the elements, of spectrographic purity, were separated in macro quantities. The principles established for the separation of cerium and yttrium are being applied to the development of methods for the large scale separation of adjacent rare earths; the details will be published in subsequent papers.

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[CONTRIBUTION FROM THE CLINTON LABORATORIES, OAK RIDGE, TENN.]

The Chemical Identification of Radioisotopes of Neodymium and of Element 61[1]

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Introduction

In the comprehensive studies of the radioactive species produced in the fission of uranium[3] it has been found that over thirty are members of the rare earth family (isotopes of yttrium and the group lanthanum through europium). The chemical and physical identification of these was an important part of the research program of the Manhattan Project. Standard oxidative separations and fractional precipitations[4] and the use of radiochemical methods based on chain relations served to distinguish the activities of yttrium, lanthanum, cerium, and some of praseodymium, and those[5] of samarium and europium. The characterization of the sequence praseodymium, neodymium, and element 61 presented very difficult problems[6] that were solved only with the intensification of ion exchange methods originally developed by Boyd and co-workers[7] and applied to the rare earth field by Cohn and co-workers.[8] In this paper is reported the successful separation of these three elements, the first to have been achieved with radioisotopes of neodymium and of element 61.

Earlier work on the Manhattan Project had revealed the presence of two unidentified fission products in the rare earth region. A soft beta emitting activity of ~4y half-life was discovered by Ballou[9] and independently by Goldschmidt and Morgan.[10] This activity was later studied by Seiler and Winsberg[6] who set the half-life at ~3.7y. These investigators considered the activity to be an isotope of praseodymium, neodymium, or element 61 on the basis of detailed qualitative chemical separations between lanthanum and praseodymium. Another unidentified rare earth activity was later discovered by Davies[11] through its characteristic gamma radiations. This was confirmed by Hume and Martens[12] who determined its half-life as ~11d and showed that the activity was not cerium. We have been able to identify these two activities as isotopes of element 61 and of neodymium, respectively, both of mass number 147. In addition the 47h 61^{149} has been identified among the fission products. All three of these activities, together with a previously unidentified 1.7h isotope of neodymium, are also produced as the result of the activation of neodymium with slow neutrons.

Chemical Identification

The 11d activity was first subjected to standard qualitative serpations[4,6] in order to limit the identification problem to a definite group of rare earth elements. Separations by carbonate digestion definitely eliminated yttrium and all rare earth elements of atomic number greater than 61. Oxidative fusion with sodium nitrate[4,6] demonstrated that the activity was not an isotope of lanthanum and must therefore be identified with praseodymium, neodymium or element 61. Finally, the activity was limited to an isotope of neodymium or element 61 by demonstration of separation from praseodymium with potassium hydroxide fusions.

Positive identification of the 3.7y and the 11d radioisotopes was then achieved by the recently developed ion-exchange method using a synthetic organic cation exchanger (Amberlite IR-1) of the sulfonated phenol-formaldehyde type. This new

(1) This document is based on work performed at the Clinton Laboratories operated under contract No. W-35-058-eng-71 for the Manhattan Project, classified reports of which are referred to here as "Manh. Proj. Rep." The information covered herein will appear in the Plutonium Project Record (Plut. Proj. Rec., Vol. 9B, papers 7.54.3, 7.54.4, 7.54.5, 7.54.6, and 11.1), in Division IV of the Manhattan Project Technical Series.

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(3) THE PLUTONIUM PROJECT, Nuclei Formed in Fission: Decay Characteristics, Fission Yields and Chain Relationships, THIS JOURNAL, **68**, 2411–2442 (1946). Reprints are obtainable from the offices of The American Chemical Society.

(4) A. A. Noyes and W. C. Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Co., New York, N. Y., 1927.

(5) L. Winsberg, Manh. Proj. Rep. CC-2310, pp. 231–244 (Jan. 1945) and CC-2966 (Apr. 1945); Plut. Proj. Rec., Vol. 9B, 7.55.1, 7.55.2, 7.56.1, 7.56.2, and 7.56.3 (1946).

(6) (a) N. E. Ballou, Manh. Proj. Rep. CC-389B (Dec. 1942), CC-920 (Sept. 1943), CC-1204 (Jan. 1944), CN-1312 (May 1945), Plut. Proj. Rec., Vol. 9B, 8.24.7 and 8.24.12 (1946); N. E. Ballou and J. A. Marinsky, *ibid.*, 8.24.11; (b) J. A. Seiler and L. Winsberg, Manh. Proj. Rep. CC-2310, pp. 227–230 (Jan. 1945); Plut. Proj. Rec., Vol. 9B, 7.54.2 (1946).

(7) (a) G. E. Boyd, J. A. Swartout, *et al.*, Manh. Proj. Rep. CN-3346 (Dec. 1945); J. A. Schubert, Manh. Proj. Rep. CN-1873 (Jan. 1945); G. E. Boyd, J. Schubert, and A. W. Adamson, THIS JOURNAL, **69**, 2818 (1947); (b) A. W. Adamson, Manh. Proj. Rep. CN-1859 (Apr. 1944); G. E. Boyd, A. W. Adamson and L. S. Myers, THIS JOURNAL, **69**, 2836 (1947).

(8) E. R. Tompkins, and J. X. Khym, W. E. Cohn, Manh. Proj. Rep. CL-WEC-10 (Dec. 1946); THIS JOURNAL, **69**, 2769 (1947).

(9) N. E. Ballou, Manh. Proj. Rep. CC-680, p. 22 (May 1943) and CC-3418 (Feb. 1946); Plut. Proj. Rec., Vol. 9B, 7.54.1 (1946).

(10) B. Goldschmidt and F. Morgan, Canadian Proj. Rep. MC-11 (Aug. 1943).

(11) T. H. Davies, Manh. Proj. Rep. M-CN-1424 (Apr. 1944).

(12) D. N. Hume and R. I. Martens, *ibid.*, CN-1311 (June 1944).

method provides very effective separations of the rare earths,[8] even between adjacent elements. The procedure involves the adsorption of the rare earth ions on a column of the resin from dilute acid solution followed by elution with 5% citric acid adjusted to a pH of about 3 with concentrated ammonia.

The order of elution of the rare earths (from lanthanum through europium) and yttrium was established in a series of experiments[8,13] using radioactive cerium, lanthanum, europium and yttrium produced in fission and radioactive praseodymium and europium produced by slow neutron activation of pure oxides. Macroscopic quantities of samarium, europium, and neodymium with spectrographic analyses were also used. The results of these experiments show clearly that the order of elution of the rare earths is the reverse of that of atomic number, and that consequently the atomic number of an unknown radioisotope can be determined from the elution curves of a group of successive rare earths. Yttrium is eluted in the region of gadolinium as might be expected from its well known behavior in precipitation work. A typical set of elution curves is presented in Fig. 1.

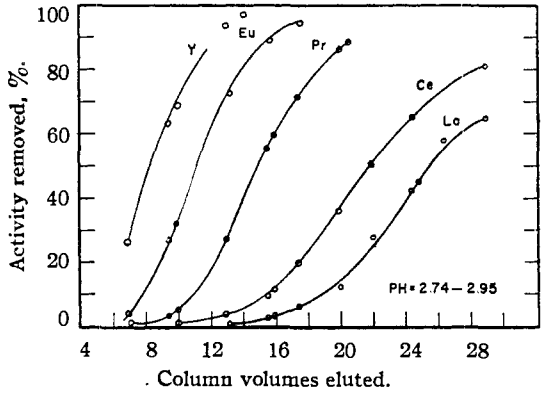

Fig. 1.—A typical set of curves showing the order of elution of the rare earths.

The 11d and the 3.7y activities were identified in the following experiment. A sample which contained essentially the praseodymium group (praseodymium, neodymium and element 61) with very little cerium, samarium, europium, and yttrium activities (by virtue of thorough chemical removal of cerium by ceric iodate precipitations[4] and of yttrium, samarium, and europium by repeated digestions with potassium carbonate[4,6]), was isolated with about 15 mg. of lanthanum carrier from a rare earth fission product elution fraction intermediate between cerium and yttrium that was supplied by Cohn and co-workers.[8] The rare earth activities in this sample were adsorbed on an Amberlite IR-1 column and eluted with a 5% solution of ammonium citrate at a pH value of 2.75. Fractions of the eluate were collected, and the observed beta and gamma activity in each fraction was plotted against the volume of eluate that had passed through the column. Four beta activity peaks were observed, as shown in Fig. 2. The gamma activity (11d half-life) was found to be associated with the third peak.

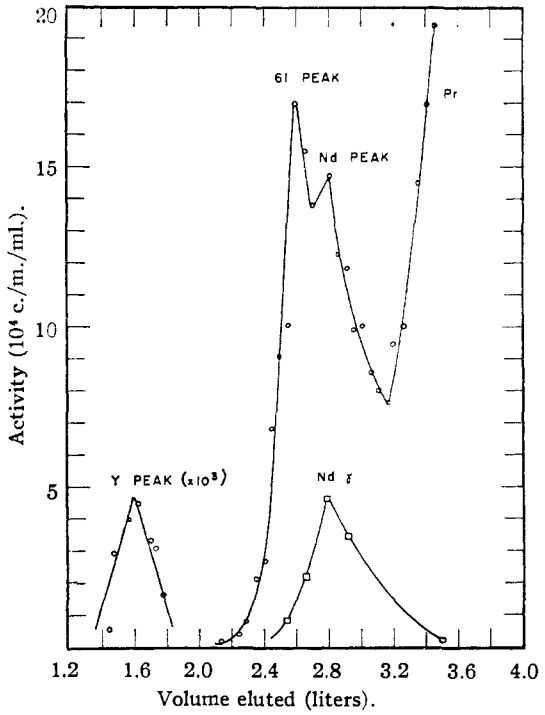

Fig. 2.—Elution curve of intermediate rare earth fraction.

The activity of the first peak was very low. It was identified as 57d Y^{91} (1.5 Mev. beta energy) from aluminum absorption curves. It is estimated from the curves that about 0.001% of the original yttrium was present in this experiment. Consideration of the fission yields and half-lives of fission product activities[3] indicates that no appreciable activity of samarium and europium would be found even though contamination from these elements should exceed that from yttrium by a factor of about one thousand. The remaining peaks must thus be ascribed to element 61, neodymium, and praseodymium in that order.

Decay and absorption data on a fraction corresponding to the top of the fourth peak showed that the activity consisted only of 13.8d Pr^{143} (1.0 Mev. beta energy), as expected. Similar studies of activities elsewhere along the distribution curve showed that the element 61 peak consisted of the activity of the long-lived soft beta emitter (0.2 Mev.), and that the neodymium peak consisted of the 11d activity with moderately hard beta rays (0.4 and 0.9 Mev.) and gamma rays.

(13) J. A. Marinsky and L. E. Glendenin, Manh. Proj. Rep. CC-2829 (June 1945); J. A. Marinsky, Plut. Proj. Rec., Vol. 9B, 11.1 (1946).

TABLE I

CHARACTERISTICS OF SOME RADIOISOTOPES OF Nd AND ELEMENT 61

Nucleus	Half-life	Decay	Class[a]	Fission yield, %	Energy of radiations in Mev. Particles	γ Radiations
$_{60}Nd^{147}$	11.0d	β^-, γ, e^-, X-ray	A	2.6	~0.4 (40%) 0.9 (60%) e^-: ~0.03	0.58 (40%) X-ray ~0.04
$_{60}Nd^{(149)}$	1.7h	β^-, γ or X-ray	B	...	1.5	γ or X-rays present
61^{147}	3.7y	β^-	A	(2.6)	0.20	no γ
61^{149}	47h	β^-, γ, e^- (?) X-ray (?)	A	1.4	1.1	0.25 (low intensity) X-ray (?)

[a] The classification corresponds to that of ref. 3, namely: A, element certain, isotope certain; B, element certain, isotope probable.

This experiment[14] was the first carried out to separate radioisotopes of element 61 from those of neighboring elements. Independent work[15] and subsequent amplification[15,16] has led to great improvements in the techniques for separating a variety of individual rare earth elements.

Similar elution experiments on activities produced by slow neutron irradiation of neodymium revealed not only the occurrence of the two radioisotopes discussed above, but also led to the identification of a 47h isotope of element 61 and a 1.7h isotope of neodymium. The 47h element 61 activity was subsequently isolated from fission products by using suitable timing and chemical techniques to eliminate interference from the 40.0h La^{140}, the 33h Ce^{143}, the 47h Sm^{153}, and the 56h Np^{239}. The 1.7h Nd, of probable mass 149, undoubtedly occurs among the fission products, but has not yet been identified there.

Physical Characteristics

Decay Energies.—Radiochemical studies were made of the four activities mentioned above in order to establish their decay characteristics, genetic relationships, fission yields, and mass assignments. These properties are presented in Table I. The decay characteristics were determined from decay curves and the absorption of the radiations in aluminum and lead. Maximum energies of the beta rays were estimated from ranges in aluminum evaluated by the method of Feather.[17] Beta-gamma coincidence counting was used to establish the coincidence of the gamma ray of the 11d activity with the softer beta component and the association of X-radiation with the emission of the harder beta component.

Genetic Relationships.—Since the two isotopes of element 61 are obtained in the slow neutron activation of neodymium as well as in the fission of uranium, it was of interest to see how these are related to the radioisotopes of neodymium. A study was made of the change in the ratio of the 3.7y element 61 activity to that of the 47h element 61 activity as a result of decay of the 11d Nd activity, under conditions for which the 1.7h activity had been removed by decay.

Very pure neodymium oxide (Hilger) was irradiated in the Clinton pile for seven days. This preparation was dissolved in 6 *N* hydrochloric acid and diluted to a definite volume. Several hours after the end of irradiation an aliquot portion was adsorbed on a resin column and eluted with a 5% solution of ammonium citrate at a *p*H of 2.75. Neodymium carrier was added to the first eluted fraction, which contained 47h element 61 with very little neodymium activity. The activities of the fraction were precipitated on neodymium fluoride and finally on neodymium oxalate. The sample was mounted as fraction I and its decay was studied. Ten days after the end of irradiation another equal aliquot was treated in the manner described above to give a similar fraction II rich in element 61.

Decay curves were followed for several months on both the fractions to determine the content in the 47h, 11d, and 3.7y activities, taking the point of reference as that of the end of the irradiation. Fractions I and II were found to contain the same amount of 47h 61 activity but the second contained less activity of 11d Nd, undoubtedly because of a small difference in *p*H of the lutriant. The observed activities, without correction for external absorption (20 mg./sq. cm.) and self-scattering (from ~25 mg./sq. cm.) are given in counts per minute (c./m.) in the first three lines of Table II. It is seen that the 3.7y activity is increased with reference to the 47h activity, which can only happen if the former is produced as a result of decay of the 11d Nd.

Correlation of the exact amounts of 3.7y activ-

TABLE II

ACTIVITIES OBSERVED IN TWO ELEMENT 61 FRACTIONS

Species	I, Separation at end of irradiation c./m.	II, Separation after 10 days of decay c./m.
11d Nd	9.0×10^4	5.0×10^4
47h 61	2.0×10^6	2.0×10^6
3.7y 61	3.5×10^2	7.0×10^2
11d Nd/740	1.2×10^2	0.7×10^2
Corr. 3.7y 61	2.3×10^2	6.3×10^2

(14) J. A. Marinsky and L. E. Glendenin, Manh. Proj. Rep. CN-2809 (Apr. 1945) and CC-2829 (June 1945).

(15) F. H. Spedding, A. F. Voigt, E. M. Gladrow, N. R. Sleight, J. E. Powell, J. M. Wright, T. A. Butler, and P. Figard, Manh. Proj. Rep. CC-2980 (Apr. 1945) and CC-2720 (May, 1945); THIS JOURNAL, **69**, 2786 (1947).

(16) (a) B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947); (b) D. H. Harris and E. R. Tompkins, *ibid.*, **69**, 2792 (1947).

(17) N. Feather, *Proc. Camb. Phil. Soc.*, **34**, 599 (1938); (b) L. E. Glendenin, *Nucleonics*, in press (1947).

ity formed during the seven-day period of irradiation and during the ten-day period of decay requires correction for the amount of this activity coming from the total decay of the 11d Nd contaminating the fractions. Taking the reasonable value of one-sixth for the ratio of counting efficiencies of the two activities and the factor 1/123 for the ratio of the half-lives, there are obtained the values given in the fourth line for the contamination correction in equivalents of 3.7y activity. The difference between these values and the observed activities in the third line gives the estimate of the true activities present in the two fractions. The activity in fraction II exceeds that in fraction I by the factor 2.7, in good agreement with the predicted value 2.96. Correspondingly the activity in fraction I is found to be 2.3×10^2 in comparison with the predicted value 2.1×10^2 computed from the activity of 11d Nd (6.65×10^5 c./m.) observed to be present before fractionation with the reference amount of 47h activity (2.0×10^6 c./m.).

It was not possible to study the occurrence of genetic relationship between 1.7h Nd and 47h element 61 by this method since their radiations are similar and the half-life of 1.7h Nd is too short to permit the required separations. It was therefore necessary to establish the relationship indirectly by varying the time of slow neutron irradiation of Nd and comparing the ratio of the two activities at the end of each bombardment with the ratio that should result from a genetic relationship. Such experiments indicated a parent-daughter relationship; however, the same neutron capture cross-section per normal atom of Nd could produce similar results.

Fission Yield.—The fission yield is defined as the percentage of the fissions (in this case of U^{235} with thermal neutrons) leading to the nucleus in question by direct formation and decay of precursors. The fission yields of the activities were determined from analysis of the decay curves of activities of the two elements isolated together from uranium that had been exposed in the pile, using neodymium carrier. The timing of the chemical operations was adjusted so that other rare earth activities were eliminated. The observed activities were corrected for decay, absorption, and degree of saturation during bombardment, and compared with the 12.8d Ba^{140} activity isolated from the same source. From the absolute fission yield value[18] of 6.1% for Ba^{140} the fission yields of 11d Nd and 47h element 61 were determined as 2.6 and 1.4%, respectively.

Mass Assignments.—The mass number of a fission product nucleus may be estimated from its fission yield since the fission yield varies rapidly with the mass over much of the fission product range. According to the yield-mass curve,[3] in which the yields of U^{235} fission product chains are plotted as a function of their masses, the fission yield values of 2.6 and 1.4% correspond to mass numbers of 147 and 149, respectively. An intense source of pure 3.7y element 61 from fission was prepared and submitted to Hayden and Lewis[19] who verified the mass assignment of 147 with the mass spectrograph. More recently the assignment of mass 149 to the 47h element 61 has been verified in the mass spectrograph by Inghram, Hess, Hayden, and Parker[20].

Discussion

Numerous studies have been made of activities from bombardments of praseodymium and neodymium in which isotopes of element 61 might be expected together with isotopes of neighboring elements from competitive nuclear reactions. Following exploratory investigations[21] the major contribution has been from Pool, Kurbatov, Quill, and co-workers[22] with important specialized studies by Wu and Segrè[23] and by Bothe.[24] The activities observed, together with the assumed nuclear reactions and the proposed assignment of the activities by element and mass number, are listed in Table III. It is apparent that considerable uncertainty persists in the assignment of the activities as can be determined by checking the reported identifications of the 1.7h Nd^{149}, the 47h 61^{149}, and the 11d Nd^{147}, whose identities have been established in this paper. This is to be expected because all assignments were made without attempts at chemical separations, which are virtually indispensable for element identification in this difficult section of the periodic system. The ion exchange column separations are certainly superior to the best standard fractionation available to these workers.

The identification of radioisotopes produced in cross bombardments (where the nuclear charge changes in the primary nuclear reaction) is in principle easier than for the (n,γ) or $(n,2n)$ reactions. The possibility of rare earth impurities in target materials cannot, however, be dismissed. Seaborg[25] in his Table of Isotopes lists all the activities in Table III only as Class E, element probable. Other reviews of the identification of radioisotopes of element 61 have been given by Seaborg[26] and Paneth.[27]

(18) M. S. Freedman and D. W. Engelkemeir, Manh. Proj. Rep. CC-1331 (Feb. 1944).

(19) R. J. Hayden and L. G. Lewis, *ibid.*, CP-3383 (Dec. 1945); *Phys. Rev.*, **70**, 11 (1946).

(20) M. G. Inghram, D. C. Hess, Jr., R. J. Hayden, and G. W. Parker, *ibid.*, **71**, 743 (1947).

(21) (a) E. Amaldi, C. D'Agostino, E. Fermi, B. Pontecorvo, and E. Segrè, *Proc. Roy. Soc., (London)*, **A149**, 522 (1935); (b) J. C. McClennan and W. H. Ranu, *Nature*, **136**, 831 (1935).

(22) (a) M. L. Pool and L. L. Quill, *Phys. Rev.*, **53**, 437 (1938); (b) H. B. Law, M. L. Pool, J. D. Kurbatov, and L. L. Quill, *ibid.*, **59**, 936 (1941); (c) J. D. Kurbatov, D. C. MacDonald, M. L. Pool, and L. L. Quill, *ibid.*, **61**, 106 (1942); (d) J. D. Kurbatov and M. L. Pool, *ibid.*, **63**, 463 (1943).

(23) C. S. Wu and E. Segrè, *ibid.*, **61**, 203 (1942).

(24) W. Bothe, *Z. f. Naturforsch.*, **1**, 179 (1946).

(25) G. T. Seaborg, *Rev. Mod. Phys.*, **16**, 1 (1944).

(26) G. T. Seaborg, *Science*, **105**, 349 (1947).

(27) F. A. Paneth, *Nature*, **159**, 8 (1947).

TABLE III

PREVIOUSLY REPORTED RADIOISOTOPES OF NEODYMIUM AND OF ELEMENT 61

Assumed reaction	Target element	Half-life	Mode of decay	Proposed assignment	Reference
n,γ	Nd	1h[a]			21
n,γ	Nd	35m			21
n,γ	Nd	21m	β^-	Nd^{151}	22
n,γ	Nd	2h[a]	β^-	Nd^{149}	22
n,γ	Nd	84h[b]	β^-	Nd^{147}	22
n,γ	Nd	2.0h[a]	β^-	$Nd^{147,149,151}$,	
n,γ	Nd	47.5h[b]	β^-	$61^{147,149,151}$, or	24
n,γ	Nd	11.1d[c]	β^-	Sm^{151}	
$n,2n$	Nd	2h[a]	β^-	Nd^{149}	22
$n,2n$	Nd	84h[b]	β^-	Nd^{147}	22
$n,2n$	Nd	2.3h[a]	β^-	61^{147} or ^{146}	22
$n,2n$	Nd	47h[b]	β^-	Nd^{149}	22
$n,2n$	Nd	10d[c]	β^-	61^{147}	22
$n,?$	Nd	108d			22
$n,2n$	Nd	2.5h	β^+	Nd^{140}	22
$n,2n$	Nd	41h[b]	β^-	Nd	22
$n,2n$	Nd	~2h[a]		Nd	22
$n,2n$	Nd	short		Nd	22
$n,2n$	Nd	47.5h[b]	β^-	$Nd^{147,149,151}$ or	24
$n,2n$	Nd	11.1d[c]	β^-	$61^{147,149,151}$	
d,p	Nd	47h[b]	β^-	Nd^{149}	22, 23
d,n	Nd	12.5h	β^-	61	22
α,n	Pr	~108d		61^{144}	22
d,n	Nd	~108d		61^{144}	22
α,n	Pr	~200d	K or I. T., γ	61^{144}	23
d,n / p,n / α,p	Nd	2.7h	β^-,γ	61	22
d,n / p,n / α,p	Nd	5.3d	β^-,γ	61	22
d,n	Nd	16d[c]	β^-,γ	61	22
$d?$	Nd	~1y	γ	..	22

[a] Presumably 1.7h Nd^{149}. [b] Presumably 47h 61^{149}. [c] Presumably 11d Nd^{147}.

Added interest in the identification of isotopes of element 61 derives from the fact that significant quantities of the natural element have not been separated, and that stable isotopes may not occur. The problem of the natural existence of element 61 has been reviewed by Yost, Russell and Garner,[28] who state, "the evidence for the existence in nature of element 61 is somewhat circumstantial rather than conclusive, and the isolation of this element cannot be regarded as having been effected."

Considerable quantities of 61^{147} can be prepared, however, as the result of the industrial application of nuclear power. A uranium pile operating at the power level of 1,000 kw. produces $\sim 3 \times 10^{16}$ fissions per second. From the data in Table I, it is seen that 2.6% of these will lead to chain 147. There is produced, therefore, ~16 mg. per day of Nd^{147}, which, after suitable decay, is transformed into 61^{147} of sufficient half-life for isolation and chemical study. The activity associated with 1 mg. of the species is 0.66 curie, but the radiations consist solely of soft β rays that are easily shielded and should not interfere too greatly with chemical operations.

We wish to express our gratitude to Dr. D. N. Hume for his generous advice and encouragement in this research. The collaboration of Mr. J. X. Khym on the order of elution experiments and the coöperation of Drs. W. E. Cohn and E. R. Tompkins in furnishing rare earth concentrates are gratefully acknowledged.

Summary

Studies of the elution characteristics of rare earth ions from Amberlite IR-1 absorption columns, using buffered citrate solutions, have shown that the order of elution is the reverse of atomic number, with yttrium falling near gadolinium. The position in the elution sequence can be used to identify individual rare earth elements, and useful separations can be achieved.

Column separations on fission product mixtures containing activities of praseodymium, neodymium, and element 61 have led to the first positive chemical identification of isotopes of element 61 of 47h and 3.7y half-life.

Radiochemical studies and fractionations have established the decay characteristics, genetic relation, and mass assignments of 11d Nd^{147}, 3.7y 61^{147}, 1.7h $Nd^{(149)}$, and 47h 61^{149}.

Other radiochemical work on neodymium and element 61 has been reviewed.

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(28) D. M. Yost, H. Russell, Jr., and C. S. Garner, "The Rare Earth Elements and Their Compounds," Chapter 4, John Wiley and Sons, New York, N. Y., 1947.