, $C_{11}H_{12}N_2O$, are reported: $La_2(S_4O_6)_3 \cdot 4C_6H_{12}N_4$, m above 250° , colorless crystals moderately soluble in H_2O ; $Ce_2(S_4O_6)_3 \cdot 4C_6H_{12}N_4$, very similar to the La compound; $Pr_2(S_4O_6)_3 \cdot 4C_6H_{12}N_4$, green crystals; $La_2(S_4O_6)_3 \cdot 6C_{11}H_{12}N_2O$, colorless crystals moderately soluble in H_2O ; $Pr_2(S_4O_6)_3 \cdot 6C_{11}H_{12}N_2O$, similar to the La compound. Each compound is prepared by dissolving a rare earth nitrate in cold H_2O to form a concentrated solution, adding approximately twice as much by weight of the organic compound dissolved in H_2O , filtering and adding saturated $Na_2S_4O_6$ solution.
267. Gordon, L., and Shaver, K. J. The application of strong chelating agents in the separation of thorium and the rare earths, for period January 1, 1952 to September 30, 1952. U.S. AEC. NYO-3555, 97 pp., October 29, 1952. Crerar Met. Abstr. 2, No. 3, 46, 1953. A method using EDTA was employed for separating the rare earths from thorium and phosphate ions. The rare earths removed contain 2-4% thorium. Complexing agents other than EDTA were found less satisfactory. Trace quantities of rare earths, however, may be chelated with nitrilotriacetic acid. With EDTA the oxalate method can be used to separate the cerium and yttrium groups with efficiency comparable to the double sulfate method. An improved spectrophotometric method for Ce(IV) is based on ultraviolet absorption of cerium following oxidation with alkaline H_2O_2 in the presence of EDTA. Thorium interference has a negligible effect. Graphs and tables are given.

268. Gordon, L., and Shaver, K. J. Fractionation of some rare earth pairs. Anal. Chem. 25, 784-7, 1953. CA 47, 7364i, 1953. Results obtained from some rare earth pairs in the presence of EDTA as a complexing agent are compared with results obtained similarly with methyl oxalate. There is no appreciable difference in the degree of fractionation although the order of oxalate solubilities is reversed. The separation of members of the cerium and yttrium groups in the presence of the complexing oxalate agent can be used with an efficiency comparable to the double sulfate.
269. Gotte, H. A new method for the rapid separation of the rare earths and of element 93 from uranium splitting. Angew. Chem. A60, 19-20, 1948. CA 42, 6233c, 1948. Cf. CA 41, 5014f. Methods for the separation of the rare earths as well as of element 93 are based on complex formations with dibenzoylmethane. The methods are rapid enough to permit the detection of substances having half-life periods of 2 to 5 minutes.
270. Hagiwara, Z. Studies on the separation of the rare earths and their accompanying elements. IV. Indirect determination of some elements such as samarium and yttrium, etc. Technol. Repts. Tohoku Univ. 17, 83-90, 1952. Anal. Abstr. 1, No. 2, 262, 1954. Some lanthanons are quantitatively precipitated by the addition of 8-hydroxyquinoline to a solution buffered with acetic acid and ammonium acetate. On ignition these complexes are converted to oxides. The determination of samarium and yttrium is made by utilizing the difference in weight between the oxide and the oxinate.
271. Jackson, D. E. Observations on the rare earths: 8-quinolinol and substituted 8-quinolinol chelates of certain rare earth elements - and appendixes A and B (Technical Rept.) Sept. 1950. University of Illinois, Urbana ATI-95 818. UNCLASS. Investigations are reported which have been carried out on the preparation and properties of the chelates of certain rare earth elements with oxine and its 5,7-dichloro derivative.
272. James, R. A., and Bryan, W. P. Use of thenoyltrifluoroacetone in ion exchange separation. J. Am. Chem. Soc. 76, 1982-4, 1954. Nuclear Sci. Abstr. 8, 396, 1954. Conditions are established

under which thenoyltrifluoroacetone can be successfully employed as an eluting agent in ion exchange separations of rare earths. Complete separation of yttrium and europium using this reagent and very short columns is demonstrated. Possible applications of the method are discussed.

273. Keenan, T. K., and Suttle, J. F. The chelation of praseodymium by thenoyltrifluoroacetone. J. Am. Chem. Soc. 76, 2184-5, 1954. Crerar Met. Abstr. 2, No. 10, 46, 1954. In the chelation of praseodymium by thenoyltrifluoroacetone (TTA) the equilibrium constant is dependent on the nth power of (H^+) . The compound $Pr(TTA)_3$ is assumed. Two concentrations of TTA in benzene solutions were used and the pH was about 4-4.5. The equilibrium relation expressed in logarithmic form is $\log K_{eq} = \log D.R. + n \log (H^+) - 3 \log (HTTA)$. D.R. values are tabulated and graph is shown.
274. Lindner, K. Rare earth complexes. Ger. 726,041, Aug 20, 1942. CA 37, 6417.2, 1943. An aqueous solution or suspension of soluble or insoluble rare-earth compounds is treated with alkali, NH_4 or organic bases metaphosphates or polyphosphates.
275. Marsh, J. K. The purification of lutecium by fractionation of hexaantipyrinelutecium iodide. J. Chem. Soc. 577-8, 1950; cf. CA 22, 2118. CA 44, 7175i, 1950. Fractionation of crude hexaantipyrinelutecium iodide produces a rapid concentration of Lu in the head fractions. Separation of Tm, Er, Ho, and Dy by this method is less effective. The separation is attributed to large differences in complexing ability rather than to solubility differences. Fractionation from CH_3OH is less satisfactory than from H_2O .
276. Marsh, J. K. The separation of the lanthanons with the aid of ethylenediaminetetraacetic acid ("Enta Acid"). IV. Sodium lanthanon sulfate precipitation from sodium lanthanon enta (EDTA) solution. J. Chem. Soc. 4804-11, 1952; cf. CA 46, 3446c. CA 47, 6297d, 1953. The double-sulfate separation of rare earths is improved by adding EDTA. Separation depends on equilibrium of cationic and complexed lanthanons in solution. La is concentrated more strongly in the first fraction and Lu in the last. The place of Yt varies with conditions. $CuSO_4$ is used to combine EDTA in later fractions

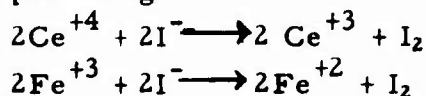
- when the excess cannot be removed by crystallization. Analyses for 12 rare earths in 27 fractions of a large separation are given.
277. Martell, A. E., and Plumb, R. C. Complexes of various metals with ethylenediamine tetraacetic acid. *J. Phys. Chem.* 56, 993-96, 1952. *Crerar Met. Abstr.* 1, No. 5, 43, 1953. Previously, the relative tendencies of various metals to form complexes with EDTA in buffer solutions were reported. The experimental method consists of treating an EDTA solution with two metal ions, the amounts of all three being equal. The result is a comparison of the stability of the two metal complexes. The method is interpreted theoretically for conditions of precipitation of excess ion and presence of a single solution phase. Data on rare earth complexes cover Pr, Nd, La, Y and mixtures of these. Structural formulae of polydentate EDTA chelates of the rare earth metals, mathematical calculations, graphs and tables are shown.
278. Mattern, K. L. Complex ions of lanthanum in aqueous solutions. U. S. AEC. UCRL-1407, 92 pp., 1953. *Crerar Met. Abstr.* 2, No. 4, 54, 1953. Complexing of lanthanum by certain anions (a large number) was studied by observing the decrease in the thenoyltrifluoroacetone (TTA) complex as the lanthanum concentration diminished. This species had the best properties for spectrophotometric determinations. Values for complexing constants of the ion species of chloride, sulfate, chlorate, succinate, citrate acetate, tartarate, phthalate, and lactate were determined. Graphs and tables included.
279. Mehrotra, R. C., and Dhar, N. R. Hexametaphosphates. I. Preparation and properties of sodium hexametaphosphate and a study of the extent of complex formation with calcium ions by conductivity data. *Proc. Natl. Inst. Sci. India* 16, 59-65, 1950. *CA* 44, 8278f, 1950. Pure Na hexametaphosphate (I) was prepared by the method of P. Pascal (*CA* 18, 505) by heating $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ to 700° , and rapid quenching of the melt. Five % solution of I in H_2O reacts with salts of Ca, Sr, Ba, Mg, Zn, Mn, Pb, Al, Be, La, Th, Zr, Ce, Fe, and UO_2 forming solution complexes by the following mechanism: $\text{Na}_2 [\text{Na}_4(\text{PO}_3)_6] + \text{BX} \rightleftharpoons \text{Na}_2 [\text{Na}_2\text{B}(\text{PO}_3)_6] + \text{Na}_2\text{X};$

$\text{Na}_2 [\text{Na}_2\text{B}(\text{PO}_3)_6] + \text{BX} \rightleftharpoons \text{Na}_2 [\text{B}_2(\text{PO}_3)_6] + \text{Na}_2\text{X}$, where BX stands for CaC_2O_4 , CaCO_3 , etc. The reactions indicated by the equations were followed by conductivity measurements. II. A study of the complexes formed by sodium hexametaphosphate with strontium, barium, and lead ions by conductivity data. Ibid 67-9. Sr, Ba, and Pb sulfates dissolve in I with the formation of $\text{Na}_4\text{B}(\text{PO}_3)_6$, where B is Sr, Ba, or Pb. Only Pb tended to react a stage further, forming $\text{Na}_2\text{Pb}_2(\text{PO}_3)_6$.

280. Moeller, T., and Brantley, J. C. Rare earths. LVIII. Reaction between neodymium and ethylenediamine tetraacetate ions in aqueous solution. J. Am. Chem. Soc. 72, 5447-51, 1950; cf. CA 45, 1463a. CA 45, 4596b, 1951. Evidence for an anionic complex formed from Nd and $[\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2^-)]_2$ in the ratio 1:1 was obtained from absorption spectra, electrometric titration with NaOH, and electrophoretic migration. Each Nd adsorption band from 5100 to 10,000 Å is resolved into two or more bands in the presence of EDTA.
281. Moeller, T. Coordination chemistry of the rare earth metal ions. Record Chem. Prog. 14, 69-81, 1953. Crerar Met. Abstr. 2, No. 4, 53, 1953. Trivalent rare earth ions seem to be generally 6-coordinate. The suggested octahedral geometry might be studied optically resolving active species. β -diketone chelates, if octahedral, should be assymetric and also give crystallizable, optically active salts. Coordinating with EDTA changes the absorption spectra of trivalent neodymium, gadolinium, holmium and erbium ions. β -diketone derivatives and oxine form chelated inner complexes. Cationic chelates are formed by tartarates, citrates, EDTA, iminodiacetic acids and nitriloacetic acid. Data are tabulated.
282. Nakatsuka, Y., and Kudo, I. 8-Hydroxyquinolate of tetrapositive neodymium. J. Chem. Soc. Japan, Pure Chem. Sect. 72, 655, 1951; cf. Ramsey, et al., CA 44, 9294d. CA 46, 6981b, 1952. $\text{Nd}(\text{NO}_3)_3$ dissolved in an ammoniacal solution of 8-hydroxyquinoline-7-sulfonic acid was anodically oxidized according to the method of N and Chang (Acta Chim. Taiwan. 1, 37, 1948). The electrolyzed solution was mixed with an excess of 8-hydroxyquinoline and heated

below 100° in a sealed tube. The yellow crystalline precipitate, dried at room temperature, agreed well with the formula $\text{Nd}(\text{C}_9\text{H}_6\text{NOH})_4 \cdot \text{H}_2\text{O}$. The quadrivalence of Nd was confirmed bromometrically, after decomposition of the substance in HCl containing KBr. $\text{Nd}^{4+} + \text{Br}^- = \text{Nd}^{3+} + \text{Br}$ and $\text{C}_9\text{H}_6\text{-NOH} + 4\text{Br} = \text{C}_9\text{H}_4\text{Br}_2\text{NOH} + 2\text{HBr}$. Thus, for the complete bromination of 1 mole of $\text{Nd}(\text{C}_9\text{H}_6\text{NOH})_4$ addition of 15 gram atoms of Br is necessary. This is the first Nd(IV) compound reported.

283. Nakazuka, Y. Mutual separation of rare earth of cerium series. Japan, 3708, Oct. 27, 1950. CA 46, 10562h, 1952. Soluble salts of rare earth elements of the lanthanide series (La, Ce, Pr, Nd, Sm part or all) are treated with NH_4OH solution of 8,5(or7) $\text{HO}(\text{HO}_3\text{S})\text{C}_9\text{H}_5\text{N}$ to form intramolecular complex salts of these elements, and they are separated by use of their difference of basicity and by the use of oxidation of Ce, Pr, and Nd from valency 4 to 5.
284. Perros, T. P., and Naeser, C. R. A complex praseodymium fluoride readily soluble in dilute acids. J. Am. Chem. Soc. 71, 3847-8, 1949. CA 44, 9852i, 1950. KHF_2 (10g) was melted in a Pt crucible, 0.5 g PrF_3 dissolved in the melt, and the cooled melt extracted with water containing a little NH_4OH leaving a pale-green residue, which dissolved with warming in 3 N HCl. When Pr_6O_{11} was added to the melt the reaction was vigorous and the green residue showed the same characteristics.
285. Pribil, R., Simon, V., and Dolezal, J. Uses of complexones in chemical analysis. Paper 23: Iodometric determination of cerium, manganates and chromates. Chem. Listy 46, 88-90, 1952. Crerar Met. Abstr. 1, No. 5, 42, 1952. The proposed determination of Ce in the presence of Fe (as in mischmetal) is based on the property of one of the so-called complexones, viz. EDTA, to react with Fe^{+2} in the presence of I_2 with the formation of both I^- ions and complex ferrocplxone ions. The solution containing Ce and Fe is treated with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in order to oxidize into Ce^{+4} and Fe^{+3} , whereupon KI is added producing



As said above, the addition of the complexone solution (of a sufficiently low pH value) will lead both to the formation of ferro-complexone ions and the conversion of the equivalent quantity of I_2 back into I^- ions. The remaining free iodine is equivalent to the Ce content and can be titrated, eg. with $Na_2S_2O_3$.

286. Ramsey, W. J., et al. Praseodymium and neodymium complexes with 8-quinolinol-5-sulfonic acid. *J. Am. Chem. Soc.* 72, 2782-3, 1950. *CA* 44, 9294d, 1950. A 20-cc solution containing 0.08 g $Pr(NO_3)_2$ (I) was added to 100 cc 0.5 N NH_4OH containing 1.5 g 8-quinolinol-5-sulfonic acid (II) and a similar solution without I were let stand overnight exposed to air. Both solutions similarly became reddish brown. Anodic oxidation for 20 minutes in a porous cup at 6 v and 0.2 amp caused both to darken to opaqueness. No precipitate formed in either solution. Thus the color change is no indication of oxidation of I. To opaque solutions of I, $Nd(NO_3)_3$ (III), and mixtures of I and III, prepared as above, were added 10 g Na_2CO_3 and 3 g glucose, the mixture was heated 1.5 hours on a steam bath. For I alone, $Pr_2(CO_3)_3$ (IV) did not precipitate quantitatively, 10-50% remaining in solution. The precipitated IV was determined by conversion to the oxalate and ignition to Pr_6O_{11} . Glucose was not necessary to precipitate part of IV. For III alone, $Nd_2(CO_3)_3$ (V) partially precipitated; V, converted to the oxalate and ignited, decomposed to Nd_2O_3 (light blue). With I + III, no semiquantitative separation was observed. Thus, the oxidation states of Pr and Nd greater than 3 and their separation as proposed by Nakatsuka and Chang (*Acta Chimica Teiwanica* 1, 37, 1949) are not tenable. Adding a concentrated solution of $PrCl_3$ to a concentrated solution of the NH_4 salt of II in excess NH_4OH and concentrating the resulting solution by evaporation gave a complex compound containing Pr, N, and S but no Pr^{III} derivative of II.
287. Ryabchikov, D. I., and Terent'eva, E. A. Complex compounds of rare earth metals and some organic amines. *Compt. rend. acad. sci. U. S. S. R.* 51, 291-4, 1946. *CA* 40, 6362.1, 1946. Ce, La, Pr, Nd, Y and Er form complex compounds with organic amines, having a coordination number of six. With phenyldimethylpyrazolone (anti-pyrene) the product is $[M-(C_{11}H_{12}ON_2)_6]X_6$, where X is the acid

radical and M is the metal. The N-dimethylantipyrene (pyramidone) molecule has two N atoms connected to Me groups and can take up two of the coordination places in the metal atom, forming, for instance, $[\text{Ce}(\text{C}_{13}\text{H}_{17}\text{ONO}_3)_3](\text{NO}_3)_3$. Attempts to make analogous compounds with compounds with pyridine, of the formula $\text{M}''' \cdot 6\text{R} \cdot \text{N} \cdot \text{X}_3$, were not successful.

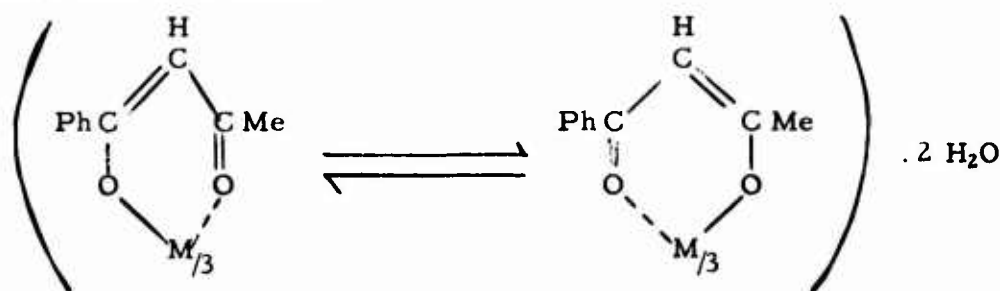
- 288 Ryabchikov, D. I., and Trent'eva, E. A. Complex formation of rare earth elements. *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk*, 44-55, 1949. CA 43, 4969d, 1949. Absence of precipitation by the usual precipitating reagents, F^- , $\text{C}_2\text{O}_4^{2-}$, OH^- , $[\text{Fe}(\text{CN})_6]^{4-}$ (in the order of decreasing effectiveness) was taken as a criterion of complex formation. With most of the salts of the organic acids studied, elements of the "Ce group" (La, Ce, Pr, Nd, Sm) give first insoluble precipitates, which dissolve on addition of an excess of the salt, whereas elements of the "Y group" (Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu, Y) are not precipitated. (1) With NH_4OAc , nitrates of the rare earth elements give not very stable complexes of the form $[\text{M}_3\text{Ac}_3](\text{NO}_3)_6 \cdot n\text{H}_2\text{O}$; with NH_4 stearate, only insoluble simple salts. $(\text{CO}_2\text{H})_2$ gives very weak complexes; with the higher homologs (malonic, succinic, glutaric and adipic acids), the Y-group elements form soluble complexes, not precipitated by $\text{Fe}(\text{CN})_6^{4-}$, the Ce group gives insoluble simple salts. Pimelic, azelaic, and sebacic acids give no complexes, only insoluble precipitates. Maleic and citraconic acids, both cis, form soluble complexes, whereas the trans fumaric acid gives, with $\text{La}(\text{NO}_3)_3$, only a precipitate, insoluble in an excess. Phthalic, tetrachlorophthalic, and diphenic acids give only insoluble precipitates. The precipitates obtained with tartaric and with mucic acid are readily soluble in an excess, forming highly stable complexes. Among the amino acids, glutamic and aspartic acids form the most stable complexes. Sulfonic acids of the benzene, naphthalene, and anthracene series give no complexes with rare earths. (2) With K citrate, elements of the Ce group give first a precipitate which dissolves in an excess to form a complex $\text{K}_3[\text{M}(\text{C}_6\text{H}_5\text{O}_7)_2]$. Complex citrates synthesized include: $\text{K}_3[\text{La}(\text{C}_6\text{H}_5\text{O}_7)_2]$; $\text{K}_3[\text{Nd}(\text{C}_6\text{H}_5\text{O}_7)_2]$; $\text{Na}_3[\text{Nd}(\text{C}_6\text{H}_5\text{O}_7)_2] \cdot 3\text{H}_2\text{O}$, synthesized by adding

2 moles of finely powdered citric acid to 1 mole NdCl_3 solution, neutralization with NaOH , and separation with EtOH ; $(\text{NH}_4)_3[\text{Nd}(\text{C}_6\text{H}_5\text{O}_7)_2] \cdot 3\text{H}_2\text{O}$; $\text{Ca}_3[\text{Nd}(\text{C}_6\text{H}_5\text{O}_7)_2]_2$, and $\text{Ca}_3[\text{La}(\text{C}_6\text{H}_5\text{O}_7)_2]_2$ by precipitation with $\text{Ca}(\text{NO}_3)_2$; $\text{Ce}[\text{Nd}(\text{C}_6\text{H}_5\text{O}_7)_2]$, by precipitation with CeCl_3 . In these complexes, the coordination number is obviously 6, and each molecule of citric acid is linked to the central atom by the O atoms of the 3 CO_2H groups. In alkaline solution the complexes are very stable, and are not precipitated by either $\text{C}_2\text{O}_4^{--}$ or F^- . (3) With antipyrine (ap), elements of the Ce group form complexes $[\text{Meap}_6]\text{X}_3$, where $\text{M} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$, and also Er and Y , and $\text{X}^- = \text{Cl}^-, \text{NO}_3^-, \text{ClO}_4^-, \text{Br}^-, \text{I}^-, \text{IO}_3^-$, and $1/3[\text{Cr}(\text{CNS})_6]^{---}$. The complex perchlorates are less soluble in H_2O than the corresponding simple perchlorates, but are soluble in organic solvents. No salts of the ap complexes could be obtained with F^- , H_2PO_2^- , SO_4^{--} , or $\text{C}_2\text{O}_4^{--}$; these anions disrupt the complex, e.g. $2[\text{Ce ap}_6]\text{Cl}_3 + 3\text{K}_2\text{SO}_4 \longrightarrow \text{Ce}_2(\text{SO}_4)_3 + 6\text{ ap} + 6\text{ KCl}$. Salts of the anion $[\text{Cr}(\text{CNS})_6]^{---}$ can be obtained also by adding separately ap and the chloride of the rare earth element to a solution of $\text{K}_3[\text{Cr}(\text{CNS})_6]$. While in these complexes, one molecule of ap occupies only one coordination place, elements of the Y group can also form complexes with one molecule of ap occupying 2 places, e.g., $[\text{Er ap}_3][\text{Cr}(\text{CNS})_6]$, and an analogous compound with Y. In the ap complexes, the anion X cannot be replaced by $[\text{Fe}(\text{CN})_6]^{----}$, which reacts rapidly according to $[\text{M ap}_6]\text{Cl}_3 + \text{K}_4[\text{Fe}(\text{CN})_6] \longrightarrow \text{MK}[\text{Fe}(\text{CN})_6] + 6\text{ ap} + 3\text{ KCl}$. (4) With pyramidone (pd), the complexes are of the form $[\text{M pd}_3]\text{X}_3$, where $\text{M} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Er}$; Y and $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{IO}_3^-, \text{NO}_3^-, \text{ClO}_4^-$; one molecule of pd always occupies 2 coordination places. All these complexes form, with $\text{K}_3[\text{Cr}(\text{CNS})_6]$, sparingly soluble precipitates $[\text{M pd}_3][\text{Cr}(\text{CNS})_6]$. (5) With pyridine (py), complexes could only be isolated in the form of precipitates. $[\text{M py}_6][\text{Cr}(\text{CNS})_6]$, where $\text{M} = \text{Ce}, \text{Nd}, \text{Er}$. (6) Concentrated solutions of salts of La, Ce, Pr, and Nd give, with a saturated solution of $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$, precipitates of the form $\text{M}[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 8\text{H}_2\text{O}$, with the rare metal outside the coordination sphere. Other rare elements, and dilute solutions of the above four, react according to $3\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] + 2\text{M}(\text{NO}_3)_3 \longrightarrow \text{M}_2(\text{C}_2\text{O}_4)_3 +$

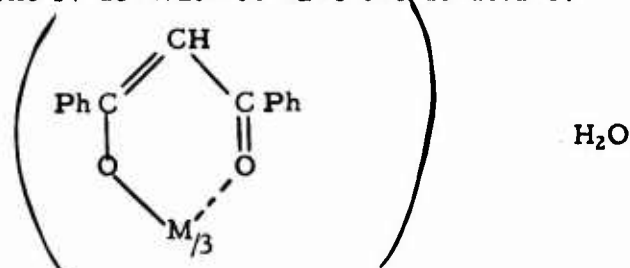
$3K_3 [Cr(C_2O_4)_2(NO_3)_2]$, and Th reacts according to $K_3 [Cr(C_2O_4)_3] + Th(NO_3)_4 \rightarrow Th(C_2O_4)_2 + Cr(NO_3)_3 + KNO_3 + K_2C_2O_4$. (7) The following are indications of some degree of complex formation in double salts of rare earth elements. Alkali nitrates give no precipitate with rare earth salts. In the presence of a 20-fold excess of NH_4NO_3 , $(NH_4)_2C_2O_4$ gives a precipitate instantaneously with nitrates of the Ce group, but only on longer standing with nitrates of the Y group. In contrast to the Ce group, elements of the Y group form highly soluble double sulfates in the presence of (15-20-fold) excess K_2SO_4 or Na_2SO_4 , and are not precipitated by $K_4 [Fe(CN)_6]$ or NH_4OH , whereas $(NH_4)_2C_2O_4$ gives only a slight opalescence. The precipitate formed by K_2CO_3 in salts of the Ce group is soluble in an excess, but the complex is disrupted by $(NH_4)_2C_2O_4$. In the Y group, the precipitate is dissolved only by a great excess (10-15-fold) of K_2CO_3 , but the complex is more stable, in particular is not decomposed by $(NH_4)_2C_2O_4$ or even NaF. $K_4 [Fe(CN)_6]$ gave, after 10 days' standing, a precipitate, apparently $KY [Fe(CN)_6]$.

289. Sacconi, L., and Ercoli, R. Some complexes of the rare earths with β -diketones. Gazz. chim. ital. 79, 731-8, 1949. CA 44, 3832f, 1950. The following compounds were prepared: Benzoylacetone (I) derivatives: $La(C_{10}H_9O_2)_3 \cdot 2H_2O$, straw color, m 108-9°; $Pr(C_{10}H_9O_2)_3 \cdot 2H_2O$, green-yellow, m 106-8°; $Nd(C_{10}H_9O_2)_3 \cdot 2H_2O$ (II), pale lilac, m 106-8°; $Sm(C_{10}H_9O_2)_3 \cdot 2H_2O$, straw color, m 103-5°; $Gd(C_{10}H_9O_2)_3 \cdot 2H_2O$, colorless, m 100-1°; $Ce(C_{10}H_9O_2)_4$ (III), brown-red, m 187-8°; $Th(C_{10}H_9O_2)_4$, colorless, m 215-16°. Dibenzoylmethane (IV) derivatives: $La(C_{15}H_{11}O_2)_3 \cdot H_2O$, straw-yellow, m 142-5°; $Pr(C_{15}H_{11}O_2)_3 \cdot H_2O$, yellow, 149-51°; $Nd(C_{15}H_{11}O_2)_3 \cdot H_2O$ (V), lilac-green dichroism, 147-50°; $Sm(C_{15}H_{11}O_2)_3 \cdot H_2O$, golden yellow, m 148-9°; $Gd(C_{15}H_{11}O_2)_3 \cdot H_2O$, green-yellow by transmitted light, rose-yellow by reflection, m 214-16°; $Ce(C_{15}H_{11}O_2)_4$ (VI), brown-red, m 192-3°; $Th(C_{15}H_{11}O_2)_4$, yellow, m 192-3°. In preparing them, an excess (3-4 moles) of I or IV is used to avoid precipitation of hydroxides or basic salts. Examples: 3 g I in 20 cc EtOH, added to 2 g $Nd(NO_3)_3 \cdot 6H_2O$ (VII) in 3 cc water + 5 cc EtOH (heat is evolved), 12 cc water added, neutralized with saturated alcoholic NH_3 , and the precipitate (addition of water to the filtrate gives more precipitate) washed with EtOH and water, gives

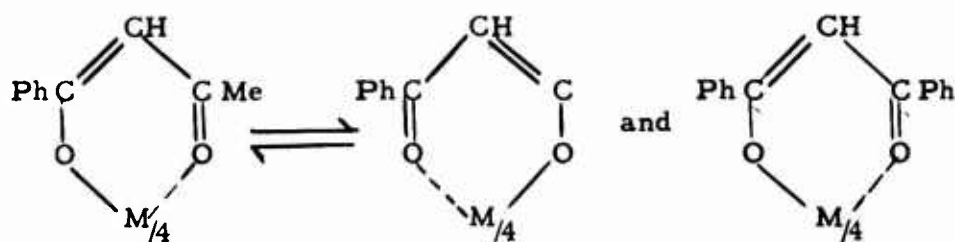
2.2 g II. Alcohol IV (3.6 g in 40 cc), added to 2 g VII in a few drops of water and 6 cc EtOH, made alkaline with alcoholic NH_3 , the precipitate (4 g) dried over H_2SO_4 in vacuo, suspended in 70 cc EtOH, heated on a steam bath, air passed through to remove NH_3 , and allowed to stand, precipitates 2.9 g of V. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (VIII) and 6 g I in 70 cc EtOH, made alkaline with alcoholic NH_3 , heated on a steam bath, and the precipitate purified by C_6H_6 or CHCl_3 -petroleum ether, yield 2.4 g III. VIII (2 g) and 4 g IV in 110 cc EtOH yield 4.5 g VI. The I derivatives of Nd, Sm, and Gd are internal complexes of the probable structure:



The IV derivatives have the structure:



The structures of the Ce and Th derivatives are:



The tendency of trivalent Ce to oxidize to quadrivalent Ce during the formation of the complexes offers the possibility of separating Ce from the trivalent earth metals. I is preferable to IV for this purpose. When an alcohol solution of the nitrates and I is neutralized with alcoholic NH_3 , and the mixture is heated, III precipitates; the La, Pr, Nd, and Sm derivatives are too soluble in hot EtOH to pre-

precipitate, and, on prolonged boiling, decompose and form oily droplets. III is slightly soluble in, and can be crystallized from, C_6H_6 , whereas the others are very soluble. To separate Ce from the trivalent metals, the precipitate which is formed by addition of alcoholic NH_3 to the alcohol solution of the nitrates and I is recrystallized repeatedly from C_6H_6 . This gives pure III.

290. Schwarzenbach, G., and Biedermann, W. Complexons. VII. Titration of metals with nitrilotriacetic acid, H_3X . Indication of end point by pH effects. *Helv. Chim. Acta* 31, 331-40, 1948. *CA* 42, 4481a, 1948. When an excess of a neutral solution of a salt of nitrilotriacetic acid of the type $K_2(HX)$ is treated with the salt of a multivalent metal M, a complex of M and X is formed and a H ion is liberated. This can be titrated alkalimetrically, to determine the metal by the shift in the titration curve from pure $K_2(HX)$. Potentiometric, conductimetric, or indicator methods can be used. When the number of equivalents of base added per metal, a , is 1, the following pH values represent the range during which sharp rise in titration curve occurs: Ca 6.8-9.0, Cd 4.5-6.3, Co(II) 4.7-7.9, Cu(II) 4.5-8, Hg(II) 4.5-9, Mn(II) 6.0-8.4, Ni 4.6-7.5, Pb(II) 5.0-8.0, Zn 4.9-8.0, Mg 7.5-9.0. For Ce (III) 7.0-8.2, La(III) 7.4-8.6, and Al 7.0-8.0, a may be 1 or 2. Cr (III) and Fe(III) cannot be titrated owing to formation of the complex ion $MXOH^-$. Formation of MX_2 sometimes complicates the titration. If the pH of the solution is brought to about 5, the ion X^{-3} may be used instead of HX^{-2} . In this case, base need not be added before the titration. Mg cannot be titrated by this method. The values for the other metals are Ca 8.5-9.6, Cd 5.0-7.0, Co 6.0-8.7, Cu 5.0-8, Fe(II) 6.7-8.7, Mn 7.9-9.2, Ni 5.5-7.8, Pb 5.0-9, Zn 6.2-8.0, Ce 8.4-9.5, La 8.5-10.1, Al 7.0-8.0.
291. Schwarzenbach, G., and Biedermann, W. VIII. Titration of metals with uramildiacetic, H_3Z . Indication of end point by pH effects. *Helv. Chim. Acta* 31, 456-9, 1948. *CA* 42, 4481d, 1948. cf. *CA* 40, 4312.2. Formation of a complex from HZ^{-2} or Z^{-3} liberates H ion, which can be determined by alkaline titration. In this case best results for most metals are obtained when a is 1, but for La and Ce, a should be 2. The pH ranges for the sharp rise in titration curves are as follows,

for HZ and Z ions, respectively, in each case: Cu 5.1-6.1, 6.1; Ce 4.7-7.8, 6.5-8.5; Cd (a = 1 or 2) 4.7 and 9.0, 7.5 and 9.2; Co 4.8-8.1, 5.5-8.5, La 5.0-8.0, 6.5-8.5; Mg 5.3-8.1, 6.5-8.5; Mn 4.6-7.1, 6.5-8.5; Ni 4.6-8.0, 6.0-8.5; Zn 4.6-8.0, 6.0-8.5, Al (a = 1 and 2) 4.5 and 5.2-7.2, 4.5 and 6.5.

292. Schwarzenbach, G., and Biedermann, W. IX. Titration of metals with ethylene-diaminetetraacetic acid, H_4Y . Indiation of end point by pH effects. *Helv. Chim. Acta* 31, 459-65, 1948. CA 42, 4481f, 1948. In this case, either $K_2(H_2Y)$ or $K_3(HY)$ can be used with formation of the complex and 2 or 1 H ions, respectively. Best results are obtained with the H_2Y ion. When a = 2 for Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, Zn, Ce, and La, the normal pH of 5.0 of $K_2(H_2Y)$ falls to about 3 when the bivalent metal is added. With $K_3(HY)$ and a = 1, the fall is from 8.5 to 3.5-6.5. Na_4Y does not give satisfactory results. Al, Fe(III), and Cr(III) form hydroxo complexes, which make the method difficult for them. The Cr complex, $Cr(HY)H_2O$ (which is strongly acidic) can be isolated. The H_2O is part of the complex, since it cannot be removed in a high vacuum at 100°.
293. Schwarzenbach, G. Stability of complex compounds of the rare earths. *Angew. Chem.* 66, 142, 1954. *Crerar Met. Abstr.* 2, No. 10, 49, 1954. The various methods for the determination of the stability of rare earth complex compounds are discussed. The results in agreement with earlier investigations, seem to indicate that gadolinium constitutes an exceptional element in this respect. This paper was presented before the 13th International Congress for Pure and Applied Chemistry, Stockholm (July 29 to August 4, 1953) and Uppsala (August 5 to August 7, 1953).
294. Stern, K. G., and Steinberg, M. A. Desoxyribonucleic acid complexes of rare earths. *Biochim. et Biophys. Acta* 11, 553-58, 1953. *Crerar Met. Abstr.* 2, No. 3, 52, 1953. Spectrophotometric and tracer studies were used to study the reactions of lanthanum, neodymium, promethium and samarium salts with the high polymer sodium salt of desoxyribonucleic acid. One part of lanthanum or neodymium reacts with 9 parts of desoxyribonucleic acid replacing much of the sodium. The elementary composition of the complexes produced was determined,

but their structure is not elucidated the trivalent rare earth atom may combine with three acidic phosphate groups on the same molecule, or on alternate molecules. The latter explains better the insolubility of the complex. Data are tabulated

295. Stites, J. G., McCarty, C. N., and Quill, L. L. The rare earth metals and their compounds. VIII. An improved method for the synthesis of some rare earth acetylacetonates. J. Am. Chem. Soc. 70, 3142-3, 1948. CA 43, 2106g, 1949. A concentrated solution of the rare earth chloride is treated with 50% in excess of the theoretical amount of acetylacetone at a pH just below that required for precipitation of the corresponding rare earth hydroxide; this pH is maintained during 12 hours' stirring. Crystalline acetylacetonates of high purity are obtained in 83-98% yield. Yield is a function of the pH of the solution.
296. Stites, J. R., Jr. The rare earth metals and their compounds. The normal and modified acetylacetonates. Univ. Microfilms (Ann Arbor, Mich.), Pub. No. 1268, 124 pp. Microfilm Abstr. 9, No. 2, 40-1, 1949. CA 43, 8928e, 1949. No abstract.
297. Suttle, J. F., and Keenan, T. F. The chelation of praseodymium as a function of pH using thenyltrifluoroacetone. U.S. AEC LA-1104, 1 pp, 1950. Crerar Met. Abstr. 3, No. 5, 36, 1953. The equilibrium equation for the chelation of praseodymium with thenyltrifluoroacetone (TTA) is: $\log K_{ep} = \log D.R. + n \log H^+ - 3 \log HT$. A plot of $\log D.R.$ versus $\log H^+$ should give a line with slope "n", representing the average charge on the praseodymium species. This slope decreases with increasing atomic number and basicity of the rare earths. The experimental K_{eg} for praseodymium is 3.34×10^{-9} which is in reasonable agreement with the theoretical value. Preliminary studies show a possibility of separating praseodymium from lanthanum and chelation. 11 references.
298. Vickery, R. C. Separation of lanthanons by means of complexes with amino acids. J. Chem. Soc. 2058-61, 1950; cf. CA 44, 9853d. CA 45, 2358g, 1951. Of the amino acids studied, histidine and glycine are the only ones to coordinate with lanthanon hydroxides in neutral or NH_3 solutions. If excess lanthanon hydroxide is digested with

amino acid, the lanthanons are fractionally precipitated from the resulting solution by $\text{H}_2\text{C}_2\text{O}_4$ in order of inverse atomic numbers; if sufficient excess of amino acid to dissolve all the lanthanon hydroxide is used, $\text{H}_2\text{C}_2\text{O}_4$ precipitates the lanthanons in order of atomic numbers with degree of separation comparable to that obtained by Marsh with EDTA. By the latter method with histidine as the coordinating agent La and Sm concentrate rapidly at the head and tail of the series. Pr and Nd are separated to some extent, whereas the heavier lanthanons are not fractionated satisfactorily. Fractionation with glycine is less efficient. Crystalline complexes of lanthanon with glycine, $\text{Ln}(\text{NH}_2\text{CH}_2\text{CO}_2)_3$, histidine, $\text{Ln}(\text{C}_3\text{H}_3\text{N}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COO})_3$, cystine, $\text{Ln}_2[(\text{SCH}_2\text{CH}(\text{NH}_2)\text{COO})_2]_3$, glutamic acid, $\text{Ln}_2(\text{OOCCH}_2\text{CH}(\text{NH}_2)\text{COO})_3$, and aspartic acid, $\text{Ln}_2(\text{OOCCH}_2\text{CH}(\text{NH}_2)\text{COO})_3$, were prepared.

299. Vickery, R. C. Polynuclear complexes of lanthanon sulfates. J. Chem. Soc. 1101-4, 1950. CA 44, 9853d, 1950. La, Nd, and Pr are separated from a solution of Na lanthanon double sulfate in aqueous NH_4OAc by fractional decomposition with H_2SO_4 or HCl , but there is no correlation between amount of acid and extent of decomposition. Ce spreads through all the fractions. It was not possible to obtain separations by fractional crystallization of these solutions $\text{Sm}[\text{Sm}(\text{NH}_4)_3(\text{AcO}_3)](\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ and the corresponding Pr complex were isolated by crystallization from H_2O ; however, La, Ce(III), Ce(IV), and Nd did not yield well-defined compounds. The solutions and crystals containing Nd exhibit a blue fluorescence under a Hg lamp, a property which can serve as a qualitative test for Nd.
300. Vickery, R. C. Lanthanon complexes with ethylenediamine tetraacetic acid. J. Chem. Soc. 1817-21, 1951. CA 45, 9415c, 1951. Formation of complexes from lanthanon oxalates in a solution of the NH_4 salt of EDTA followed by fractional acidification gave excellent separation of La and good concentration of Sm; Pr and Nd were resolved to a certain extent. Precipitation by an excess of oxalic acid did not yield such good results even in the presence of excess EDTA. The use of nonaqueous solvents did not improve the separation of the lanthanons. Complex formation from sulfates and alkali double sulfates yielded only mediocre separation. Complex formation from tungstates,

molybdates, chromates, vanadates, and complex cyanides, and subsequent precipitation were further complicated by the formation of anionic complexes of the metallic ion. Two forms of $(\text{NH}_4)_3 [\text{EDTA La}(\text{C}_2\text{O}_4)]$ have been prepared: an α -form obtained from solutions where complex formation and crystallization occurred below about 50° ; and a β -form, which was formed at a higher temperature. The β -form is more stable and soluble.

301. Vickery, R. C. Lanthanon complexes with ethylenediaminetetraacetic acid. II. J. Chem. Soc. 421-5, 1952; cf. CA 45, 9415c. CA 46, 4946d, 1952. Complexes of the NH_4 salt of $[\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2]_2$ EDTA with Pr, Nd, Sm, Gd, Dy, Er, and Yb were made by mixing solutions of either the chloride or the perchlorate of the lanthanon with a solution of NH_4 EDTA. The absorption spectra of these solutions were studied spectrophotometrically. The "internal" Stark effect splitting of the absorption spectra occurs only with Nd and Er. This phenomenon may be due to a perturbation of the lanthanon ionic field; this hypothesis is examined on the basis of lanthanon paramagnetism. Spectrophotometric data on the Nd nitrilotriacetic acid complex are presented.
302. Vickery, R. C. Lanthanon complexes with ethylenediamine-N, N', N'-tetraacetic acid. III. J. Chem. Soc. 1895-8, 1952; cf. CA 46, 4946d. CA 47, 6741h, 1953. The stability constants (K) of the lanthanon (Ln) complexes (I) of $[\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2]_2$ (EDTA) were determined on samples twice recrystallized from H_2O , then precipitated from NH_4OH solution by acid. For this series, $K = \frac{[\text{LnH}_2\text{A}]}{[\text{Ln}^{3+}] [\text{HA}^{3-}]}$. The prime dissociation is $\text{LnHA} \rightarrow \text{LnA}^- + \text{H}^+$, with LnA^- being a 3-ionic, 3-coordinate complex. In dilute solutions below pH 6.0, the amphoteric-ion nature of LnA^- is negligible. Dilute solutions of EDTA (10^{-3}M) and I ($0.2 \times 10^{-5}\text{M}$) with HNO_3 ($2.563 \times 10^{-3}\text{N}$) and KCl (to ionic strength 0.1M) were titrated with 1.248N NaOH at 20° , a pH meter being used. From the pH curves the amount of free H^+ was determined. The equations are derived giving the average number of ligands, A, attached to the metal, and n (EDTA attached to Ln/total Ln) involving known and determined data. From plots of the formation curve of the systems, n versus $\log 1/[\text{A}]$ (cf. CA 44, 10567c), at a value of $n = 0.5$ (equal amounts of LnHA_{x-1} and LnHA_x), the K's are read as the corresponding $\log 1/[\text{A}]$ value.

Results for log K were as follows for the different lanthanons: La 15.30, Ce 16.05, Pr 16.55, Nd 16.75, Sm = Gd 17.2, Dy 17.75, Er 18.15, Yb 18.70, and Y 18.0. From log K, ΔF was found for complex formation, the Bjerrum quantity (cf. CA 44, 6758e) being used. Complex configuration is likely octahedral with the ligands bound in 5-member chelate rings.

303. Vickery, R. C. Lanthanum complexes with hydrazine-N N-diacetic acid. J. Chem. Soc. p. 385-8, 1954. IAI p. 177, July 1954. A study has been made of the stable complexes formed between the lanthanons and hydrazinediacetic acid. Solid complexes have been prepared which exhibit a Ln:acid ratio of 1:3 and over all stability constants have been derived for some of the normal complexes formed; these range from 6.6 for the lanthanum complex to 7.7 for the ytterbium complexes. The complexes formed are of little value in macro scale separation of the lanthanons.
304. Wheelwright, E. W., Spedding, F. H., and Schwarzenbach, G. The stability of the rare earth complexes with ethylenediamine tetraacetic acid. U.S. AEC ISC-279, 25 pp., 1952. Crerar Met. Abstr. 1, No. 11, 56, 1953. In order to get the stability constants of rare earth-EDTA complexes, the equilibrium among the di-hydrogen cupric EDTA complex, uncomplexed cupric ions, the monohydrogen rare earth-EDTA complex and rare earth cations are studied. The rare earth complex stability constant was obtained by an indirect potentiometric method. The procedure and solutions used are described. A polarographic method for determining cupric ion concentration in supporting KNO_3 solutions, and thereby supporting the other entities, was found more effective as well as easier. Results show that the difference between individual rare earth elements is large, with an especially large increase for La^{+3} to Ce^{+3} paralleling the rapid decrease of ionic radius. The irregularity around gadolinium is thought to be an effect of steric hindrance of the anionic carboxyl groups. Tables are given.

305. Wheelwright, E. J., Spedding, F. H., and Schwarzenbach, G.

Stability of rare earth complexes with ethylenediamine tetraacetic acid. J. Am. Chem. Soc. 75, 4196-201, 1953. Crerar Met. Abstr. 2, No. 3, 52, 1953. The stability constant of the complexes formed between the rare earths (RE) metal ions and the anion EDTA of ethylenediaminetetraacetic acid were measured at 20° and at an ionic strength $\mu = 0.1$ by two independent supplemental methods: (1) a potentiometric method, more accurate for the lighter RE, which involved the formation constants of copper with the anion of H_4EDTA and of copper with the trihydrochloride of B,B,B''-triaminotriethylamine, and (2) a polarographic method, more accurate for the heavier RE, consisting in the determination of the amount of free Cu in the presence of both Cu and RE complexes ($M EDTA^-$). The difference in $K_M EDTA^-$ between the individual metals is surprisingly large. Typical values for $\log K_M EDTA^-$ by methods (1) and (2), respectively, are: Ce 15.39 ± 0.06 and 15.6 ± 0.4 ; Gd 16.70 ± 0.08 and 16.6 ± 0.15 ; Lu 19.06 ± 0.4 and 19.65 ± 0.12 .

XII SOLUBILITY STUDIES

306. Fischer, W., Wernet, J., and Zumbusch-Plisterer, M. The solubility of the chlorides of the rare earths in hydrochloric acid as the basis of a new separation possibility. *Z. anorg. Chem.* 258, 157-61, 1949. *CA* 44, 407h, 1950. The high solubility of ScCl_3 (15.4 g Sc_2O_3 /100 cc solution) in HCl-saturated (1 atm) solutions of H_2O , $\text{Et}_2\text{O} \cdot \text{H}_2\text{O}$, or $\text{EtOH} \cdot \text{H}_2\text{O}$, permitted the separation of Sc from Al, Y, the lanthanides, and other elements whose chlorides were precipitated under these conditions.
307. Hagiwara, Z. Studies on the separation of the rare earths and their accompanying elements. I. By using the hydrolysis of a buffered solution. *Technol. Repts. Tohoku Univ.* 17, 58-69, 1952. *Anal. Abstr.* 1, No. 2, 260, 1954. A study is made of the hydrolysis of buffered solutions containing urea, ammonium salts and organic acids in order to utilize the difference of basicity of the rare earths for their separation.
308. Hagiwara, Z. Studies on the separation of the rare earths and their accompanying elements. III. Separation of cerium from the rare earths. *Technol. Repts., Tohoku Univ.* 17, 77-82, 1952. *Anal. Abstr.* 1, No. 2, 261, 1954. The separation which is based on the hydrolysis of urea in hot buffered solution, is discussed in detail. The behavior of the basic precipitate of cerium at various pH values is also studied.
309. Moeller, T. Observations on the rare earths. LV. Hydrolysis studies upon yttrium and certain rare earth (III) sulfate solutions at 25°. *J. Phys. Chem.* 50, 242-50, 1946, cf. *CA* 40, 805.3. *CA* 41, 3007h, 1947. The hydrolysis of La, Ce, Pr, Nd, Sm, Eu, Gd, Yb, and Y sulfate solutions at various concentrations was investigated by direct determination of H-ion concentration with a pH meter. Plots of pH against log concentration for all 9 elements deviated from the linear relationship expected; this is ascribed to the use of concentrations instead of activities. Hydrolysis increases generally with decrease in cation radius. Greatest degree of hydrolysis is exhibited by $\text{Y}_2(\text{SO}_4)_3$. In all instances, extent of hydrolysis is small.

310. Moeller, T., and Quinty, G. Radiometric determination of the solubilities of thorium and certain rare earth metal hypophosphates. J. Am. Chem. Soc. 74, 6123, 1952. CA 47, 11060f, 1953. cf. CA 47, 11060e, 1953. ThP_2O_6 is quantitatively insoluble in at least 4N HCl whereas $\text{Nd}_4(\text{P}_2\text{O}_6)_3$ and $\text{Y}_4(\text{P}_2\text{O}_6)_3$ under comparable conditions are sufficiently soluble to permit separations.
311. Moeller, T., and Zimmerman, P. A. Rare earths; some observations on solutions of certain rare earth metal salts in basic solvents. J. Am. Chem. Soc. 75, 3940-3, 1953. Crerar Met. Abstr. 2, No. 2, 70, 1953. Anhydrous $\text{La}(\text{NO}_3)_3$, NdBr_3 , NdI_3 and acetates of Nd and Y are moderately soluble in both ethylenediamine and monoethanolamine but only slightly in morpholine. General solubility decreases in the order acetates, nitrates, iodides, and bromides. Monoethanolamine is a better ionizing solvent for weak electrolytes (acetates) and ethylenediamine is better for strong electrolytes.
312. Monk, C. B. Electrolytes in solutions of amino acids. V. Solubilities of calcium, barium, and lanthanum iodates in glycine, alanine, and glycyglycine. Trans. Faraday Soc. 47, 1233-40, 1951; cf. CA 45, 8329b. CA 46, 4327g, 1952. The solubilities at $25^\circ \pm 0.03$ were determined. The results are discussed in terms of the Debye-Huckel theory, the ion-dipole modification of Kirkwood (CA 28, 5316.8) and Scatchard's (CA 21, 1216) solubility relation. Ba glycinate and alaninate dissociation constants are given.
313. Templeton, C. G. The distribution of rare earth nitrates between water and hexyl alcohol at 25° . J. Am. Chem. Soc. 71, 2187-90, 1949. CA 43, 8807h, 1949. Temperature control was within $\pm 0.05^\circ$, and 24 hr was allowed for attainment of equilibrium with constant agitation. Approximately 1 g of each layer was evaporated to dryness and then ignited and weighed as the oxide. Mole fractions X' (of R^{3+} in H_2O) and X'' [of $\text{R}(\text{NO}_3)_3$ in alcohol] were calculated for the respective phases on the assumption that the solvents are completely immiscible and the salt is completely ionized in the aqueous phase and exists as an unionized molecule in the alcohol layer. Values of X'' plotted versus X' on a log-log scale yield straight lines of the form $\log X'' = \text{constant} + A_r \log X'$, where A_r , the value of

the slope, varies from 4.3 to 4.8. For all nitrates studied, there is an increased extractability into the alcohol with increasing atomic number. Separation values as high as 1.88 should be expected for Nd/La when $X'_{\text{Nd}} = X'_{\text{La}} = 0.06$ mole fraction. [Errors communicated by the author are as follows: Table I column 3 for Ce [574, 548, 515, 485, 446, 400, 361, and 330 (all $\times 10^{-4}$)]; column 4 for Ce [176, 143, 103, 77, 51, 34, 20, and 15 (all $\times 10^{-4}$)]; column 3 for Pr [533, 533, 517, 452, 432, 431, 393, 363, 329, and 308 (all $\times 10^{-4}$)]; column 4 for Pr [168, 166, 146, 87, 66, 60, 44, 31, 21, and 15 (all $\times 10^{-4}$)]. In Figure I the Ce line should be above the La line and the Pr line closer to the one for Nd. Summary, paragraph 2, read: For all the rare earth nitrates investigated there is an increased extractability into the alcohol with increasing atomic number]

XIII. SPECTROGRAPHIC STUDIES

314. Butement, F. D. S. Absorption and fluorescence spectra of bivalent samarium, europium, and ytterbium. Trans. Faraday Soc. 44, 617-26, 1948. CA 43, 2509i, 1949. The absorption spectra were photographed from 900 to 2000 A on a Hilger medium spectrograph and the molar extinction coefficients in aqueous solution deduced. The absorption spectra include SmCl_2 in water and in solid NaCl, SrCl_2 , and BaCl_2 ; EuCl_2 in H_2O and in SrCl_2 or in BaCl_2 ; YbCl_2 in H_2O . The fluorescence spectra include SmCl_2 in SrCl_2 , and in BaCl_2 ; EuCl_2 in SrCl_2 , and in BaCl_2 ; YbCl_2 in SrCl_2 , and in BaCl_2 . The assignment of bands to possible electronic transitions is discussed. All 3 ions show heavy diffuse bands owing to $4f \rightarrow 5d$, or $6s$ transitions, and Sm^{++} and Eu^{++} show narrow, weak bands which can be correlated with those of the isoelectronic Eu^{+++} and Gd^{+++} , respectively.
315. Feldman, C. Note on the arc spectrum of element 61. J. Am. Chem. Soc. 71, 3841-2, 1949. CA 44, 9797e, 1950. The arc spectrum of 3 samples of the chloride of element 61 was examined. The strongest arc lines in the 3000-3450 A region are: 3366.05 weak, 3377.64 weak, 3391.25 medium, 3418.67 weak, 3427.42 strong, 3441.09 weak, 3449.81 medium. All lines are ± 0.03 A.
316. Fassel, V. A. Quantitative spectrographic analysis of the rare earth elements. III. Determination of major constituents in complex mixtures. J. Optical Soc. Am. 39, 187-93, 1949. CA 43, 2889a, 1949. cf. CA 42, 5795f, 1949. A method is described for determining Y and Gd in complex mixtures in the concentration range 8-100%. The procedures involve the high-current direct current arc excitation of mixtures of rare earth oxide, -ceric oxide, and graphite. Selected lines of Ce are used as internal standards. The choice of Ce as internal standard was based on the relative ease with which any Ce if present in a mixture, could be separated from the mixture and then introduced to a definite extent. Precision studies showed a standard deviation of about $\pm 2.5\%$ for single determinations.

317. Fassel, V. A., and Wilhelm, H. A. The quantitative spectrographic analysis of the rare earth elements. I. Determination of samarium in neodymium. II. Determination of europium in samarium. J. Optical Soc. Am. 38, 518-26, 1948. CA 42, 5795f, 1954. Spectrographic methods applicable to the determination of small amounts of rare earth impurities in other rare earths are described. The specific examples discussed are the determination of Sm in Nd and of Eu in Sm. The procedures involve the high current direct current arc excitation of rare earth oxide-graphite mixtures. Selected lines of the major rare earth constituent are used as internal standards. Studies on the variation of the analytical intensity ratio during excitation and the effect of large changes in arc current, percentage of graphite, and weight of sample charge of the intensity ratio values are included.
318. Gatterer, A., et al. Atlas of persistent spectra. Separate from Astrophys. Lab. of the Vatican Observatory, Vatican City. I. Spectra of thirty chemical elements. 53 pp., 28 charts. CA 44, 1329e, 1950. The arc and spark spectra are given for Ag, Al, Ba, Bi, C, Ca, Cd, Co, Cr, Cu, Mg, Mn, Mo, Ni, Pb, Rb, Si, Sn, Sr, Ti, Tl, V, W, and Zn. The arc spectra are given for Ba, Ca, Co, Cr, Mn, Mo, Ni, Rb, Sr, Ti, and V, and the spark spectra for Au, As, B, P, Pt, and Sb. The ultimate lines of Li, Na, K, and Cs are included as impurities in the spectrum of Rb. II. Spectra of rare earths. 80 pp., 42 charts. The spectra are given of the rare earths and of Sc, Y, Zr, and Th. III. Spectra of rare metals and some metalloids. 10 pp., 21 charts. The arc and spark spectra are given of Au, As, Be, Ga, Ge, Hf, In, Ir, Cb, Os, Pd, Pt, Re, Rh, Ru, Sb, Ta, Te, U, Cl, Br, I, S, Se, and Hg.
319. Hirt, R. C. and Nachtrieb, N. H. See Ref. 153.
320. Hirt, R. C., and Nachtrieb, N. H. Spectrographic determination of rare earth elements in uranium compounds. Anal. Chem. 20, 1077-8, 1948. CA 43, 1684a, 1949. Seven rare earth elements were studied spectrographically to determine their wave lengths and sensitivities. To avoid interference from U lines, the U was removed by an ether extraction of uranyl nitrate, the rare earth precipitated as a fluoride,

and purified with NaOH. The spectrographic determination was carried out by the Cu-spark method, with a Jarrell-Ash Wadsworth automatic spectrograph.

321. Klinkenberg, P. F. A. Spectra of the rare earth elements. *Physica* 13, 1-15, 1947; cf. CA 40, 6988.1. CA 41, 6146a, 1947. Calculations based on relations which were derived from the vector model show a considerable difference between the multiplet separations in the configurations $4f^x 6s^2$ and $4f^{x-1} 5d 6s^2$ of some neutral rare earth spectra. In some cases they allow conclusions to be made on the character of the ground state from only a few intervals found between the most prominent lines. Applied to the case of terbium I the ground configuration of this spectrum turns out to be $4f^8 5d 6s^2$. A few low levels are given. The calculations are extended to the ground terms of Tb II $4f^8 5d 6s^9H$ and ^7H , and their relative positions are estimated. Empirical regularities can be interpreted in accordance with the results on Tb I. Levels of both ^9H and ^7H are found.
322. McClelland, J. A. C. Determination of rare earths. *Analyst* 75, 392, 1950; cf. CA 44, 971h. CA 44, 8820d, 1950. Since the publication of the former paper on the spectrographic determination of rare earths by the intermittent-arc technique, it has been found that Cu as supporting electrode, in place of graphite, makes the operating conditions simpler and gives spectra relatively free from interfering background, at the cost of a slight loss in sensitivity. Cu is easily obtained in a state of purity and, unlike graphite, does not vary with its origin and so affect the determination of rare earths. It does not give the band spectrum that graphite does, a wider choice of spectral lines results and the consumption of electrode material is reduced.
323. McClelland, J. A. C. Applications of the intermittent alternating current arc. II. Determination of rare earths. *Analyst* 74, 529-36, 1949. CA 44, 971i, 1950. To the solution of the sample obtained by treatments with HF and other mineral acids add NH_4OH and ignite the filtered and washed precipitate. To it add 0.25 g of Fe_2O_3 of suitable particle size. The quantity of Fe_2O_3 should be at least 10 times that of the rare earth oxides. Triturate the mixture of oxides with 1 g of $KHSO_4$ and transfer the powder to a cupped graphite

electrode which has a crater 1-1.5 mm deep and leveled off. Heat the electrode on a hot plate until fusion starts and spread the mass evenly over the surface with a steel blade, to give a smooth coating to the electrode. Precise directions are given for using the electrode in a large Littrow spectrograph. The suitable spectral lines are listed for determining 17 rare earth and associated elements by comparison with spectral lines of Fe. With samples containing 0.1-0.7% of the element, the results are usually within 10% of the truth.

324. Meggers, W. F., Scribner, B. F., and Bozman, W. R. Absorption and emission spectra of promethium. J. Research Natl. Bur. Standards 46, 85-98, 1951, (Research Paper No. 2179). CA 45, 3714f, 1951. Five mg Pm separated from fission products at the Oak Ridge Natl. Lab., were lent by the U.S. Atomic Energy Commission for this investigation. The absorption spectrum of this sample in solution was plotted between 3500 and 10,000 Å; the principal bands have wave lengths 494.5, 548.5, 568.0, 685.5, 735.5 mμ (= 0.5 mμ). Small portions of the sample were dried on Cu electrodes employed in photographing a.-c. arc and spark spectra with a concave grating of 22 ft radius. Excepting Sm, into which Pm decays, no other rare earths could be detected in this sample, but common chemical contaminants were troublesome. Between 2200 and 6900 Å the wave lengths and relative intensities of more than 2200 new spectral lines were determined, but it was not possible to differentiate Pm I and Pm II lines with the light sources employed. The strongest Pm lines have wave lengths 3892.16, 3910.26, 3919.09, 3957.74, and 3998.96 ± 0.02 Å. Hyperfine structure is believed to be present in some Pm lines, indicating that the Pm nucleus possesses mechanical and magnetic moments. Confirming the findings of the Oak Ridge Natl. Lab., both the absorption and the emission spectrum identify this fission product as a new element of rare earth type; they provide positive proof that the element with atomic number 61 has been discovered.
325. Moeller, T., and Brantley, J. C. Rare earths. Spectrographic estimation of certain rare earth elements. Anal. Chem. 22, 433-41, 1950. CA 44, 5756i, 1950. Absorption spectra have been investigated over the range 2200 to 10,000 Å for Sc, Y, Th, La, Ce, Pr, Nd, Sm,

Eu, Gd, Er, Tm, Yb, and Lu in aqueous solutions of the chlorides, nitrates, acetates, and perchlorates. Specific data are shown for the chlorides (and for $\text{Er}(\text{ClO}_4)_3$) of those ions which show absorption in the ultraviolet, visible, or near infrared. Data are also given for the effects of slit width on band resolution, for the effects of concentration on absorption, for wavelength of bands free from interference by other rare earth metal ions, for sensitivity of detection at these wave lengths and for the effects of added ions. A spectro-photometric procedure adaptable for the estimation of Pr, Nd, Sm, Eu, Tm, and Yb to within 1% is outlined. Information relative to the estimation of Gd and Er, where larger errors are encountered, is also presented.

326. Parker, G. W., and Lantz, P. M. Absorption spectrum of element 61, promethium. *J. Am. Chem. Soc.* 72, 2834-6, 1950. CA 44, 8795e, 1950. The absorption bands of Pm in the visible spectrum resemble those of Nd both in number and intensity but are distinctly separable from them by at least 8 m μ . The absorption bands of Pm are in the same position and of the same magnitude for both the chloride and nitrate solutions. The most prominent absorption bands for a solution of Pm are at 493.5 ± 0.5 , 548.5 ± 0.5 , 568.0 ± 0.2 , and 685.0 ± 0.1 , 702.7 ± 0.3 , 737.2 ± 0.2 , and 785.0 ± 0.1 m μ .
327. Peed, W. F., Spitzer, E. J., and Burkhart, L. E. The L spectrum of element 61. *Phys. Rev.* 76, 143-4, 1949; cf. CA 43, 4133a. CA 43, 8268f, 1949. The lines are: $L\alpha_2$, 2287.9 ± 0.4 ; $L\alpha_1$, 2277.5 ± 0.3 ; $L\beta_1$, 2075.4 ± 0.4 ; $L\beta_3$, 2037.9 ± 0.4 ; $L\beta_2$, 1951.8 ± 0.6 ; $L\gamma_1$, 1795.2 ± 0.9 x.u. Lines presumed to be β_4 , α_2 , β_7 , and α_9 , were observed, but wave lengths were not determined.
328. Schuurmans, Ph. Methods of analysis in the spectra of the rare earths and in the very complex spectra of thorium and uranium. *Physica* 12, 589-94, 1946, (in English). CA 41, 5016f, 1947. The complexity of the spectra of the rare earths is due to the presence of f-type electrons in their electron configurations in which the coupling is intermediate between (ls) and (jj). This causes a departure from the Lande interval rule in multiple terms, but nevertheless leaves a regularity between the component levels that is helpful in predicting

the location of new levels. In the case of U the Zeeman effect in some well-resolved lines indicates that one of the low levels is $^7M_2^0$ which can appear only in configurations containing f electrons.

329. Short, H. G., and Dutton, W. L. Determination of rare earth elements and yttrium in uranium compounds. Anal. Chem. 20, 1073-6, 1948. CA 43, 1281a, 1949. Most of the U is removed by extracting $UO_2(NO_3)_2$ with ether. The rare earths are then precipitated as fluorides and purified as hydroxides. The final determination is then made with the spectrograph. With a 50-g sample, 0.2 parts of Th can be determined in the presence of 10^6 parts of Gd. Treat 10 g of the original material with 50% HNO_3 . If necessary, filter off any residue, fuse it with $K_2S_2O_7$ in a Pt crucible, dissolve the cold melt in HCl , and evaporate the excess acid on the steam bath. Precipitate the rare earths in this solution as described below. Evaporate the main solution until crystallization of $UO_2(NO_3)_2$ begins, then cool and break up lumps with a glass rod. Dissolve as much as possible with 70 ml of Et_2O . Transfer to a separatory funnel, leaving as much as possible of the residue in the beaker. Wash this with 10 ml more of Et_2O . Add sufficient water to give 1 ml of aqueous layer, shake, allow the layers to form, and drain off the aqueous solution into the original beaker. Repeat the extraction after adding 1 ml more of water. Reject the Et_2O solution containing the U. Evaporate off the ether carefully from the aqueous fraction, add a little water and 2 drops of HNO_3 . Evaporate nearly to dryness, transfer to a Pt dish and dilute to 50 ml with water, add 15 ml of 40% HF and allow to stand overnight. Filter through paper on a waxed funnel and into a waxed beaker. Wash once with water and ignite in a Pt crucible. Wash out the Pt dish with 1-2 ml of hot concentrated H_2SO_4 and add the solution to the Pt crucible. Evaporate to fumes of H_2SO_4 to remove F. Dissolve the residue in 10% HCl and transfer the 5-10 ml of solution to a beaker. Add 0.1 g of salicylic acid and a slight excess of NH_4OH . After 30 minutes, filter off the insoluble hydroxides and wash with 4% NH_3 solution. Ignite, dissolve in a little concentrated HCl , and evaporate in a depression of a 5-mm Cu rod. Examine in a large Hilger automatic Littrow spectrograph and establish

the quantities of the rare earth elements

330. Spicer W. M. , and Ziegler, W. T. Spectrochemical determinations of lanthanum in praseodymium metal. Anal. Chem. 21, 1422-3, 1949 CA 44, 1847c, 1950 A sample of supposedly pure Pr metal was suspected to be grossly contaminated with La. It was decided to analyze spectrographically for La with Mn 3438.974 A as an internal standard With mixtures of pure La and Mn chlorides and Cu electrodes, intensity ratios of this line and La 4086.7 A gave a linear log-log working curve. Closely agreeing results on the Pr metal gave an average La content of 37.0%. This figure was later verified by chemical assay
- 331 Smith D. M. Spectrographic analysis of rare and high-purity materials. Analyst 71, 368-76, 1946 CA 40, 6015.4, 1946. The use of the spectroscope for testing materials of high purity is outlined and various difficulties mentioned, such as the masking of lines and the presence of faint lines of doubtful origin. Various methods of arc excitation are discussed.
- 332 Smith, D. M. , and Wiggins, G. M. Some improvements in the technique of spectrographic analysis of high-purity materials. Spectrochim. Acta 3, 327-40, 1948. CA 43, 2539c, 1949. A review of work with the intermittent a.-c. arc and the constant current d.-c. arc. The C arc in steam is used for the analysis of rare earth oxides. Sometimes the concave mirror has advantages as a mode of spectrographic slit irradiation and line-intensity variations across the arc gap and variations with time of running the arc have been studied. A method for the complete qualitative analysis of volatile elements and compounds, by using certain exposure periods during the continuous running of the arc, is suggested.
- 333 Smith, D. M. , and Wiggins, G. M. Analysis of rare earth oxides by means of emission spectra. I. Persistent lines in arc spectra of rare earth elements Analyst 74, 95-101, 1949. CA 43, 5337f, 1949. The persistent lines of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb, and Y were determined. There are 5-9 lines for each element. In the photographs faint lines, probably due to impurities, were also present. II. A technique for the suppression of

cyanogen bands in carbon arc spectra of rare earth oxides. Ibid.

101-4. Detailed directions are given for photographing spectra in an atmosphere of steam

334. Spitz, E. W., et al. Spectrographic determination of certain rare earths in stainless steels. Anal. Chem. 26, 304-7, 1954. The addition of a mixture of rare earth oxides or metals to molten steel has created an interest in the determination of the residual rare earths in the steel. A spectrographic method using a direct current arc, following electrochemical and chemical separations, has been developed which permits the determination of as little as 50 γ of total rare earths in a 1-g sample of steel. Electrolytic separation with a mercury cathode is used to remove the major interfering components from the sample solution. The less than milligram amounts of cerium, lanthanum, neodymium, and praseodymium which remain in solution are concentrated by precipitation with ammonium hydroxide, using ferric iron as a carrier. The combined hydroxides are dissolved in a minimum of hydrochloric acid, and uranium and sodium chloride are added to serve as the internal standard and as the spectroscopic buffer, respectively.

XIV. PARAMAGNETIC SUSCEPTIBILITY

335. Altshuler, S. A., Kurenev, V. Ya., and Salikhov, S. G. Paramagnetic resonance absorption in crystalline powders of some rare earth compounds. Doklady Akad. Nauk S.S.S.R. 70, 201-4, 1950. CA 44, 3755i, 1950. The energy, Q , absorbed as a function of a constant magnetic field H , 200-3000 oersteds, superposed perpendicularly on a weak magnetic field oscillating at $\nu_1 = 6.75 \times 10^8$ hertz, was determined by the method of reaction on the generator. Curves with a maximum were found with $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and anhydrous $\text{Pr}_2(\text{SO}_4)_3$. For the first 2 salts the position of the maximum is the same, $H = 1200$; dehydration shifts it to 700 oersteds. This confirms that the cubic symmetry of the crystalline electrical field in the hydrated sulfate and nitrate is due to H_2O molecules, and that dehydration lowers the symmetry of that field. Likewise, the curves of $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ nearly coincide; however, the position of the common single maximum, 700 oersteds, cannot very well be taken to indicate cubic symmetry of the crystalline electrical field, as a calculation of the transition probabilities between sub-levels of Nd^{+++} in a cubic field predicts a series of lines of almost equal intensities. The same difficulty obtains with $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, maximum at $H = 600$. $\text{Ce}(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$ has a maximum at $H = 700$, as against $H = 1650$, calculated for the main maximum for cubic symmetry; however, if a rhombic field is assumed to be superposed on the main cubic field, that line cannot appear except at very high H , and only the actually observed maximum can be expected in the given range of H . The curve of Sm_2O_3 has a maximum at $H = 1400$, the theoretical interpretation of which is not clear. At $\nu_2 = 2.38 \times 10^8$ hertz, the curves retain the same shape, only the maxima are shifted ν_1/ν_2 times to lower H .
336. Benoit, R., and Blum, P. Paramagnetic properties of borides of some of the rare earths. Compt. rend. 234, 2428-30, 1952. CA 46, 9357e, 1952. The magnetic moments of CeB_6 , NdB_6 , GdB_6 , YbB_6 , YB_6 , and LaB_6 were determined between 350° and 1000° . YB_6 and LaB_6 have zero moments. In the temperature range of 350 - 760° the following

moments were observed: CeB_6 2.91, NdB_6 3.82, GdB_6 7.63, and YbB_6 4.58 Bohr magnetons. The corresponding Curie temperatures were 344, 455, 49, and 2°K, respectively.

337. Bleaney, B., et al. Paramagnetic resonance in gadolinium ethylsulfate. *Phil. Mag.* 42, 1062-4, 1951. *CA* 46, 6484g, 1952. A report of a number of measurements on Gd ethylsulfate diluted with La ethylsulfate. Experiments at 1.3-cm wave length showed that the spectrum consists of 7 roughly equally spaced lines, whose splitting varies approximately as $(3 \cos^2 \theta - 1)$ with the angle θ between the external magnetic field and the crystalline hexagonal axis. This shows that in the Hamiltonian the predominant term is P_2^0 , with axial symmetry not cubic symmetry. Thus Gd is comparable to Mn, where the splitting of the ^6S state, previously interpreted by a cubic field, is known to be mainly axial in symmetry.
338. Bleaney, B., Elliott, R. J., and Scovil, H. E. D. Dipole-dipole interaction in the rare earth ethyl sulfates. *Proc. Phys. Soc. (London)* 64A, 933-5, 1951. *CA* 46, 9979g, 1952. Paramagnetic resonance spectra of several rare earth ethyl sulfates show interesting features in line shape which can be related to spin-spin and spin-lattice effects in the crystal. The former gives usually a broadening of the resonance lines which is due to the magnetic fields in neighboring ions, randomly superimposed. This broadening consists really of a closely spaced fine structure, some detail of which can be resolved if the crystal is diluted with an isomorphous diamagnetic salt. The ethyl sulfates are sufficiently dilute themselves to give some resolution. The spectrum of neodymium ethyl sulfate at 20°K is shown.
339. Bogle, G. S., Cooke, A. H., and Whitley, S. Paramagnetism of cerium ethyl sulfate at low temperatures. *Proc. Phys. Soc. (London)* 64A, 931-2, 1951. *CA* 46, 9908h, 1952. Single crystals of $\text{Ce}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ were investigated at liquid-He temperatures by measurements of susceptibility and by paramagnetic resonance experiments. This substance shows no paramagnetic resonance at temperatures above 20°K because the spin-lattice relaxation time is so short that the absorption lines are broadened to such an extent as to be undetectable. In the concentrated salt the $\pm 5/2$ state lies lowest, con-

trary to the case of the dilute salt. This is confirmed by susceptibility measurements, which were made on 4 single crystals mounted together with their hexagonal axes parallel. Ce ethyl sulfate is of value for cooling substances on which it is desired to make magnetic experiments at temperatures below 1°K, for example the investigation of the phase diagram of a superconductor, or nuclear resonance experiments.

340. Bogle, G. S., Duffus, H. J., and Scovil, H. E. D. The nuclear electrical quadrupole moment of erbium¹⁶⁷. *Proc. Phys. Soc.* 65A, 760-1, 1952. CA 46, 10870b, 1952. Measurements are extended on the paramagnetic resonance spectrum of Er ethyl sulfate diluted with La ethyl sulfate. A value of the nuclear quadrupole moment is derived as $(10.2 \pm 3) \times 10^{-24} \text{ cm}^2$.
341. Chambers, W. H., Sheriff, R. E., and Williams, D. The nuclear magnetic moment of praseodymium¹⁴¹. *Phys. Rev.* 78, 482-3, 1950. CA 44, 7144i, 1950. The moment is 4.5938 ± 0.0023 .
342. Cotton, A., and Tsai, B. The magnetic separation of diamagnetic or paramagnetic substances and the attainment of magnetic fields of high gradient. *Ann. phys.* 17, 337-59, 1942. CA 38, 4480.2, 1944. Objects suspended in liquid O in the field of an electromagnet suffer a vertical displacement, a position being reached that represents equilibrium between the force of gravity and the magnetic field. This behavior is discussed as a means of separation of diamagnetic or paramagnetic substances. The method is judged too costly for a general separation procedure but valuable for specific problems, e. g., separation of rare earth metals. The procedure is also of value in studying the magneto-optical and electro-optical properties of fine crystalline suspensions in liquid O because the magnetic field prevents settling of such suspensions. The method can also be used to determine magnetic susceptibilities, either relative or absolute, for at the position of equilibrium the relation $H(H/z) = (d - d_1)/(k_1 - k)g$ is valid, where H has its usual meaning, z is the distance along the vertical perpendicular to the axis of revolution of the pole pieces, g is the gravitational constant, d and d₁ are the densities of the object and liquid O, respectively, and k and k₁ are the magnetic

susceptibilities of the object and O, respectively. Graphs showing the variation of H and $H(H/z)$ with z for the large electromagnet of the Academy of Sciences are given. Liquid air can be used in place of liquid O as the medium but has the disadvantages of a changing boiling temperature and composition, of having a lower density than O, and of being much less paramagnetic. Solutions of paramagnetic salts (e.g., $Mn(NO_3)_2 \cdot 6H_2O$ in water) can also be used because they can be prepared to give densities higher than that of liquid O. Methods of attaining high field gradients are critically reviewed, special consideration being given to the effect of the size of the instrument on the gradient obtained and to the problem of the study of very small objects.

343. Douglas, D. L., and Yost, D. M. The magnetic susceptibility of europium and samarium amalgam. *J. Chem. Phys.* 18, 1418-19, 1950. *CA* 44, 10400h, 1950. Magnetic susceptibilities of dilute Eu and Sm amalgams were determined at approximately 25°. The effective Bohr magneton number of the Eu amalgam is approximately 8.3, in good agreement with theory. The value for the Sm amalgam (2.28-2.38) is definitely higher than that given by Klemm and Bommer (*CA* 31, 4172.4) for the pure metal, nor does it agree with the values of Selwood (*CA* 29, 1693.1) for Sm(II) and Sm(III) compounds (3.62 and 1.55, respectively).
344. Elliott, R. J., and Stevens, K. W. H. A preliminary survey of the paramagnetic resonance phenomena observed in rare earth ethyl sulfates. *Proc. Phys. Soc. (London)* 64B, 205-7, 1951. *CA* 46, 9357d, 1952. The results of some preliminary theoretical investigations using a crystalline electrical field hypothesis to account for the magnetic properties at low temperatures. Data are discussed for Ce^{+++} , Nd^{+++} , Sm^{+++} , Gd^{+++} , Dy^{+++} , Er^{+++} , and Y^{+++} .
345. Elliott, R. J., and Stevens, K. W. H. The paramagnetism of cerium ethyl sulfate: theory. *Proc. Phys. Soc. (London)* 64A, 932-3, 1951; cf. *CA* 46, 9357d. *CA* 46, 9908g, 1952. The theory of the resonance phenomena in rare earth ethyl sulfates was taken to 2nd order in perturbation theory and applied to Ce ethyl sulfate.

346. Elliott, R. J., and Stevens, K. W. H. The paramagnetism of samarium ethyl sulfate; theory. Proc. Phys. Soc. 65A, 370-1, 1952. CA 46, 10726b, 1952. From paramagnetic resonance observations the magnetic moment and quadrupole moment is calculated for both the isotopes.
347. Elliott, R. J., and Stevens, K. W. H. The theory of the magnetic properties of rare earth salts: cerium ethyl sulfate. Proc. Roy. Soc. (London) 215A, 437-53, 1952. CA 47, 4670e, 1953. The theory of a Ce^{3+} ion in a crystal is considered as that of a free ion with a single 4f electron outside closed shells, and the effect of the surrounding lattice is included as a static crystalline electrical field. It is applied to the Et sulfate for which experimental data are available. In the concentrated salt the order of the two low-lying doublets is inverted from that in the dilute salt. This is caused by a small change in one of the field parameters that might readily come about as the result of a small change in the positions of the surrounding radicals. Calculation of susceptibility and Verdet constant agree with experiment and thus support the proposed theory.
348. Elliott, R. J., and Stevens, K. W. H. The theory of magnetic-resonance experiments on salts of the rare earths. Proc. Roy. Soc. (London) A218, 553-66, 1953. CA 47, 9768d, 1953. The theory of paramagnetic resonance in rare earth crystals is presented, with the assumption, that the crystalline electrical field splitting is less than the spin-orbit splitting. The first problem considered has been that of finding the ground states. This has not been exhaustively treated. Enough formulas and multiplying factors have been given to reduce any such problems to its simplest form. The nuclear-electronic interactions can be correlated with the terms of the 'spin-Hamiltonian.'
349. Elliott, J. F., Legvold, S., and Spedding, F. H. The ferromagnetic properties of the rare earths metals. U.S. AEC ISC-378, 58 pp., June 1953. Crerar Met. Abstr. 2, No. 6, 37, 1954. The magnetic moments (in fields of 4000-18,000 oersteds between 20.4°-320°K) and absolute saturation magnetic moments of gadolinium, dysprosium and erbium are tabulated. The Curie point of gadolinium as

determined by the ballistic method and as defined by the disappearance of spontaneous magnetization differed. Gadolinium is magnetically "harder" than iron. Dysprosium is ferromagnetic below 90°K; erbium is ferromagnetic at 20.4°K. The magnitudes of the magnetic moments of dysprosium and erbium indicate that the orbital angular momentum contributes to ferromagnetism. The anomalous behavior of the magnetization vs $1/H$ curves of dysprosium are noted and discussed. Tables, graphs and diagrams are shown. 40 references.

350. Elliott, R. J., and Stevens, K. W. H. The magnetic properties of certain rare earth sulfates. *Proc. Roy. Soc. (London)* 219, 387-404, 1953. *Crerar Met. Abstr.* 2, No. 3, 51, 1953. The theory of magnetic properties of rare-earth ions in crystals is applied to ethyl sulfates. Magnetic susceptibility and resonance results are discussed. Observations are explained by using fields of C_{3h} symmetry which vary systematically with the rare earth ion tested; a mathematical treatment is presented. Neodymium, samarium, gadolinium, dysprosium, erbium and ytterbium were the rare earths studied. Data are tabulated.
351. Garif'yanov, N. S. Resonance paramagnetic absorption in a single crystal of gadolinium nitrate. *Doklady Akad. Nauk S.S.S.R.* 84, 923-5, 1952; cf. Zavoiskii, *CA* 40, 1708.7. *CA* 46, 9980h, 1952. According to the theory of Kittel and Luttinger (*CA* 42, 1821g) the Gd^{3+} ion, being in the $^8S_{1/2}$ state, and the spin-orbital coupling being weak, should suffer in the electrical field of the crystal a small splitting δ of the ground state, of the order of radio frequencies. The spectrum of resonance paramagnetic absorption in Gd^{3+} salt crystals should consist of a few lines, the position of which on the curve of the coefficients of paramagnetic absorption X'' as a function of the static magnetic field H should permit determination of the symmetry and direction of the intra-crystalline electrical field and of δ . Curves of $X''(H)$ were determined by reflection in 9.378×10^9 hertz for the orientations (100), (110), and (111), of a crystal of $Gd(NO_3)_3 \cdot 6H_2O$ (I) relative to the octahedron formed by H_2O ; the salt is triclinic, containing in the elementary cell, 2 Gd, 6N, 18 O atoms, and 12 molecules H_2O . With pure I, the absorption lines are

too broad for a resolution of the maxima. It is possible, however, with crystals grown from a saturated solution containing 1 weight part of I with 10 parts of the diamagnetic $\text{La}(\text{NO}_3)_3$. The experimental positions of the maxima were compared with those calculated by the formulas of de Boer and Lieshout (CA 44, 2810d), with $\delta = 0.176 \text{ cm}^{-1}$, on the assumption of a cubic symmetry of the electrical field produced around the Gd^{3+} ion by the 6 H_2O molecules. Systematic deviations, in excess of possible experimental errors, indicate that this assumption is not strictly valid. Paramagnetic resonance was observed also, in 9.378×10^9 , 3.750×10^9 , 4.882×10^8 , 2.02×10^8 , 1×10^7 hertzes, in powders of other salts of Gd^{3+} . All these salts gave a broad absorption band (width 2000-2500 oersteds), with the effective g factor values: I 2, $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ 2.1, $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ 1.99, Gd_2O_3 1.98.

352. Hilal, O. M. M., and Sugden, S. Magnetic susceptibilities of the rare earth elements. I. Yttrium. J. Chem. Soc. 135-6, 1949. CA 43, 6479g, 1949. Measurements of the magnetic susceptibility of successive fractions were used to follow the purification of Y by fractional precipitation by NH_3 carried in a current of air. The limiting value for the Y ion at room temperature is $10^6 \chi = 0.21 \pm 0.02$. This method of purification, for which full experimental details are given, proved to be much more rapid than the bromate method of fractional crystallization. The magnetic measurements were made by the Gouy method. The purity of the final product was checked spectroscopically.
353. Jagannadham, A. V. Diamagnetic susceptibilities of paramagnetic ions. Proc. Rajasthan Acad. Sci. 1, 6-8, 1950. CA 45, 9948d, 1951. Diamagnetic susceptibilities were calculated by the method of Angus (CA 26, 4218) for the paramagnetic ions of the Fe, rare earth, Pt, and Pd groups of metals. The results (in e.m.u. $\times 10^6$) follow:
 Sc^{++} 25.83, Ti^{++} 22.19, Ti^{+++} 11.59, V^{++} 21.56, V^{+++} 14.78, V^{4+} 9.23, Cr^{++} 21.11, Cr^{+++} 15.38, Mn^{++} 20.69, Mn^{+++} 18.01, Mn^{4+} 12.16, Fe^{++} 19.51, Fe^{+++} 15.59, Co^{++} 18.41, Ni^{++} 17.45, Cu^{++} 16.38, Ce^{+++} 27.36, Pr^{+++} 27.29, Nd^{+++} 27.19, Pm^{+++} 26.91, Sm^{+++} 26.53, Eu^{+++} 26.24, Gd^{+++} 25.78, Tb^{+++} 25.19, Dy^{+++} 24.79,

Ho⁺⁺⁺ 24.78, Er⁺⁺⁺ 24.37, Tm⁺⁺⁺ 23.79, Yb⁺⁺⁺ 23.57; Mo⁺⁺⁺ 24.85, Mo⁴⁺ 34.68, Ru⁺⁺⁺ 34.03, Ru⁴⁺ 27.10, Rh⁺⁺⁺ 34.84, Pd⁺⁺ 38.01; W⁺⁺⁺ 47.98, W⁴⁺ 35.17, Os⁺⁺ 58.80, Os⁺⁺⁺ 47.53, Ir⁺⁺⁺ 46.34, Ir⁴⁺ 38.32, Pt⁺⁺ 52.77, Pt⁴⁺ 57.60, U⁴⁺ 46.14.

354. Legvold, S. Some magnetic and electrical properties of gadolinium, dysprosium and erbium metals. *Revs. Mod. Phys.* 25, 129-30, 1953. *Crerar Met. Abstr.* 2, No. 3. 48, 1953. Results of preliminary work on the ferromagnetic properties of the rare earths are reported. Magnetization curves of hexagonal close-packed gadolinium are shown. The Gd Curie point is $16 \pm 1^\circ\text{C}$. Electrical resistivities from 2.2-293°K were determined on gadolinium, erbium and dysprosium rods. Curves are shown; those of gadolinium and dysprosium show abrupt changes in slope at 300°K and 155°K, respectively. Erbium has an unusually high resistivity at room temperature. Tables are given.
355. Mukherji, A. The principal magnetic susceptibilities of single crystals of rare earth salts at low temperatures. I. Cerium salts. *Indian J. Phys.* 23, 217-28, 1949. *CA* 44, 6326g, 1950. Cerium double salt susceptibilities were determined from 85 to 300°K. The results are discussed in terms of crystalline field theory. The deviation of the effective mean square moment of the cerous ion from the Hund value for the free ion can be explained on the assumption of a single suitable cubic field, which is independent of temperature. The mean square moment is almost wholly determined by the cubic part of the field, the rhombic part having little effect. The variation in cubic field magnitude in passing from hydrated salts to anhydrous halides is in the right direction. The X₁-axis of CeNH₄(SO₄)₂·4H₂O rotates by about 15° as the temperature is lowered from 300 to 85°K. II. Praseodymium salts. *Ibid.* 309-20. Pr₂(SO₄)₃·8H₂O and Pr₂Mg₃(NO₃)₁₂·24H₂O susceptibilities were determined from 85 to 300°K. The observed magnetic moment at all temperatures can be explained on the basis of a single suitable cubic field. Large observed anisotropies point to the existence of a strongly asymmetric rhombic field. Rhombic splitting is not small compared to cubic splitting. The X₁-axis of praseodymium sulfate rotates about 63° as the tempera-

ture is lowered. III. Neodymium salt. Ibid. 410-20. $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Nd}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ susceptibilities were determined from 85 to 300°K. Although a single cubic field of the fourth degree could explain the mean susceptibility, the absolute magnitude of this field estimated from magnetic data would not be correct. Estimation of the cubic part of the field, assumed to be wholly fourth degree, from magnetic data gave varying results from crystal to crystal. The influence of fourth- and sixth-degree terms on Stark splitting and the large magnetic anisotropy indicate that the low energy levels observed in absorption spectra cannot be attributed to the cubic field alone. The X_1 -axis of the sulfate rotates about 7° as the temperature is lowered. IV. Samarium salts. Ibid. 445-52. $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Sm}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ susceptibilities were determined from 85 to 300°K. The results are discussed in terms of crystal field theory. The magnetic anisotropy of Ce, Pr, and Nd increases with decreasing temperature; in samarium salts it first increases, passes through a maximum, and then decreases. This behavior is attributed to the small separation (930 cm^{-1}) between the ground level and next higher level of the Sm^{++} ion.

356. Rabideau, S. W. Magnetic susceptibilities of praseodymium oxides. J. Chem. Phys. 19, 874-6, 1951. CA 46, 305e, 1952. The magnetic susceptibilities of the 3 oxides of praseodymium, Pr_2O_3 , PrO_2 , Pr_6O_{11} , were measured with the Faraday magnetic balance over a range of temperatures from 80 to 300°K. The sesquioxide and the dioxide have moments of 3.55 and 2.48 Bohr magnetons, respectively, and obey the Weiss modification of the Curie law, $X(T + \Delta) = C$, over the range of temperatures studied with corresponding values of Δ equal to 55.0° and 104°. A curvature was noted in the plot of $1/X$ versus T for the oxide Pr_6O_{11} . Thus the Weiss-Curie law does not adequately express the relation between the susceptibility and the temperature for this oxide. A moment of 2.8 Bohr magnetons was calculated for Pr_6O_{11} from the slope of the above plot between 200° and 300°K.
357. Sahney, R. C., Aggarwal, S. L., and Singh, M. Structure of the periodates. III Magnetic study of the paramagnetic periodates of

Cu, Ni, [Co], Ce and Y J. Indian Chem. Soc. 24, 193-6, 1947. CA 42, 8551i, 1948. The method of preparation of the paramagnetic periodates of Cu, Ni, Co, Ce, and Y is outlined and the analyses of the prepared salts are given. The susceptibilities, $X_m \times 10^{-6}$, at 32° measured by the modified Guoy's balance are: copper periodate 6.803, nickel paraperiodate 20.744, cobalt dimesoperiodate 23.67, tetrahydrated cerium mesoperiodate 5.143, tetrahydrated yttrium mesoperiodate 9.072. On the assumption that these compounds obey Curie's law in the limited temperature range of the experiments, the effective magnetic moment, μ_B , in Bohr magnetons was calculated for each of the metal ions by the equation $\mu_B = 2.84 \sqrt{X_M T}$, after due allowance had been made in each case for the diamagnetic contributions of the periodate ion and H₂O mols. The results are: Cu⁺⁺, 1.731; Ni⁺⁺, 3.174; Co⁺⁺, 3.67; Ce⁺⁺⁺, 2.356; Y⁺⁺, 2.909. These values are compared with the theoretical results calculated by Hund's, Van Vleck's, and the Bose-Stoner formulas. From the general agreement of the experimental values of μ_B with those calculated theoretically it is concluded that these compounds are the true simple salts of periodic acid rather than the complex salts.

358. Sanchez, A. E. Magnetic behavior of the chlorides of praseodymium and neodymium in solid form or in solution. Rev. acad. cienc. exact., fis. y nat., Madrid 34, 202-41, 1940. CA 45, 3211a, 1951. The magnetic susceptibility of anhydrous PrCl₃ was determined up to 300°, that of NdCl₃ up to 426°. Both follow the Weiss law. The magnetic moments are: PrCl₃ 18.26, NdCl₃ 19.15. Measurements on aqueous solutions of either compound at temperatures up to 150° show deviations from this law which are ascribed to distortion of the angular orbital momentum by the electrical field of water molecules.
359. Stevens, K. W. H. Matrix elements and operator equivalents connected with the magnetic properties of rare earth ions. Proc. Phys. Soc. (London) 65A, 209-15, 1952. CA 46, 10725f, 1952. A theory is developed for calculating the matrix elements of crystal field potentials. Calculations are included and data given for the following ions

Ce^{+++} , Pr^{+++} , Nd^{+++} , Pm^{+++} , Sm^{+++} , Eu^{+++} , Gd^{+++} , Tb^{+++} , Dy^{+++} , Ho^{+++} , Er^{+++} , Tm^{+++} , Yb^{+++} . The data are obtained in terms of one-electron radial integrals.

360. Sugden, S., and Tailby, S. R. The magnetic susceptibilities of the rare-earth elements. II. Samarium. III. Gadolinium. IV Thulium. J. Am. Chem. Soc. 136-7, 137-8, 139-40, 1949. CA 43, 6479i, 1949. Suitable compounds of Sm, Gd, and Tm were purified by successive fractional crystallizations. In each case the process was followed by measurements of the magnetic susceptibility. Full experimental details of the chemical purification and fractionating processes are given. The values at 20° of $10^6 \chi$ for the various ions are: Sm 6.72 ± 0.03 , Gd 168.4 ± 0.2 , and Tm 136.5 ± 0.1 . These results are in good agreement with theoretical values.
361. Trapnell, B. M. W., and Selwood, P. W. Magnetic susceptibilities of europium sesquioxide and of uranium dioxide at low temperatures. Nature 169, 840-1, 1952. CA 46, 10726i, 1952. Susceptibility measurements in the temperature range 20-80°K with Eu_2O_3 favor a screening constant of 34 for the Eu^{+3} ion. The susceptibility of Eu follows the Van Vleck (Theory of Electric and Magnetic Susceptibilities (CA 26, 5826, 1932)) theory fairly well down to 80°K, but moderate deviations in a positive direction are observed at lower temperatures. The Weiss constant of UO_2 is determined as 220°. UO_2 shows no indication of a magnetic anomaly corresponding to an antiferromagnetic Curie point down to 20°K.

XV. ACTIVATION AND X-RAY STUDIES

362. Bomke, H., and Reddemann, H. Absorption of slow neutrons in rare earths and in cadmium. *Z. Physik* 120, 56-68, 1942. CA 37, 4007.2, 1943. The total cross section for thermal neutrons is determined for pure samples of 13 rare earths. The values found in units of 10^{-24} sq cm are: Y, 4; La, 10; Tb, 15; Nd, 72; Sm, 7040; Eu, 2700; Gd, 22,550; Dy, 780; Ho, 52; Er, 185; Tm, 114; Yb, 50; Lu, 65. The absorption cross section of Cd for slow neutrons is 2640×10^{-24} sq cm.
363. Browne, C. I., et al. The decay series neodymium¹⁴⁰ — praseodymium¹⁴⁰ — cerium¹⁴⁰. *Phys. Rev.* 85, 146-7, 1952. CA 46, 4388b, 1952. Nd¹⁴⁰, prepared by bombarding Pr oxide with 19-m.e.v. deuterons, was separated by citrate elution from Dowex 50 cation-exchange resin at 83°. The Pr¹⁴⁰ β^+ spectrum has a maximum energy of 2.23 ± 0.02 m.e.v. There may be a component of ~ 1 m.e.v. The e^- spectrum contains a line at 28.9 ± 0.5 e.kv. due to Auger conversion of K-shell vacancies in Pr or Ce or both. The x-ray spectrum has the intensity ratios $\text{PrK}\alpha_{1,2}:\text{CeK}\alpha_{1,2}:\text{PrK}\beta_1:\text{CeK}\beta_1 = 100:50:28:11$. In Pr¹⁴⁰ $K/\beta^+ = 1.0 \pm 0.1$. The Pr¹⁴⁰ decay is allowed, and $\Delta I = 1$. Nd¹⁴⁰ decays 26% by L-capture and 74% by K-capture. Pr¹⁴⁰ decays 58% by β^+ -emission, 37% by K-capture, and 5% by L-capture; $\beta^+/K = \sim 1.6$. The decay energy of Nd¹⁴⁰ is 105 ± 40 e.kv. Pr¹⁴⁰ is in the S₁ state; $\beta^+/e^- = \sim 50$, $K/e^- = \sim 100$, and $W_K = 0.90$.
364. Chatterjee, S. D., and Olcott, R. N. Absence of spontaneous emission of neutrons from samarium. *Phys. Rev.* 85, 147-8, 1952. CA 46, 4388d, 1952. Yagoda and Kaplan reported spontaneous emission of neutrons from Sm, with a half life $\sim 10^{16}$ years (CA 43, 8857f). With 782 g Sm as the oxalate, in 2 different experimental arrangements, no evidence of the spontaneous emission of neutrons from Sm was found. Possible sources of the neutrons reported by Y and K are discussed.
365. Colmer, F. C. W., and Littler, D. J. Pile neutron absorption cross sections of some of the elements. *Proc. Phys. Soc. (London)* 63A, 1175-6, 1950. CA 45, 2786h, 1951. Measurements have been made

- with a pile oscillator in a graphite low-energy pile. Absorption cross sections are reported for Al, Sb, A, As, Ba, Bi, B, Br, Ca, Ce, Cl, Cr, Co, Nb, Cu, Gd, Hf, I, Fe, Pb, Li, Mg, Mn, Mo, Ni, N, Pd, P, Pt, K, Se, Si, Na, Sr, S, Ta, Sn, Ti, W, V, Zn, and Zr.
366. Duckworth, H. E. Some possible rare stable isotopes. *Phys. Rev.* 75, 1438, 1949. *CA* 43, 5297d, 1949. The weights of the lightest known isotopes of elements of even atomic number are plotted against their atomic numbers from $_{46}\text{Pd}$ to $_{82}\text{Pb}$. Most of them lie on 3 straight lines: $_{48}\text{Cd}^{106}$ - $_{60}\text{Nd}^{142}$, $_{62}\text{Sm}^{144}$ - $_{74}\text{W}^{180}$, and $_{76}\text{Os}^{184}$ - $_{82}\text{Pb}^{204}$. The results are discussed, and searches for stable $_{52}\text{Te}^{118}$, $_{64}\text{Gd}^{150}$, and $_{78}\text{Pt}^{190}$ are indicated.
367. Duffield, R. B., and Langer, L. M. The β -spectrum of lanthanum ^{141} . *Phys. Rev.* 84, 1065-6, 1951. *CA* 46, 3867f, 1952. There are β end-points at 2.43 ± 0.03 and 0.91 ± 0.04 m.e.v. The relative intensity of the 0.91-m.e.v. radiation is 5%. There is a α -ray of 1.3-1.6 m.e.v. A decay scheme is given for the series $\text{La}^{141} \rightarrow \text{Ce}^{141} \rightarrow \text{Pr}^{141}$.
368. Edwards, R. R., and Coryell, C. D. β -Decay of cerium ^{144} as the acetylacetonate to praseodymium ^{144} . Brookhaven Natl. Lab., Conf. Chem. Effects of Nuclear Transformations (Hot Atom Chem.) AECU-50, (BNL-C'7) 52-62, 1948. *CA* 45, 4147e, 1951. The 275-day Ce^{144} decays with a 0.348 m.e.v. β to 17-minute Pr^{144} which emits 3.07-m.e.v. β -rays. If the latter is removed from the system by any process the residue exhibits growth which can be easily followed in short time experiments. Ce acetylacetonate dissolved in CS_2 or CCl_4 and containing excess acetylacetone showed complete removal of Pr by H_2O if shaken continuously during the decay, but no removal from CCl_4 and only 30% removal from CS_2 if shaken briefly after a similar decay period in the solvent alone. Likewise no removal into an aqueous solution was found if decay in crystalline Ce acetylacetonate was followed by solution in CCl_4 and immediate extraction or on prolonged shaking with H_2O in the absence of excess acetylacetone. The addition of carrier Pr acetylacetonate did not prevent extraction of "hot" Pr from a system shaken continuously with H_2O and containing excess acetylacetone.

The data may be explained by assuming that the decay leads primarily to PrA_3^+ (A = acetylacetonate), which reacts with CeA_3 to give $\text{PrA}_3 + \text{CeA}_3^+$, both stable in both phases; or in the presence of excess acetylacetone reacts to give PrA_4 , which reacts with H_2O . Alternatively the acetylacetonate acts to carry H_2O into the organic phase, where reaction takes place.

369. Goldstein, A., Schuman, R. P., and Robinson, W. Fission yields of members of chain 141. Natl. Nuclear Energy Ser., Div. IV, 9, Radio-chem. Studies: The Fission Products, Book 2, 1188-90, 1951. CA 46, 6003, 1952. In an investigation to determine whether the fission yield of a given decay chain varies along the chain, the fission yield of the fission product chain of mass 141 (3-sec. $\text{Xe}^{141} \rightarrow$ short-lived $\text{Cs}^{141} \rightarrow$ 18-min. $\text{Ba}^{141} \rightarrow$ 3.5-hr. $\text{La}^{141} \rightarrow$ 28-day $\text{Ce}^{141} \rightarrow$ stable Pr^{141}) was measured separately at Ba, La, and Ce, by 2 different methods. The ratio of the Ba yield to the Ce yield was 0.82. There was no evidence (within relatively large error) that the La yield was less than the Ce yield.
370. Grant, P. J., and Hill, J. M. Decay of holmium¹⁶⁶. Nature 163, 524-5, 1949. CA 43, 5297c, 1949. Ho^{166} produced by slow-neutron bombardment decays by β -emission to Er^{166} . This decay was investigated with a magnetic-lens β -ray spectrometer and by coincidence and absorption methods. The half life observed was 26.8 ± 0.4 hours. The maximum energy of the β -spectrum was 1.88 m.e.v. It was found that both K and L conversions occur.
371. Hayden, R. J., Reynolds, J. H., Inghram, M. G. Reactions induced by slow-neutron irradiation of europium. Phys. Rev. 75, 1500-7, 1949. CA 43, 5296h, 1949. Eu was irradiated with slow neutrons and analyzed by mass-spectrometric techniques. The cross sections depend linearly on the value of 2600 barns taken for normal Eu. For the Eu isotopes of mass 151 through 155 the cross section, half life, and K/ β values are given. CA 40, 6338.2, 41, 2326f; 42, 8076c.
372. Heath, R. L. K-shell conversion coefficient of cerium¹⁴¹. Phys. Rev. 87, 1132-3, 1952. CA 46, 10926d, 1952. The ratio of the 36-e.kv. K x-ray intensity to the 141-e.kv. γ -ray is 0.46 ± 0.02 . The K/L

conversion ratio is 5 ± 1 . The transition is chiefly M_1 , with some E_2 radiation.

373. Kelly, W. C. Internal conversion in praseodymium¹⁴⁴, indium¹¹⁴, barium¹³⁷, and cadmium¹¹⁰. Phys. Rev. 85, 101-3, 1952. CA 46, 4387f, 1952. β -Ray spectrometer measurements were made of the internal-conversion ratio α_K/α_L for 4 nuclear transitions. Values obtained are: 5.3 ± 0.1 for the 132-e.kv. transition in Pr¹⁴⁴, 1.30 ± 0.05 , 192 e.kv., In¹¹⁴; 4.57 ± 0.05 , 662 e.kv., Ba¹³⁷; and 14 ± 2 , 656 e.kv., Cd¹¹⁰. Tentative assignments of multipolarity are given.
374. Koehler, W. C., and Wollan, E. O. Slow neutron scattering cross sections for rare earth nuclides. Phys. Rev. 91, 597-9, 1953. Crerar Met. Abstr. 2, No. 2, 63, 1953. Coherent neutron scattering amplitudes determined for some rare earths are tabulated with total scattering cross-sections and other data. Nuclides studied were La¹³⁹, Ce¹⁴⁰, Ce¹⁴², Pr¹⁴¹, Nd¹⁴², Nd¹⁴⁴, Nd¹⁴⁶, Sm¹⁵², and Sm¹⁵⁴. Data on six isotopes of erbium included.
375. Long, J. K., and Pool, M. L. Radioactive promethium¹⁴⁸ and promethium¹⁵⁰. Phys. Rev. 86, 137, 1952; cf. CA 38, 2876.1. CA 46, 4388c, 1952. A 48-day activity is assigned to Pm¹⁴⁸, formed by the reaction Nd¹⁴⁸(p,n)Pm¹⁴⁸. There are negative β -particles of 1.7 ± 0.1 and 0.6 ± 0.1 m.e.v., and a γ -radiation of ~ 0.54 m.e.v. A 2.7-hour activity is assigned to Pm¹⁵⁰, formed by the reaction Nd¹⁵⁰(p,n)-Pm¹⁵⁰. There is a β end point at 2.4 ± 0.2 m.e.v.
376. Mandeville, C. E., and Shapiro, E. Disintegration of Nd¹⁴⁷, Ce¹⁴⁴, Pr¹⁴⁴ and Ce¹⁴³. Proc. Natl. Inst. Sci., India 17, 45-56, 1951. CA 46, 41c, 1952. Characteristics, radiation energies and coincidence rates have been determined by conventional absorption and coincidence methods.
377. McCullough, J. D. An x-ray study of the rare earth oxide systems: Ce^{IV}-Nd^{III}, Ce^{IV}-Pr^{III}, Ce^{IV}-Pr^{IV}, and Pr^{IV}-Nd^{III}. J. Am. Chem. Soc. 72, 1386-90, 1950. CA 44, 5178a, 1950. An x-ray study of the oxide systems Ce^{IV}-Nd^{III}, Ce^{IV}-Pr^{III}, Ce^{IV}-Pr^{IV}, and Pr^{IV}-Nd^{III} was carried out. Solid solutions with the fluorite structure are formed in all cases and lattice constants were deter-

mined as a function of composition. For the oxide systems M^{IV} - M^{III} there is an upper solubility limit varying from 50 to 67 atomic % of the trivalent metal. Pr is readily oxidized to Pr^{IV} in the presence of Ce^{IV} , but more difficultly in the presence of Nd^{III} . In no case was there evidence for the oxidation of Pr beyond the +4 state, even under O_2 pressures as high as 50 atms. Evidence was given in support of the existence of Pr_6O_{11} as a separate and distinct phase in the Pr- O_2 system.

378. McGowan, F. K. Lifetime of an excited state of dysprosium¹⁶⁰ and upper limits for some other nuclei. Phys. Rev. 85, 142, 1952. CA 46, 4388e, 1952. An excited state in Dy^{160} with a half life of $(1.8 \pm 0.2) \times 10^{-9}$ sec. was observed. The maximum β -energy is ~ 900 e. kv. L and M internal-conversion electrons corresponding to an 85-e. kv. transition were observed. No γ -rays of higher energy were found. Upper limits of the half lives of some other excited nuclear states are reported ($\times 10^{-9}$ sec.): Te^{123} , 159 e. kv., < 1.0 ; Te^{125} , 35 e. kv., < 2.0 ; Ho^{165} , 95 e. kv. < 0.8 ; Hg^{198} , 411 e. kv., < 0.4 ; Tl^{203} , 280 e. kv., < 0.4 .

379. McGowan, F. K. Measurement of some K-shell internal-conversion coefficients. Phys. Rev. 85, 151-2, 1952. CA 46, 4388e, 1952. Some experimental and theoretical K-shell conversion coefficients are compared:

Nuclide	E_γ , e. kv.	$T_{1/2}$, sec.	$\alpha_{exp} K$	$(\alpha_2 K)_{extrap.}$
Dy^{160}	85	1.8×10^{-9}	1.65 ± 0.2	1.75
Ho^{165}	95	$< 0.8 \times 10^{-9}$	≤ 2.9	1.40
Er^{166}	81	1.7×10^{-9}	1.9 ± 0.3	1.94
Yb^{170}	85	1.6×10^{-9}	1.5 ± 0.2	1.65

380. Meinke, W. W., and Anderson, R. E. Activation analysis of several rare earth elements. Anal. Chem. 26, 907-9, 1954. Crerar Met. Abstr. 2, 43, 1954. Europium can be determined in the presence of samarium and dysprosium in the presence of holmium more easily by activation analysis using appropriate radioactive bombardment than by spectrophotometry. All other lanthanons except lutetium causes less than 1% error.....

381. Meitner, L. The behavior of some rare earths on irradiation with neutrons. Arkiv. Mat. Astron. Fysik 27A, No. 17, 18 pp., 1940. CA 35, 377.7, 1941. The effective cross section for capture of thermal neutrons by Dy was found to be 870×10^{-24} sq cm $\pm 10\%$. The number of active Dy¹⁶⁵ atoms formed was only about 0.3 of the number of neutrons absorbed; evidently other Dy isotopes capture thermal neutrons with the same order of efficiency as Dy¹⁶⁴. Dy¹⁶⁵ was found to emit γ - as well as β -radiation. A sample containing Dy + Ho gave on irradiation the 156-min. period of Dy¹⁶⁵ plus the 33-hr period of Ho¹⁶⁶. Another sample also supposed to contain Ho gave no 33-hr period, but a 46-hr period attributable to Sm. The cross-section for neutron capture of this sample was measured, and found to be 9600×10^{-24} , too high for Dy or Sm; the sample was concluded to contain Gd also, which has the highest cross section of the rare earths. Its x-ray spectrum showed that the sample consisted of Dy, Sm, and Gd with a little Tb; evidently neutron irradiation may provide a method for analysis of mixtures of rare earths. The maximum energies of β -rays from Dy¹⁶⁵, Ho¹⁶⁶ and Sm¹⁵³ were found to be respectively, 1.40, 1.9 and 0.9 m.e.v.
382. Mulholland, G. L., and Kohman, T. P. Possible natural radioactivity of neodymium. Phys. Rev. 85, 144-5, 1952; cf. CA 42, 2855b. CA 46, 4388a, 1952. The maximum specific β -activity of natural Nd is 0.003 disintegrations/sec./g, corresponding to a half life of 2×10^{15} years for Nd¹⁵⁰. The maximum α -activity is 0.02/sec/g. 18 references.
383. Pool, M. L., and Krisberg, N. L. Radioactive cerium and praseodymium. Phys. Rev. 73, 1035-41, 1948. CA 42, 5768b, 1948. A 140 ± 1 -day half life is assigned Ce¹³⁹. It decays by K-electron capture to La¹³⁹. Two γ -rays of 0.184 and 0.8 m.e.v. are associated with Ce¹³⁹. The 0.184-m.e.v. γ -ray is found to be partially internally converted, giving electrons of approximately 0.145 and 0.178 m.e.v. A 30.6 ± 0.7 -day half life is assigned to Ce¹⁴¹, which is found to decay by the emission of a 0.66-m.e.v. β^- particle and a γ -ray of approximately 0.2 m.e.v. to stable Pr¹⁴¹. A 1.4 ± 0.1 -day half life is assigned to Ce¹⁴³, which decays by the emission of a

1.3-m e.v. β^- -particle and a 0.6-m.e.v. γ -ray to Pr^{143} . A 13.5 ± 0.1 half life is assigned Pr^{143} , which decays to stable Nd^{143} by emission of a 0.83-m.e.v. β^- -particle. The saturation intensity ratio of the $\text{Ce}^{142}(\text{d}, \text{n})\text{Pr}^{143}$ reaction to the $\text{Ce}^{142}(\text{d}, 2\text{n})\text{Pr}^{142}$ reaction is found to be 2.9.

384. Pringle, R. W., et al. The natural activity of lanthanum. *Phys. Rev.* 84, 1066-7, 1951; cf. *CA* 44, 7160g. *CA* 46, 4387h, 1952. La^{138} has γ -energies of 535 ± 15 , 807 ± 15 , and 1390 ± 30 e.kv., with relative intensities 0.3:0.65:1. There is a Compton edge near 1100 e.kv. There is an x-ray of 32 ± 1 e.kv. The half life is 2.0×10^{11} years. A scheme for the decay of La^{138} to Ba^{138} and to Ce^{138} is given.
385. Robinson, B. L., and Madansky, L. Coincidence studies in the decay of lanthanum¹⁴⁰. *Phys. Rev.* 84, 1067-8, 1951; cf. *CA* 46, 1884h. *CA* 46, 4387i, 1952. The 1.60-m.e.v. γ -ray is in coincidence with the 0.82-m.e.v. γ -ray and with the most energetic β -rays. The angular correlation of these 2 γ -rays was examined, 90-180°, and agrees with theoretical calculations. Spins are assigned on the basis of angular correlations. A partial decay scheme is proposed for $\text{La}^{140} \rightarrow \text{Ce}^{140}$.
386. Stover, B. J. New neutron-deficient radioactive isotopes of the light rare earth region. *Phys. Rev.* 81, 8-13, 1951. *CA* 45, 2329a, 1951. In this region, 7 new neutron-deficient radioactive isotopes were produced by proton bombardment in a cyclotron and a linear accelerator; their radiations were studied by absorption curve and magnetic counter methods. Additional data were obtained for Ce^{135} and Ce^{137} . The results are:

Nuclide	Half life	Radiations(m. e. v.)	Produced by
La^{134}	6.5 ± 0.25 min.	β^+ , 2.7; K	Ce^{134} decay
Ce^{133}	6.30 ± 0.1 hr.	β^+ , 1.3; K; γ , 1.8	$\text{La}(\text{p}, 7\text{n})$
Ce^{134}	72.0 ± 0.5 hr.	K	$\text{La}(\text{p}, 6\text{n})$
Pr^{138}	120 ± 5 min.	e^- , 0.24; β^+ , 1.4; K; γ , 0.16, 1.3	$\text{Ce}(\text{p}, 3\text{n})$
Pr^{139}	4.50 ± 0.2 hr.	β^+ , 1.0; K; γ , 1.0	$\text{Ce}(\text{p}, 2\text{n})$
Nd^{138}	22 ± 2 min.	β^+ , 2.4; K	$\text{Pr}(\text{p}, 4\text{n})$
Nd^{139}	5.50 ± 0.2 hr.	e^- , 0.28; β^+ , 3.1; K; γ , 1.1	$\text{Pr}(\text{p}, 3\text{n})$
Ce^{135}	22 hrs.	β^+ , 0.80	$\text{La}(\text{p}, 5\text{n})$
Ce^{137}		e^- , 0.24	$\text{La}(\text{p}, 3\text{n})$

387. Straub, C. P. Removal of radioactive materials from waste solutions
 Sewage and Ind. Wastes 23, 188-93, 1951. CA 46, 355c, 1952
 Radioactive wastes from the production phases of the national atomic energy program, from laboratories and hospitals, and from atomic-bomb explosions respond in varying degree to methods commonly known to sanitary engineers. Evaporation will remove all activity from the liquid portion and concentrate it in the sludge or slurry. Coagulation with alum removes 10% I^{131} , 98% P^{32} , 10 of Sr^{89} , 45-98 of Y^{91} , 98 of Ce^{144} , 98 of Y^{90} , and 10 of Sr^{90} . Phosphate coagulation gave results as follows: Zn^{65} , 99; Sr^{89} , 98, Y^{91} , 99; Sb^{124} , 67; Ce^{144} , 99; W^{185} , 10. Sand filtration removed 85-98% P^{32} and only 1-25% I^{131} . Ion-exchange materials are effective; activated sludge removes 96% Pu and about the same amount I^{131} . Other methods are suggested for removal of radioactive materials.
388. Wilkinson, G., and Hicks, H. G. Radioactive isotopes of the rare earths. I. Experimental techniques and thulium isotopes. Phys. Rev. 75, 1370-8, 1949. CA 43, 5296i, 1949. Experimental techniques used in the chemical separation and identification of radioactive isotopes of the rare earth elements are described. The isotopes are produced by the bombardment of rare earth oxides and Ta with α -particles, deuterons, and protons. Some Tm isotopes were investigated:

Isotope	166	167	168
Decay	K $\beta^+ e^-$	Ke $^-$	Ke $^-$ (β^-)
Half-life	7.7 ± 0.1 hrs.	9.6 ± 0.1 days	85 ± 2 days
Radiation energy, m.e.v.			
Particles	2.1 (β^+) 0.24, ~ 1 (e^-)	0.21 (e^-)	0.16, 0.5 (e^-)
γ -rays	L, K x-rays 1.7	L, K x-rays 0.22, 0.95	L, K x-rays 0.21, 0.85
Produced by	Ho- α -3n	Ho- α -2n	Ho- α -n
	Er-p-n	Er-p-n	Er-p-n
		Ta-d-5z, 16a	Tm-n-2n

Cross section (α -particles on Ho), barns			
38 m.e.v.	1.1	0.007	0.0001
30 m.e.v.	0.0005	0.1	0.003
19 m.e.v.	---	0.001	0.2

cf. CA 43, 1647f, 43, 4124ai.

AW:jm