1949

A scheme of analysis for the ceric rare earths

Herschel Gordon Frye
University of the Pacific

Recommended Citation

Frye, Herschel Gordon. (1949). *A scheme of analysis for the ceric rare earths*. University of the Pacific, Thesis. https://scholarlycommons.pacific.edu/uop_etds/1093

A SCHEME OF ANALYSIS
FOR THE
CERIC RARE EARTHS

By

Herschel Gordon Frye

June

1949

A Thesis
Submitted to the Department of Chemistry
College of the Pacific

In partial fulfillment
of the
Requirements for the
Degree of Master of Arts

APPROVED: Chairman, Thesis Committee

DEPOSITED IN THE COLLEGE LIBRARY:

DATED: Librarian

TABLE OF CONTENTS

CHAPTER PAGE

I. THE PROBLEM 1

II. THE ELEMENTS OF THE CERIUM GROUP 3

III. A REVIEW OF METHODS OF ANALYSIS IN USE . 7

IV. THE NATURE OF THE RESEARCH 15

V. THE PROPOSED SCHEME OF ANALYSIS 23

VI. CONCLUSIONS 27

BIBLIOGRAPHY 29

APPENDIX 41

CHAPTER I

THE PROBLEM

The elements numbered 57 to 71 have presented a problem in analytical chemistry unparalleled by that of any other group since their discovery over the span of the nineteenth century. The striking similarities in chemical behavior of the fifteen elements comprising this series have almost completely baffled analysts in every attack, and it is only with the increased use of those newer methods, best described as being of a strictly physical nature, that much real progress has been achieved. Where time-honored classical wet methods have failed rather disappointingly, newer methods based upon the use of the spectrograph and similar instruments have given much promise to the chemist interested in these elements. It is unfortunate that such determinations leave much to be desired in the way of quantitative accuracy, although as a criterion of purity, spectrographic data are of prime importance to the analyst.

The problem, then, is to develop a method for the separation and determination of the rare earth elements based upon wet method techniques rather than upon the use of the spectrometer or other physical measuring instrument. The attack on the rare earth group as a whole would present almost insuperable obstacles to the worker pressed for time, and therefore only the elements comprising the cerium group have been chosen as a subject for research undertaken. As commonly accepted, this series consists of lanthanum, cerium, praseodymium, neodymium, element 61, and samarium. Europium might also be included, but its nature is much that of a transition element between the cerium and yttrium groups. The cerium group has been chosen because of the ready availability of the various salts (except those of element 61, of course) and because of the rather wide occurrence of the member elements in such minerals as monazite. Had time been available, an additional reason might have been the relatively simple spectra in the carbon or copper arc of these first elements of the whole rare earth series.

Since most promise has been shown by the use of organic reagents, the greater part of the work has been done in this direction. An attempt has been made to select a representative cross-section of organic compounds used under a variety of conditions. Principal results are set forth in Table III of the appendix.

CHAPTER II

THE ELEMENTS OF THE CERIUM GROUP

Intelligent approach to the problem, whether typically physical or chemical in nature, must first concern itself with the properties of the elements under consideration. A review of the periodic table reveals that one would expect to find only one element, lanthanum, occupying the third period position in the sixth orbit series between barium and hafnium. The latter two indeed fall well into the series in which they have been placed. Perhaps the most striking aspect is the great increase in atomic weight between lanthanum and hafnium, although the two elements occupy adjacent positions in the table. It is here, in the position of atomic number 57, that the rare earth group of fifteen remarkably similar elements is found. So alike are these elements chemically that ordinary means of separation are almost worthless, and even the tedious process of fractional crystallization produces pure salts only with repeated fractionation and much effort on the part of the operator.

Electronic studies have determined that the rare earths, except lanthanum, are unlike other atoms in that they contain a varying number of so-called 4f electrons in the N shell. The number of these 4f electrons increases from one in the case of cerium to a maximum of fourteen in the case of lutecium. Lanthanum, the first member of the series, has no 4f electrons and is not considered a rare earth by some spectroscopists. These electrons occupy circular orbits so that the azimuthal quantum number is equal to the total quantum number, and since they are in a shell located rather deep within the atom, they contribute little to the chemical activity of the elements. The increase in atomic number and atomic weight does not contribute additional electrons in the outermost shell, and this number remains at three throughout the entire series, giving rise to the monotonous regularity of the chemical and physical properties exhibited by the members of the group.

The 4f electrons contribute nothing to the chemical reactivity, but they do contribute much to the complexity of the atomic spectra. The arc spectra of all the rare earths except lanthanum include a great number of lines, and spectrographic analysis is tedious and demanding on both operator and instrument. Electronic configurations of the elements of the cerium group are listed in Table I of the appendix, although the nature of this study has little bearing on such data as these.

The physical set-up of the rare earth atom leads to greater attraction between nucleus and planetary electrons due to the relative proximity with which the additional electrons are located in regard to the nucleus. This increased attraction within the atom leads to that particular phenomenon known as the lanthanide contraction, in which increasing atomic number gives both atoms and ions of decreasing radius. This leads to a situation in which the rare earth holmium, atomic number 67, has an ionic radius almost exactly equal to that of yttrium, atomic number 39. Indeed, when the two elements occur together, they are almost impossible to separate.

Little need be said concerning the occurrence of the rare earths. There are a number of minerals in which they occur together with thorium, yttrium, uranium, and similar elements, usually as complex salts. The principal source of the cerium group is the mineral monazite, which is a complex phosphate containing a preponderance of cerium and much thorium. Other minerals of note are the silicates gadolinite, cerite, and allenite, the phosphate xenotime, the fluoride ytterocite, and the columbate-tantalates fergusonite and samarskite. Deposits of these minerals are limited in amount but widespread. The best monazite areas are located in Brazil and India, although there are considerable deposits in Florida and Idaho in this country. It has been estimated that cerium is present to the extent of 0.00155 per cent of the lithosphere and is therefore more abundant than such everyday elements as mercury, tin, cadmium, antimony, bismuth, and tungsten[1]. Europium, the least plentiful of the known rare earths, occurs to the extent of only 0.0001 per cent of the lithosphere. Perhaps other important deposits remain hidden in little explored areas, but the limited use to which the members of this group of metals may be put could never cause a cerium rush to another land.

Data concerning the physical properties of the rare earth elements of the cerium group may be found in the appendix (Table II), for it seems unnecessary to include such a listing within the text of the thesis.

---

[1] Yost, Russell, and Garner, *The Rare Earth Elements and Their Compounds* (New York: John Wiley and Sons, 1947) page 40.

CHAPTER III

A REVIEW OF METHODS OF ANALYSIS IN USE

The nature of the problem and the available equipment indicated an attack from a typical wet methods point of view rather than an approach making use of expensive pieces of optical or photometric apparatus. Much has already been done along these purely physical lines by workers here and abroad making use of established methods such as chromatographic absorption[2], arc spectroscopy[3], spectrography[4], x-ray spectrography[5], and infra red emission spectroscopy[6]. While these methods are perhaps less tedious than ordinary chemical means of sep-

---

[2] Lang and Nagel, Zeitschrift fur Elektrochemie 104, 1936. Pages 390-400.

[3] Rodden, Journal of Research, National Bureau of Standards 26, 1941. Page 557. See also: Bauer, Zeitschrift fur anorganische und allgemeine Chemie 221, 1935. Page 209. See also: McCarty, et. al., Industrial and Engineering Chemistry, Analytical Edition 10, 1938. Page 184. See also: Gatterer and Junkes, Spectrochimica Acta 1, 1939. Page 31. See also: Lopez de Azcona, Boletin del Instituto Geologico y Minero de Espan 15, 1941. Page 270. See also: Fassel and Wilhelm, Journal of the Optical Society of America 38, 1948. Pages 518-526.

[4] Meggers, Review of Modern Physics 14, 1942. Page 96.

[5] Kimura, Journal of the Chemical Society of Japan 54, 1933. Pages 213-219. See also: Shinoda, Journal of the Chemical Society of Japan 58, 1937. Pages 1483-1486.

[6] Meggers, Analytical Chemistry 21, 1949. Pages 29-31.

arations, still they leave much to be desired by way of quantitative accuracy. As an absolute criterion of purity, however, such data are without peer.

Fractional crystallization has long been the classic method for the preparation of pure rare earth salts, time consuming and wasteful as such an approach is. Some of the limitations of fractional crystallization as a method of separation of the rare earths are reviewed by Spedding and others[7] in a recent paper describing ion exchange as a promising method. Salts most extensively used in such fractionations are the double nitrates[8], although bromates, phosphates, and sulfates have been used with success[9]. With such methods, of course, quantitative accuracy is impossible to achieve.

It would be foolish indeed to proceed in search of the answer to such a problem as has been outlined in

---

[7] Spedding, et. al., Journal of the American Chemical Society 69, 1947. Pages 2786-2792.

[8] Jantsch, Zeitschrift fur anorganische Chemie 76, 1912. Page 321. See also: Prandtl and Rauchenberger, Zeitschrift fur anorganische und allgemeine Chemie 120, 1922. Page 120.

[9] Selwood, Journal of the American Chemical Society 55, 1933. Page 4900. See also: Marsh, Journal of the Chemical Society 1939, 1939. Page 554. See also: James, et. al., Journal of the American Chemical Society 49, 1927. Page 132.

chapter I without first completing a very thorough search of the pertinent literature as far back as library facilities allow. Such a search reveals that a great many analysts have turned their talents in the direction of rare earth research and have attacked the problem from almost every conceivable avenue of approach. In the previous paragraphs, the discussion has concerned itself mainly with those methods which might be considered strictly instrumental in nature, and most of the work of the last ten years has been directed along these lines. This does not imply that the classical wet methods have been neglected; such is far from the case. Indeed, almost every possible rare earth compound has been prepared in an attempt to find differences of chemical behavior distinct enough to afford a useful basis for a new separation.

A number of methods have been developed for the separation of the rare earth group as a whole from such elements as thorium and uranium, which almost invariably occur in rare earth minerals. Thorium may be separated from the rare earths by boiling the mixture with a solution of hydrogen peroxide which has been made slightly acid[10], or by the use of an organic compound such as

---

[10] Hopkins, The Chemistry of the Rarer Elements (Boston: D.C. Heath and Co., 1923) page 99.

hexamethylenetetramine[11]. Pyridine has been suggested[12] as a precipitant for the quantitative separation of thorium from the rare earths of the cerium group. Procedures such as the basic acetate method fail because elements such as thorium and yttrium are incompletely precipitated. Organic reagents such as cupferron, sebacic acid, and the sodium salt of diethyldithiocarbamic acid have been proposed for the separation of the rare earths from uranium[13].

A number of the reagents commonly used for the separation of some other metal have been applied to the rare earths with varying success. Thus, Studies have been made using aluminon[14], oxalic acid, and 8-hydroxyquinoline[15]. Most of these methods fail because they lack the necessary specificity. Aluminon, for example, gives similar reactions for aluminum, the rare earths, yttrium, thorium, and gallium. The use of certain of the alkaloids such as morphine has

---

[11] Ismail and Harwood, Analyst 62, 1937. Page 185

[12] Moeller and Kremers, Chemical Reviews 37, 1945. Page 139.

[13] Short and Dutton, Analytical Chemistry 20, 1948. Pages 1073-1076.

[14] Cory and Rogers, Journal of the American Chemical Society 49, 1927. Page 216. See also: Middleton, Journal of the American Chemical Society 48, 1926. Page 2125. See also; Yoe, Journal of the American Chemical Society 54, 1932. Page 1022.

[15] Yoe and Sarver, Organic Analytical Reagents (New York, John Wiley and Sons, 1941) page 137.

been attempted[16] with but little success. Brucine was tried in the present research with negative results. All of the above methods fail because they are not specific for the rare earths as a group, let alone useful for the desired intra-group separations.

Methods for the separation of the various rare earths from members of their own group are even less numerous and efficient. Reported separations of lanthanum from praseodymium and neodymium make use of ammonium chloride[17], ammonia alone[18], ammonia with a metallic nitrate such as that of cadmium or nickel[19], or the oxides or carbonates of basic metals such as magnesium[20]. Appleton and Selwood have separated lanthanum and neodymium thiocyanates by means of a n-butanol and water mixture[21], but the method is by no means quantitative. Piperadine

---

[16] Ibid., page 242.

[17] Prandtl and Rauchenberger, Berichten der Deutschen Chemischen Gesellschaft 53, 1920. Pages 843-853.

[18] Wierda and Kremers, Transactions of the American Electrochemical Society 48, 1925. Page 159.

[19] Prandtl and Rauchenberger, Zeitschrift fur anorganische und allgemeine Chemie 129, 1923. Pages 176-180.

[20] Neish and Burns, Canadian Chemistry and Metallurgy 5, 1921. Page 69.

[21] Appleton and Selwood, Journal of the American Chemical Society 63, 1941. Page 2029.

has been suggested as a reagent for the separation of neodymium from lanthanum[22], and Brauner[23] claims a good separation of praseodymium from lanthanum by alkali fusion of the nitrates at high temperature, the praseodymium being oxidized to a higher valency state and rendered insoluble in concentrated ammonium nitrate solution. The lanthanum salt is soluble in the reagent.

More recent separations make use of differing reaction rates. Thus, the anhydrous rare earth bromides react with ethyl benzoate at 154° C. to yield ethyl bromide and the insoluble rare earth benzoates[24]. The method is only fair for the separation of lanthanum and neodymium. Kruger and Tschirch have developed a colorimetric method of doubtful value for lanthanum which depends on the formation of a blue color with the addition of ammonia to the nitrate solution in the presence of acetate or propionate ion[25]. No verification could be achieved in the research under discussion here. Praseo-

---

[22] Baskerville and Stevenson, _Journal of the American Chemical Society 26_, 1904. Page 54.

[23] Brauner, _Collection of Czech Chemical Communications 5_, 1933. Pages 279-286.

[24] Young, Arch, and Shyne, _Journal of the American Chemical Society 63_, 1941. Page 957.

[25] Kruger and Tschirch, _Berichten der Deutschen Chemischen Gesellschaft 63B_, 1930. Pages 826-836.

dymium, neodymium, samarium, ytterbium, and erbium do not interfere, but the other rare earths do.

Yoe[26] and Mellan[27] list reagents such as gallic acid, ethylenediamine, and pyrogallol as group reagents, and pyrocatechol, diphenylamine, benzidine, and carminic acid as specific for cerium. Cacotheline is said to be specific for europium[28]. A recent article reports that samarium may be separated from the other rare earths by the reduction of ethanolic solutions of the trichlorides with magnesium and hydrochloric acid[29]. Some promise is shown by the use of complex arsenicals such as 2-(o-arsonophenylazo)-p-cresol and 3-(o-arsonophenylazo)-4,5 dihydroxy- 2,7 naphthalenedisulfonic acid[30]. Elements such as thorium, uranium, and zirconium do not interfere with the test. Sodium azide precipitates thorium quantitatively from rare earth mixtures[31].

---

[26] Yoe, op. cit., page 190

[27] Mellan, Organic Reagents for Inorganic Analysis (Philadelphia: Blakiston, 1941) page 305.

[28] Yoe, op. cit., page 217.

[29] Clifford and Beachell, Journal of the American Chemical Society 70, 1948. Pages 2730-2731.

[30] Kuznetsov, Journal of Applied Chemistry (USSR) 13, 1940. Pages 1257-1261.

[31] Moeller and Kremers, op. cit., page 142.

In spite of the vast amount of research that has been done with the rare earths, the only really useful methods are those making use of fractional crystallization. Methods based on delicate pH control[32] or on color reactions[33] are of value in some cases, but the number of interfering ions is great. Thus, fractionation is left supreme[34]. It is unfortunate that this best method of obtaining pure salts of the rare earths is so tedious and wasteful, and at best, fractionation is hardly quantitative. Perhaps the answer to the problem lies in the application of ion exchange[35] to such separations, but again the process is costly and time consuming, however valuable it may be for the preparation of spectroscopically pure rare earth salts.

---

[32] Trombe, Comptus Rendus hebdomadaires des seances l'Acadamie des Sciences 215, 1942. Pages 539-541.

[33] Yoe and Sarver, *op. cit.*, page 203. See also: Mellan, *op. cit.*, pages 307-309.

[34] Yost, Russell, and Garner, *op. cit.*, page 41.

[35] Spedding, et. al., Journal of the American Chemical Society 69, 1947. Page 2777. See also: Spedding, et. al., Journal of the American Chemical Society 70, 1948. Pages 1671-1672. See also: Kunin, Analytical Chemistry 21, 1949. Pages 87-96. See also: Beamish, Analytical Chemistry 21, 1949. Pages 147-148.

CHAPTER IV

THE NATURE OF THE RESEARCH

A review of the literature such as has been briefly described in chapter III would indicate that almost every avenue of attack possible has been attempted by other workers in the field of rare earth analysis. The nature of the elements themselves is such that inorganic means of approach seem futile, and, therefore, a number of organic compounds selected from as many of the classes of compounds as possible were tried. This preliminary part of the research might well be described as trial and error, but it was felt that the problem demanded such an approach until a firmer basis of understanding could be reached. Compounds were used from the classes of both aliphatic and aromatic acids and their amino, halogen, and hydroxy substitution products, alcohols, aldehydes, primary and secondary aliphatic and aromatic amines, certain dyes, ketones, and phenols. It is to be understood that no research of limited scope could attempt more than a mere selection of such compounds in the brief amount of time alloted. Many of the reagents previously described in the literature were verified under different conditions and concentrations. Thus, the aluminon reaction was carried out in both ammonium hydroxide and in acetic acid - ammonium acetate solution.

All tests were carried out with solutions of the rare earth nitrates[36] of such concentration that one milliliter of the solution contained approximately one milligram of the salt. In the preliminary study, controls were carried of aluminum, barium, and calcium nitrates of the above concentration. The final investigation made use of similar solutions of cadmium, chromium, iron, strontium, and thorium in addition to those mentioned above. The control cations were selected from those likely to occur in rare earth minerals; however, an attempt was made to select representatives from the various groups. The results of the preliminary investigation are tabulated in the appendix (Table III).

Results were, for the most part, uninformative. Cerium often gave definite selective reactions, as might well be expected since the element was in the quadrivalent state. In the case of this particular cation, it was felt that the existing methods of separation were adequate and quite useful. All four of the remaining rare earths gave monotonously similar reactions with reagent after reagent until a chance addition of a twenty per cent solution of

---

[36] Nitrates of cerium, lanthanum, and neodymium were obtained from Eimer and Amend, while the salts of praseodymium and samarium were purchased from the Lindsay Light and Chemical Company. All samples were the purest obtainable.

tartaric acid to an ammoniacal solution being tested with m-nitrobenzoic acid yielded a white precipitate with lanthanum and praseodymium but not with neodymium and samarium. It was from this point that the major part of the research was developed.

The nature of the ammonia - tartrate precipitate was thoroughly investigated. Here, the separation of lanthanum and praseodymium from neodymium and samarium appears to be concerned principally with a rather fine adjustment of the hydrogen ion concentration with the optimum pH at 2.7. Cerium is also partially brought down with lanthanum and praseodymium, but this element is easily determined volumetrically with standard ferrous solution and causes no inconvenience. In cases in which the ammonia was added to the solution of the rare earth nitrate before the addition of the tartaric acid, poor separations were noted. Indeed, under the very best of conditions some error is likely due to coprecipitation and incomplete precipitation, especially of lanthanum.

Various organic bases such as substituted amines and anilines were used in place of the ammonia with good results. Perhaps the best separation of all was achieved with diethylaniline. Even such a very weak base as glycine gave a separation, and here only the lanthanum was brought down immediately, thus affording basis for a fair separation of lanthanum from the other members of the group with the possible exception of some of the cerium. Repeated precipitations were found to be necessary here to insure a separation as nearly quantitative as possible.

A number of series were carried through with varying amounts of tartaric acid and of base; the results of this phase of the investigation may be found in the appendix (Table IV). One series was run in alcoholic solution, methanol saturated with ammonia being used as the base and ethanol being used in the preparation of the solutions of the rare earth nitrates and tartaric acid. Results were negative in that all of the rare earths gave similar white, gelatinous precipitates upon the addition of the alcoholic ammonia solution.

Several series were run with varying amounts of salts such as ammonium tartrate and potassium hydrogen tartrate as buffers. Results showed that the addition of such a salt had little effect on increasing the general sensitivity of the separation, although if sufficient ammonium tartrate is present, cerium will not come down. In this case, the concentrations of tartaric acid and ammonium tartrate must be approximately equal in the solution. Unfortunately, the principal separation of lanthanum and praseodymium from neodymium and samarium is also rendered less sharp, and the precipitate is more colloidal in nature than that obtained under the other unbuffered condition. Probably a low concentration of a salt such as ammonium tartrate does no harm, but neither is it of any value in the separation. Perhaps repeated precipitations in the presence of large amounts of ammonium tartrate would effectively keep all of the cerium in the filtrate during the separation, but this element is easily determined by existing volumetric methods and does no harm here. Table V of the appendix includes the information obtained from this phase of the work.

The foregoing paragraphs have outlined methods for the separation of lanthanum and praseodymium from the other rare earths and from each other. After separation, they may be ignited to the oxides and determined gravimetrically, taking care to avoid overheating with the danger of converting some of the praseodymium to Pr_6O_{11}. The neodymium and samarium may then be brought down as hydrated oxalates and ignited to the oxides. Care must also be exercised here in order that some of the samarium will not be reduced to the divalent state, with the introduction of considerable error in the results of the entire determination. Samarium can then be determined in the neodymium - samarium oxide mixture by conversion of the oxides to the trichlorides, solution of the chlorides in ethanol, and reduction with hydrochloric acid and magnesium according to the method proposed by Clifford and Beachell[37]. The samarium is reduced to the divalent state and may readily be determined volumetrically. The neodymium remains unchanged and can be calculated by difference. Europium and ytterbium interfere, but they seldom occur in appreciable amounts in cerium group minerals and thus present little problem.

It is best to determine cerium volumetrically in each fraction, since this is the preponderant constituent of most of the ceric minerals found. Cerium is present to some extent in the separation products of both the lanthanum - praseodymium and the neodymium - samarium mixtures. If the cerium is not accurately determined in each fraction, results that are too high by several per cent may be reported for the other four ceric rare earths. An addition of the values obtained for the four different fractions will give the total percentage of cerium in the original sample. Thorium, of course, must be removed at the start of the analysis by means of pyridine[38] or another of the accepted methods of separation used for this element. Yttrium may cause some difficulty, but it is seldom present in ceric minerals in larger than trace amounts.

---

[37] Clifford and Beachell, loc. cit.

[38] Moeller and Kremers, op. cit., page 139.

It must be taken into strict account, however, in the analysis of yttrium group minerals such as xenotime.

The usual rare earth mineral sample contains few elements other than yttrium, thorium, scandium, and uranium as contaminants. Elements such as yttrium are mostly removed by treatment with sodium sulfate; the double sulfates of the cerium group elements are much less soluble than those of the yttrium group. Care must be taken to avoid loss of ceric material in such a separation, of course. Minerals such as euxenite and cerite may contain considerable amounts of zirconium, which may be eliminated by adding a solution of sodium thiosulfate to the boiling solution of mineral in the presence of a very little mineral acid[39]. In this way, zirconium and thorium as well are precipitated, whereas the rare earths, aluminum, and iron are not. Scandium may be separated from the hot solution by the addition of sodium silicofluoride[40]. Elements such as copper, zinc, cadmium, and antimony must be removed as sulfides. Copper, if not removed, might tie up the ammonia and prevent complete separation of the rare earths later on. Calcium must be removed before the separation of neodymium and samarium as oxalates, of course.

---

[39] Hopkins, *op. cit.*, page 152.

[40] *Ibid.*, page 109.

Most of the other contaminants may be removed by means of a preliminary oxalate precipitation with subsequent ignition to the oxides and solution in nitric acid. In this manner, elements such as magnesium are eliminated from the sample. Iron and manganese, if not removed, may cause high results for cerium.

Decomposition of minerals is usually brought about by heating the powdered sample with concentrated sulfuric or hydrochloric acid, although in the case of the complex silicates, fusion with potassium bisulfate or sodium hydroxide must be used. Minerals containing much columbium and tantalum are fused in potassium bifluoride. The fluorides of columbium and tantalum are soluble whereas those of the rare earths are highly insoluble. In such cases, it is necessary to attack the insoluble rare earth fluoride residue with concentrated sulfuric acid as in the case above. In any event, the mineral must be first ground to a very fine powder.

The proposed analytical scheme for the rare earth elements of the cerium group is outlined and discussed in the next chapter.

CHAPTER V

THE PROPOSED SCHEME OF ANALYSIS

From the information obtained through research and set forth in chapter IV, the proposed scheme of analysis for the members of the cerium group of rare earth elements in minerals would consist of the following steps:

1) Decomposition of the mineral by acid attack or by fusion method as described in the preceding chapter or in any good analytical text.

2) A preliminary separation of the rare earths as oxalates and the elimination of the members of the hydrogen sulfide group by the appropriate reagents.

3) The removal of thorium by means of pyridine, of scandium with sodium silicofluoride, and of zirconium with sodium thiosulfate in an acid medium as previously described (page 21).

4) The separation of members of the yttrium group from the elements of the cerium group by the use of potassium sulfate. The double sulfates with potassium of the metals of the cerium group are relatively insoluble, whereas those with members of the yttrium group are quite soluble. Considerable care must be exercised here to insure complete precipitation of all the cerium group, even at the expense of some inclusion of yttrium.

5) Conversion of the purified sample to a mixture

of the nitrates and the preparation of solutions containing approximately one milligram of mixed salts per milliliter of solution.

6) Precipitation of lanthanum by the addition of eight drops of twenty per cent tartaric acid and one drop of a five per cent aqueous solution of glycine for each milliliter of solution to be tested. Much excess of either reagent is to be avoided.

7) Precipitation of praseodymium by the addition of one or two drops of fresh 1:1 ammonium hydroxide for each milliliter of the filtrate from step 6. The precipitate must be filtered at once; if allowed to stand for any length of time, some neodymium and samarium may come down. A double precipitation both here and in step 6 is wise for most accurate results.

8) Separation of the neodymium and samarium as the hydrated oxalates with subsequent ignition to the oxides. Care must be taken during the ignition to avoid reduction of some samarium to the divalent state.

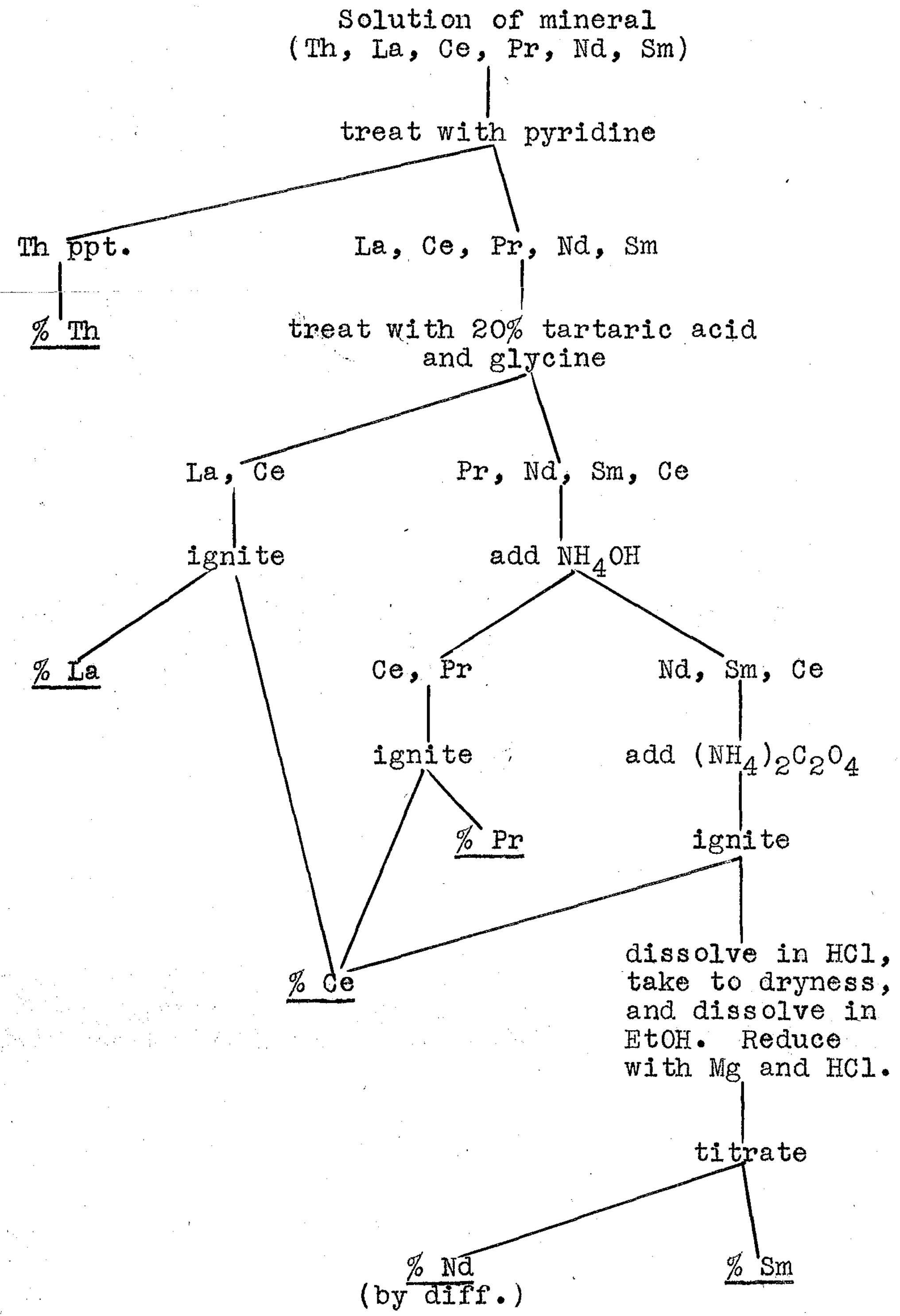
9) Reduction of the samarium in the weighed sample from step 8 with magnesium and hydrochloric acid (page 19) after solution of the mixed oxides. Samarium may then be determined volumetrically by a standard method such as permanganate and the neodymium may then be calculated by difference from the total weight in step 8. Cerium must

still be corrected for in the final results as indicated below.

10) Determinations of cerium volumetrically with standard ferrous solution. Determinations must be made individually on the lanthanum oxide (step 6), the praseodymium oxide (step 7), and the mixed neodymium and samarium oxides (step 8). The total of the three determinations will be equal to the total per cent of cerium in the original sample. Since cerium is the principal rare earth encountered in the usual mineral, it is wise to run cerium alone on some of the original untreated sample as a check on the method. Values for the other four rare earths may then be determined by correcting original values for cerium content.

Under the procedure outlined above, the rare earth elements of the cerium group may be determined with as great a degree of accuracy as is obtainable with the few fractional crystallizations that might be utilized in a control analysis. To be sure, the method leaves much to be desired and can doubtless be improved upon by future work, but it is much less tedious and wasteful than the fractionation methods ordinarily resorted to.

FLOW SHEET


Solution of mineral
(Th, La, Ce, Pr, Nd, Sm)
treat with pyridine
Th ppt.
La, Ce, Pr, Nd, Sm
% Th
treat with 20% tartaric acid and glycine
La, Ce
Pr, Nd, Sm, Ce
ignite
add NH_4OH
% La
Ce, Pr
Nd, Sm, Ce
ignite
add $(NH_4)_2C_2O_4$
% Pr
ignite
% Ce
dissolve in HCl, take to dryness, and dissolve in EtOH. Reduce with Mg and HCl.
titrate
% Nd
(by diff.)
% Sm

CHAPTER VI

CONCLUSIONS

The nature of the research has been that of an attempt to seek a method by which the rare earth elements of the cerium group may be readily separated and determined. It would be foolish to state that the method developed in this thesis is the entire answer, but is is, perhaps, a step in the direction of the development of a rapid wet method for control work where time and money are important considerations.

No procedure can be better than the analyst who does the work; this case is no exception. In the hands of a capable analyst exercising reasonable care, the results obtainable by the use of the method should be of an order of accuracy sufficiently high for routine control work. Of course, a procedure such as the one outlined here can never detect small quantities of the rare earths with the ease and accuracy of the spectrometer; neither can it separate macro quantities of relatively pure salts, as can be done using the principles of zeolite action or fractional crystallization. The method as proposed is intended merely for control work where the amount of special apparatus is limited and the training of the analysts has not necessarily been concerned with instrumental processes.

At this writing, no studies of quantitative accuracy have been run. Data obtained from direct observation of the amount and nature of the precipitates and the repeated addition of reagents have been sufficient to establish at least the semi-quantitative nature of the obtainable results. In most cases, cerium is present in great excess, and the determination of this element by means of oxidation-reduction titrimetry is both rapid and highly accurate. It is felt that more work than is at this time possible might do much to increase the value of such a scheme of analysis.

BIBLIOGRAPHY

BIBLIOGRAPHY

Books:

Browning, Philip E., *Introduction to the Rarer Elements.* New York, John Wiley and Sons, 1919. 258 pages.

DeMent, Jack, *Fluorochemistry.* Brooklyn, The Chemical Publishing Company, 1945. 796 pages.

Fernelius, W.C., editor, *Inorganic Synthesis, volume II.* New York, McGraw-Hill Book Company, Inc., 1946. 293 pages.

Fuhrman, N. Howell, *Scott's Standard Methods of Chemical Analysis.* New York, D. Van Nostrand and Company, 1925.

Hillebrand, W.F., and G.E.F. Lundell, *Inorganic Analysis.* New York, John Wiley and Sons, 1929. 929 pages.

Hopkins, B.S., *The Chemistry of the Rarer Elements.* Boston, D.C. Heath and Company, 1923. 370 pages.

Latimer, Wendell, and Joel H. Hildebrand, *Reference Book of Inorganic Chemistry.* New York, The MacMillan Company, 1930. 442 pages.

Levy, S.I., *The Rare Earths.* London, Edward Arnold and Company, 1915.

Little, H.F.V., *A Textbook of Inorganic Chemistry*, edited by Friend, volume IV. London, Griffin and Company, 1917.

Lundell, G.E.F., and James I. Hoffman, *Outlines of Methods of Chemical Analysis.* New York, John Wiley and Sons, 1938.

Mellan, Ibert, *Organic Reagents in Inorganic Analysis.* Philadelphia, P. Blakiston's Sons, 1941. 682 pages.

Mellor, J.W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, volume V. London, Longmans, Green and Company, 1924. 1004 pages.

Schwarz, Robert, *The Chemistry of the Inorganic Complex Compounds.* New York, John Wiley and Sons, 1923.

Spencer, J.F., The Metals of the Rare Earths. London, Longmans, Green and Company, 1919.

Yoe, John, and Landon A. Sarver, Organic Analytical Reagents. New York, John Wiley and Sons, 1941. 339 pages.

Yost, Don, Horace Russell, and Clifford Garner, The Rare Earth Elements and Their Compounds. New York, John Wiley and Sons, 1947. 92 pages.

Periodical articles:

Aleksandrov, G.P., and Y.P. Hokhshtein, "The Rare-earths and Thorium," Redkie Metally 4, number 6, 1935. Pages 27-31.

Appleton, D.B., and R.W. Selwood, "Fractional Partition of the Rare Earths," Journal of the American Chemical Society 63, 1941. Page 2029.

Bauer, Herbert, "The Use of the Arc Spectrum for the Analysis of Difficultly Vaporized Substances," Zeitschrift fur anorganische und allgemeine Chemie 221, 1935. Page 209.

Beamish, F.E., "Inorganic Gravimetric Analysis," Analytical Chemistry 21, 1949. Pages 144-160.

Beck, G., "A New Principle for the Fractionation of the Rare Earths with Nitriloacetate: The Separation of Lanthanum and Cerium," Helvetica Chimica Acta 29, 1946. Pages 357-360.

————, "A New Fractionating Principle for the Rare Earths with Nitriloacetate: A Displacement Method," Mikrochemie vereinigt mit Mikrochimica Acta 33, 1948. Pages 344-347.

Boss, A.E., and B.S. Hopkins, "The Rare Earths; part XXVI," Journal of the American Chemical Society 50, 1928. Page 298.

Bowles, J.A.C., and H.M. Partridge, "The Rare Earth Salts: Precipitation and pH studies with the glass electrode," Industrial and Engineering Chemistry, Analytical Edition 9, 1937. Page 124.

Brauner, Bohuslav, "A New Element of Atomic Number 61 - Illinium," Nature 118, 1926. Pages 84-85.

———, "The Characteristics of Praseodymium," Collection of Czech Chemical Communications 5, 1933. Pages 279-286.

———, and E. Svarg, "Physicochemical Studies of the Sulfates of the Rare Earths," Rozpravy II tr. ceske Akademie 41, 1931. Pages 1-20.

———, and E. Svarg, "Physicochemical Study of the Rare Earth Sulfates," Collection of Czech Chemical Communications 4, 1932. Pages 49-68.

———, and E. Svarg, "Physicochemical Study of the Rare Earth Sulfates: II Theoretical Conclusions," Collection of Czech Chemical Communications 4, 1932. Pages 239-246.

Britton, H.T.S., "An Investigation of the Chromates of Thorium and the Rare Earths: II Chromates of Lanthanum, Praseodymium, Neodymium, and Samarium," The Journal of the Chemical Society 125. Pages 1875-1880.

Charlot, G., "The Detection of Cerium and the Determination of small quantities of the Ferrous Complex with ortho-Phenanthroline," Bulletin de la Societe Chimique 6, 1939. Pages 1126-1127.

Clifford, A.F., and H.C. Beachell, "The Chemical Isolation of Samarium from Lanthanide Mixtures," Journal of the American Chemical Society 70, 1948. Pages 2730-2731.

Corey, R.B., and H.W. Rogers, "Reactions of Aluminon," Journal of the American Chemical Society 49, 1927. Page 216.

Dutt, Nihar, "The Chemistry of the Rare Earths," The Journal of the Indian Chemical Society 22, 1945. Pages 71-74.

———, "The Chemistry of the Rare Earths," The Journal of the Indian Chemical Society 22, 1945. Pages 97-101.

Duval, M. Clement, "The Thermogravity of Analytical Precipitates," Anal. Chimica Acta 1, 1947. Pages 341-344.

Fassel, V.A., and H.A. Wilhelm, "The Quantitative Spectrographic Analysis of the Rare Earth Elements," *Journal of the Optical Society of America 38*, 1948. Pages 518-526.

Gatterer, A., and J. Junkes, "The Determination of Minute Quantities of Europium in Samarium," *Spectrochimica Acta 1*, 1939. Pages 31-46.

Goldschmidt, V., M. Barth, and G. Lund, "The Geochemical Distribution Law of the Elements," *Skrifter utgitt av det Norske Videnskaps-Akademi i Oslo #7*, 1925.

Hirt, Robert, and Norman Nachtrieb, "The Spectrographic Determination of the Rare Earth Elements in Uranium Compounds," *Analytical Chemistry 20*, 1948. Pages 1077-1078.

Holleck, L., and W. Noddack, "A New Method for the Preparation of Compounds of the Bivalent Rare Earth Metals," *Angewandte Chemie 50*, 1937. Page 819.

Huttig, G.F., and M. Kantor, "Oxide Hydrates and Active Oxides, part XLIX," *Zeitschrift fur anorganische und allgemeine Chemie 202*, 1931. Page 421.

Ismail, A.M., and H.F. Harwood, "The Use of Hexamine for the Separation of Thorium from the Rare Earths, and Its Application to the Determination of Thorium in Monazite Sand," *Analyst 62*, 1937. Page 185.

Jackson, K.S., and G. Rienacker, "Solubilities of the Octahydrates of the Rare Earth Sulfates," *The Journal of the Chemical Society 1930*, 1930. Page 1687.

James, C., et. al., "Solubilities of the Rare Earth Salts," *Journal of the American Chemical Society 49*, 1927. Page 132.

Jantsch, G., and N. Skalla, "Halides of the Rare Earths," *Zeitschrift fur anorganische und allgemeine Chemie 193*, Page 391.

————, N. Skalla, and H. Grubitsch, "Halides of the Rare Earths," *Zeitschrift fur anorganische und allgemeine Chemie 216*, 1933. Page 75.

Jantsch, G., and E. Weisenberger, "Multivalent Compounds of the Rare Earths," *Monatschefte fur Chemie und Verwandte Teile anderer Wissenschaften 60*, 1932. Page 1 ff.

———, and S. Wigdorow, "Double Nitrates of the Rare Earths," *Zeitschrift fur anorganische Chemie 69*. Pages 221-231.

———, et. al., "Studies of the Rare Earth Halides," *Zeitschrift fur anorganische und allgemeine Chemie 185*, 1929. Pages 49-64.

Jensen, H., Elements 43 and 61," *Naturwissenschaften 26*, 1938. Page 381.

Kendall, J., "The Rare Earths," *Proceedings of the Royal Philosophical Society of Glasgow 59*, 1931. Pages 1-11.

Kimura, Kenjiro, "Analysis of the Rarer Elements," *Journal of the Chemical Society of Japan 54*, 1933. Page 213.

Klemm, Wilhelm, "The Classification of the Rare Earths," *Zeitschrift fur anorganische und allgemeine Chemie 209*, 1932. Pages 321-324.

———, "The Systematic Classification of the Rare Earths," *Angewandte Chemie 51*, 1938. Pages 575-576.

———, and Heinrich Bommer, "The Rare Earth Metals," *Zeitschrift fur anorganische und allgemeine Chemie 231*, 1937. Pages 138-171.

———, and H. Bommer, "The Rare Earth Metals," *Zeitschrift fur anorganische und allgemeine Chemie 241*, 1939. Pages 263-267.

———, and Paul Henkel, "Measurements with bi- and quadrivalent Compounds of the Rare Earths," *Zeitschrift fur anorganische und allgemeine Chemie 220*, 1934. Pages 180-182.

———, K. Meisel, and H.V. VonVogel, "Sulfides of the Rare Earths," *Zeitschrift fur anorganische und allgemeine Chemie 190*, 1930. Pages 123-124.

———, and Joachim Rockstroh, "Bivalent and Quadrivalent Compounds of the Rare Earths," *Zeitschrift fur anoranische und allgemeine Chemie 176*, 1928. Pages 181-199.

Kruger and ~~Deodata~~ TSCHIRCH, "The Blue Colr of Basic Lanthanum Acetate and Iodine," Berichte der Deutschen Chemischen Gesellschaft 62B, 1929. Pages 2776-2783.

———— , "The Starch-Iodine Problem: II, The Colored Iodine Compounds of the Rare Earths," Berichte der Deutschen Chemischen Gesellschaft 63B, 1930. Pages 826-836.

Kunin, Robert, "Ion Exchange," Analytical Chemistry 21, 1949. Pages 87-96.

Kuznetsov, V.I., "The Complex Forming Properties of the Azo Compounds," Journal of Applied Chemistry (U.S.S.R.) 13, 1940. Pages 1257-1261.

Liperonskii, A.S., "The Displacement of Chains of Isotopes by the Beta Radiation and Isotopy of the Rare Earths," Journal of General Chemistry (U.S.S.R.) 4, 1934. Pages 1157-1167.

Lopez de Azcona, J.M., "The Arc Spectrum in the Carbon Arcs of Cerium, Neodymium, and Praseodymium between 2200 and 5000 A for $2x10^{-4}$, $2x10^{-5}$, and $2x10^{-6}$ grams," Boletin del instituto geologico y minero de Espan 15, 1941. Page 270.

McCarty, C.N., et. al., "Observations on the Rare Earths: Quantitative Estimation of the Rare Earths by Means of Arc Spectra," Industrial and Engineering Chemistry, Analytical Edition 10, 1938. Page 184 ff.

Marsh, J.K., "The Dimethyl Phosphates of the Rare Earth Metals," The Journal of the Chemical Society 1939, 1939. Page 554.

———— , "The Rare Earth Metal Oxides: I, Direct Oxidation of Praseodymium and Terbium," The Journal of the Chemical Society 1946, 1946. Pages 15-16.

———— , "The Rare Earth Metal Oxides: II, A New Study of Oxide Precipitation by Nitrate Fusion," The Journal of the Chemical Society 1946, 1946. Pages 17-20.

———— , "The Separation of the Lanthanons," The Journal of the Chemical Society 1947, 1947. Pages 118-122.

Marsh, J.K., "The Relation of Yttrium to the Lanthanons," The Journal of the Chemical Society 1947, 1947. Pages 1084-1086.

Meggers, W.F., "Atomic Spectra of the Rare Earth Elements," Review of Modern Physics 14, 1942. Page 96.

———, "Emission Spectroscopy," Analytical Chemistry 21, 1949. Pages 29-31.

Meyer, R.J., G. Schumacher, and A. Kotowski," The Element 61," Naturwissenschaften 14, 1926. Pages 771-772.

Middleton, A.R., "Reactions of Aluminon with the Hydroxides of Beryllium, the Rare Earths, Zirconium, and Thorium," Journal of the American Chemical Society 48, 1926. Page 2125 ff.

Moeller, Therald, and Howard Kremers, "Electrochemical Studies of the Precipitation of the Trivalent Rare Earth Oxides and Hydroxides," Journal of Physical Chemistry 48, 1944. Page 295 ff.

———, and H. Kremers, "The Basicity Characteristics of Scandium, Yttrium, and the Rare Earth Elements," Chemical Reviews 37, 1945. Pages 97-159.

———, and H. Kremers, "A Double Sodium Sulfate Precipitation for the Separation of Terbium and Yttrium Earths," Industrial and Engineering Chemistry, Analytical Edition 17, 1945. Pages 44-45.

Neish, A.C., and J.W. Burns, "Precipitation of the Rare Earths by Creams of Insoluble Oxides and Carbonates," Canadian Chemistry and Metallurgy 5, 1921. Page 69.

Oka, Yosinaga, "The Fundamental Reactions in Analytical Chemistry," The Journal of the Chemical Society of Japan 59, 1938. Pages 971-1013.

Pirtea, T.I., "The Determination of Lanthanum with the Aid of 8-Hydroxyquinoline," Zeitschrift fur analytische Chemie 107, 1936. Pages 191-193.

———, "The Determination of Cerium with 8-Hydroxyquinoline," Buletinul de Chimie pura si aplicata al, Societatii Romane de Chimie 39, 1937-8. Pages 83-85.

Prandtl, Wilhelm, "Densities and Molecular Volumes of Lanthanum, Praseodymium, Neodymium, Samarium, and Europium," *Berichte der Deutschen Chemischen gesellschaft 55B*, 1922. Pages 692-694.

———, "The Search for Element 61," *Zeitschrift fur angewandte Chemie 39*, 1926. Pages 897-898.

———, "Experiences in the Preparation of the Rare Earths," *Zeitschrift fur anorganische und allgemeine Chemie 238*, 1938. Page 321 ff.

———, and Hans Ducrue, "The Solubility of the Double Nitrates of Praseodymium and Neodymium with the Bivalent Metals," *Zeitschrift fur anorganische und allgemeien Chemie 150*, 1926. Pages 105-116.

———, and Albert Grimm, "A Search for Element 61," *Zeitschrift fur anorganische und allgemeine Chemie 136*, 1924. Pages 283-288.

———, and Joseph Losch, "The Separation of the Rare Earths by Basic Precipitation," *Zeitschrift fur anorganische und allgemeine Chemie 129*, 1923. Pages 209-214.

———, and Johanna Rauchenberger, "The Separation of the Rare Earths by Basic Precipitation," *Berichte der Deutschen Chemischen Gesellschaft 53*, 1920. Pages 843-853.

———, and J. Rauchenberger, "The Separation of the Rare Earths by Precipitation with Bases," *Zeitschrift fur anorganische und allgemeine Chemie 120*, 1922. Pages 120-128.

———, and J. Rauchenberger, "The Separation of the Rare Earths by Basic Precipitation," *Zeitschrift fur anorganische und allgemeine Chemie 127*, 1922. Pages 311-314.

———, and J. Rauchenberger, "The Separation of the Rare Earths by Basic Precipitation," *Zeitschrift fur anorganische und allgemeine Chemie 129*, 1923. Pages 176-180.

———, and Georg Rieder, "The Valence of Praseodymium and Terbium," *Zeitschrift fur anorganishe und allgemeine Chemie 238*, 1938. Page 225.

Rodden, C.J., "Spectrophotometric Determination of Dysprosium, Holmium, Erbium, Thulium, and Ytterbium," Journal of Research, National Bureau of Standards 26, 1941. Page 557 ff.

Russell, R.G., and D.W. Pearce, "Fractionation of the Rare Earths by Zeolite Action," Journal of the American Chemical Society 65, 1943. Pages 595-600.

Schwarz, Robert, and H. Giese, "The Peroxides of Titanium, Zirconium, Hafnium, and Thorium," Zeitschrift fur anorganische und allgemeine Chemie 176, 1928. Page 209.

Selwood, Pierce, and B.S. Hopkins, "Observations on the Rare Earths: XXXI, Ionic Migration and Magnetism in the Separation of the Rare Earths," Transactions of the American Electrochemical Society 55 (preprint), 1929. 13 pages.

———, "Observations of the Rare Earths: XXXIV, Spectrographic Estimation of the Impurities in the Rare Earths," Industrial and Engineering Chemistry, Analytical Edition 2, 1930. Pages 93-96.

———, "A Quantitative Study of the Lanthanum-Neodymium Separation," Journal of the American Chemical Society 55, 1933. Pages 4900-4901.

Shinoda, Sakae, "Analysis of the Rarer Elements: III, Praseodymium," Journal of the Chemical Society of Japan 56, 1935. Pages 76-80.

———, "Analysis of the Rarer Elements: V, Determination of Samarium in mixtures," Journal of the Chemical Society of Japan 56, 1935. Pages 1483-1486.

———, "The Application of the X-ray Spectroscopic Method to the Chemical Analysis of the Rarer Elements: VI, Determination of Samarium and Neodymium in Rare Earth Mixtures by the Optical Wedge Method," Journal of the Chemical Society of Japan 58, 1937. Pages 989-995.

Short, H.G., and W.L. Dutton, "Determination of Rare Earth Elements and Yttrium in Uranium Compounds," Analytical Chemistry 20, 1948. Pages 1073-1076.

Spedding, F.H., et. al., "Separation of the Rare Earths by Ion Exchange: II, Praseodymium and Neodymium," *Journal of the American Chemical Society 69*, 1947. Pages 2777-2781.

————— , et. al., "Separation of the Rare Earths by Ion Exchange: Pilot Plant Scale Operations," *Journal of the American Chemical Society 69*, 1947. Pages 2786-2792.

————— , et. al., "Ion Exchange Method for the Separation of the Rare Earths in Macro Quantities," *Journal of the American Chemical Society 70*, 1948. Pages 1671-1672.

Trombe, Felix, "A New Method for Basic Precipitation Applied to the Separation of the Rare Earth Elements," *Comptus Rendus hebdomadaires des seances de l'Academie des Sciences 215*, 1942. Pages 539-541.

Trombe, Marcelle, "The pH Corresponding to the Threshold of Precipitation of the Rare Earth Elements," *Comptus Rendus hebdomadaires des seances de l'Academie des Sciences 216*, 1943. Page 888.

Vickery, R.C., "The Rare Earths," *Metallurgia 30*, 1944. Pages 215-220.

von Hevesy, G., "Regularities in the Rare Earth and Titanium Groups," *Zeitschrift fur anorganische und allgemeine Chemie 147*, 1925. Pages 217-232.

Weiser, Harry, and W.O. Milligan, "The Hydrous Oxides of Some of the Rarer Elements," *Journal of Physical Chemistry 42*, 1938. Page 673 ff.

Wenger, Paul, R. Duckert, and Y. Rusconi, "A Critical Study of Reagents for Cations: XIII, Reagents for the Cations of the Rare Earths and Yttrium," *Helvetica Chimica Acta 28*, 1945. Pages 274-278.

Wierda, J., and H.E. Kremers, "The Concentration of Praseodymium Material and the Preparation and Properties of Metallic Praseodymium," *Transactions of the American Electrochemical Society 48*, 1925. Page 159.

Yoe, John, "Some Observations on Reactions Between Certain Metallic Ions and the Ammonium Salt of Aurin Tricarboxylic Acid," *Journal of the American Chemical Society 54*, 1932. Pages 1022-1024.

Young, R.C., A. Arch, and W.V. Shyne, "Reactions of the Anhydrous Rare Earth Bromides with Ethyl Benzoate, and the Separation of Neodymium from Lanthanum," _Journal of the American Chemical Society 63_, 1941.

Other Sources:

Chemical Abstracts, all volumes to date.

APPENDIX

TABLE I

ELECTRONIC CONFIGURATIONS OF THE CERIC RARE EARTHS

Element	Atomic number	N-shell configuration				
		4f	5s	5p	5d	6s
Lanthanum	57	0	2	6	1	2
Cerium	58	2	2	6	0	2
Praseodymium	59	3	2	6	0	2
Neodymium	60	4	2	6	0	2
---	61	5	2	6	0	2
Samarium	62	6	2	6	0	2

TABLE II

PHYSICAL PROPERTIES OF THE CERIC RARE EARTHS

Element	Symbol	Color of ion	Atomic radius	Density
Lanthanum	La	colorless	1.870 A	6.194
Cerium*	Ce	colorless	1.81 A	6.78
Praseodymium	Pr	yellow-green	1.824 A	6.776
Neodymium	Nd	red-violet	1.818 A	7.004
Element 61	--	------	-----	-----
Samarium	Sm	pale yellow	-----	6.93

* Trivalent cerium is colorless; usual cerium salts encountered in the laboratory are ceric salts in which the valence of the element if four plus. These salts are red-orange in color.

Above data is from Yost, Russell, and Garner, _op. cit._, pages 3 and 20.

TABLE III

USE OF ORGANIC REAGENTS

Reagent used with Ammonia	Al	Ba	Ca	Ce	La	Nd	Pr	Sm
Adipic acid	w	w	-	w	w	w	w	w
Alizarin red S	o	-	-	r	r	r	r	r
Aluminon (in EtOH)	-	r	r	o	r	r	r	r
Aluminon (in HAc:NaAc)	r	-	-	t	r	r	r	r
p-Aminobenzoic acid	w	-	-	w	w	w	w	w
p-Aminophenol	b	b	b	b	b	b	b	b
Anthranilic acid	w	w	g	y	w	w	w	w
Cacotheline	y	-	-	y	y	y	y	y
Cacotheline (in HAc:NaAc)	y	-	-	y	y	y	y	y
Carbamine chloride	w	w	-	y	w	w	w	w
Carminic acid	r	p	p	br	pu	pu	pu	pu
Catechol	-	-	-	pu	yg	yg	yg	yg
Cinnamic acid	w	w	-	y	w	w	w	w
Citric acid (sat. sol.)	-	-	-	y	-	-	-	-
Cupferron (in EtOH)	w	w	-	w	w	w	w	w
Cupferron (in H_2SO_4)	-	w	-	-	-	-	-	-
Cyclohexanol	w	-	-	w	w	w	w	w
Dimethylamine	w	w	-	y	w	w	w	w
Diphenylamine	w	w	-	y	w	w	w	w
Diphenylcarbamine	w	-	-	y	w	w	w	w
Furfural	br	br	br	br	br	br	br	br
Gallic acid	br	br	br	br	br	br	br	br

TABLE III (continued)

Reagent with Ammonia	Al	Ba	Ca	Ce	La	Nd	Pr	Sm
Gallic acid (in HAc:NaAc)	y	bg	br	br	t	t	t	t
Glutamic acid	w	w	-	y	w	w	w	w
Glutaric acid	w	w	-	w	w	w	w	w
8-Hydroxyquinoline (in HCl)	y	-	-	br	y	y	y	y
8-Hydroxyquinoline (in EtOH)	y	w	-	br	yg	yg	yg	yg
8-Hydroxyquinoline (in HAc:NaAc)	-	-	-	br	-	-	-	-
Maleic acid	w	w	-	y	w	w	w	w
Malonic acid	-	w	-	w	-	-	-	-
m-Nitrobenzoic acid	w	-	-	w	w	w	w	w
Oxalic acid	-	w	w	y	w	w	w	w
Pyrogallol (in EtOH)	-	br	br	br	r	r	r	r
Pyrogallol (in HAc:NaAc)	-	-	-	b	f	f	f	f
Quinoline	w	w	-	w	w	w	w	w
Sulfanilic acid	w	w	-	y	w	w	w	w
Succinic acid	w	w	-	w	w	w	w	w
Tartaric acid	-	-	-	y	w	-	w	-

CODE

b - blue
bg- blue-green
br- brown
f - flesh
g - green
o - orange
p - pink
pu- purple
r - red
ro- red-orange
t - tan
w - white
y - yellow
yg- yellow-green
yw- yellow-white

TABLE IV

STUDIES OF TARTRATE PRECIPITATION

Series	Reagents (drops/ml. test solution)	Al	Ba	Cd	Ca	Ce	Cr	Fe	La	Nd	Pr	Sm	Sr	Th
1	8 Tartaric acid, 1 Ammonia	-	-	-	-	-	-	-	w	-	w	-	-	-
2	8 Tartaric acid, 2 Ammonia	-	-	-	-	y	-	-	w	-	w	-	-	-
3	8 Tartaric acid, 4 Ammonia	-	-	-	-	y	-	-	w	-	w	-	-	-
4	8 Tartaric acid, 1 Ethanolamine	-	-	-	-	-	-	-	w	-	w	-	-	-
5	8 Tartaric acid, 1 Aniline	-	-	-	-	y	-	-	w	-	w	-	-	-
6	8 Tartaric acid, 1 Methylamine	-	-	-	-	y	-	-	w	-	w	-	-	-
7	8 Tartaric acid, 1 sec-Butylamine	-	-	-	-	y	-	-	w	-	w	-	-	-
8	8 Tartaric acid, 1 iso-Butylamine	-	-	-	-	-	-	-	cl	-	cl	-	-	-
9	8 Tartaric acid, 1 Dimethylamine	-	-	-	-	-	-	-	w	-	cl	-	-	-
10	8 Tartaric acid, 1 Diethylamine	-	-	-	-	-	-	-	w	-	w	-	-	-
11	8 Tartaric acid, 1 beta-Naphthylamine	-	-	-	-	cl	-	-	-	-	-	-	-	-
12	8 Tartaric acid, 1 5% Glycine	-	-	-	-	-	-	-	w	-	-	-	-	-
13	8 Tartaric acid, 1 tri-n-Butylamine	-	-	-	-	cl	-	-	cl	-	cl	-	-	-

TABLE V

TARTRATE PRECIPITATION IN THE PRESENCE OF TARTRATES

Series	Reagents (drops/ml. test solution	Al	Ba	Cd	Ca	Ce	Cr	Fe	La	Nd	Pr	Sm	Sr	Th
101	8 Tartaric acid, 1 Ammonia	-	-	-	-	-	-	-	w	-	w	-	-	-
102	8 Tartaric acid, 2 Ammonium tartrate, 1 Ammonia	-	-	-	-	cl	-	-	w	-	w	-	-	-
103	8 Tartaric acid, 4 Ammonium tartrate, 2 Ammonia	-	-	-	-	-	-	-	w	-	cl	-	-	-
104	8 Tartaric acid, 2 Ammonium tartrate, 4 Ammonia	-	-	-	-	-	-	-	-	-	-	-	-	-
105	8 Tartaric acid, 8 Ammonium tartrate, 2 Ammonia	-	-	-	-	-	-	-	w	-	w	-	-	-
106	8 Tartaric acid, 4 Potassium bitartrate, 1 Ammonia	-	-	-	-	cl	-	-	w	-	w	-	-	-
107	8 Tartaric acid, 8 Potassium bitartrate, 2 Ammonia	-	-	-	-	cl	-	-	w	-	w	-	-	-
108	8 Tartaric acid, 4 Potassium bitartrate, 4 Ammonia	-	-	-	-	-	cl	-	-	-	-	-	-	-
109	10 5% Potassium tartrate, 1 Ammonia	-	-	cl	-	y	-	-	w	w	w	w	-	-

CODE: w - white precipitate
y - yellow precipitate
cl- cloudiness, but little precipitation