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Neutron activation analysis of trace rare earths in holmium oxide

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**Iowa State University of Science and Technology,
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NEUTRON ACTIVATION ANALYSIS
OF TRACE RARE EARTHS IN HOLMIUM OXIDE

by

Lee Philip Hunt

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

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INTRODUCTION

Activation Analysis

Activation analysis is a technique by which a constituent is quantitatively determined by measuring the radiation emitted from a nuclide that was produced from a selected nuclear transformation. Selection of the technique is based on sensitivity, speed, economy, convenience, or on the absence of another suitable method. As technological advances continue to accelerate and cause a demand for materials of high purity or of rigid trace constituent specifications, activation analysis has assumed an important role in the determination of such constituents in a wide variety of materials.

Activation of a sample involves its irradiation or bombardment by neutrons, charged particles, or high energy photons, so that atoms of the sample are transformed into other nuclides either of the same or of different elements. If the isotope produced from one or more constituents is radioactive and if its radioactivity can be distinguished or separated from other activities present, then the amount of this radioactivity is a measure of the parent isotope and, hence, of the parent element present in the original sample. Thermal (0.025 ev) neutrons are most widely used as activating particles because of the absence of an energy threshold for neutron reactions and because of their high probability of reaction with most nuclei. In addition, high thermal neutron fluxes (10^{13} - 10^{14} n/cm²-sec) are available in reactors. The most common reaction occurring with thermal neutrons is the (n, γ) process in which the neutron enters a nucleus and a "prompt" gamma ray

is immediately emitted. The resulting nucleus is one mass number heavier than the parent. Fast (14 Mev) neutrons can be used as activating particles but are of less general use due to the low fluxes (10^8 - 10^9 n/cm²-sec) available and to low reaction probabilities. Specificity is gained, however through reactions such as (n,p), (n, α), and (n,2n). Of even greater specificity are charged particle reactions in which reactions of the type (d,p), (d,n), (d, α), (α ,n), and (α ,p) are used.

The rate of formation of a nuclide in a neutron flux is proportional to the number of parent nuclei present (n), to the cross section, or probability of reaction (σ), and to the neutron flux (ϕ). In equation form,

$$\frac{dN}{dt} = n\phi\sigma = \frac{N_a\phi\sigma Wf}{M} \quad (1)$$

where N is the number of radionuclides present at time t, N_a is Avogadro's number, W is the mass of the trace element, M is its atomic weight, and f is the fractional abundance of the parent isotope.

The amount of an induced activity is determined by measuring the disintegration rate of the product isotope. Since radioactive decay is a random process, independent of the past or present circumstances of the sample, the rate of decay is dependent on the number (N) of atoms present at a given time (t), or

$$-\frac{dN}{dt} = \lambda N, \quad (2)$$

where λ is the decay constant characteristic of a particular isotope.

In activation analysis one is primarily concerned with the number of radioactive atoms present at the end of an irradiation since this

number determines the activity, disintegrations per second, available for detection. Since the rate of accumulation of a nuclide is equal to the rate of its formation at constant flux, minus the rate of its decay, the activity produced in a sample after irradiation for time t_1 is given by

$$A = \frac{N_a \phi \sigma W f}{M} (1 - e^{-\lambda t_1}) \quad (3)$$

assuming that the number of atoms of the parent remains constant.

At any time t_2 after the irradiation the activity becomes

$$A = \frac{N_a \phi \sigma W f}{M} (1 - e^{-\lambda t_1}) e^{-\lambda t_2} \quad (4)$$

Rearrangement of Equation 3 to the form

$$W = \frac{AM}{N_a \phi \sigma f (1 - e^{-\lambda t_1})} \quad (5)$$

provides a method of determining the sensitivity of an activation, the sensitivity being greatest under the conditions of high neutron flux and high detection efficiency of the emitted radiation.

After a sample has been activated under predetermined conditions, radiation from the constituent of interest must be detected and measured. The most commonly used device is the gamma-ray scintillation detector. When this detector is connected to appropriate electronic circuitry and readout devices, the resulting spectrometer provides one with a measurement of the counting rate and the gamma-ray spectrum of the radiation being measured. The general applicability of gamma-ray spectrometry is reduced because of poor gamma-ray peak resolution, spurious peaks due to Compton scattering, and because different nuclides may emit gamma rays of the same energy. Less extensively used in

activation analysis are the gas-filled Geiger-Mueller and proportional counters which are used primarily to measure the activity of nuclides that emit beta particles.

Analysis after irradiation is accomplished either by destructive or non-destructive means, the latter being more convenient. In a non-destructive analysis the radiation of the constituent of interest is measured in presence of the matrix. This requires that isotopes from other elements do not emit gamma rays of the same energy as those from the isotope being measured. In addition, the matrix activity must be low enough so that it does not override the activity of interest. When the above requirements are not met for the analysis of a single element, or if the analysis of several elements is desired, spectrum stripping can be used. In this process the spectrum of the interfering radiation is subtracted from the spectrum of the unknown. Although the resolution of gamma-ray spectra is generally difficult and time consuming, the availability of computer programs (1,2) has made the method practical. An alternate method of analysis is a destructive determination which involves separation of the unknown elements from the matrix and to some degree from one another. A drawback in a destructive analysis, however, can be the time required for separation.

Absolute or comparator methods can be used to calculate the amount of a constituent once its activity is known. The absolute method utilizes Equation 5. Since half-lives and particularly cross sections are not always accurately known, and since a flux monitor is required for an accurate determination of the flux, this method is seldom used.

Even with difficult or tedious measurements of activity, the error of the absolute method is seldom greater than $\pm 20\%$ (3). The commonly used comparator method involves irradiation of a pure sample of the unknown element for the same time and at the same flux as the unknown sample so that each receives an identical radiation exposure. If the two samples are counted under identical conditions, the weight of the unknown element can be calculated from Equation 6,

$$W_x = \frac{W_s R_x}{R_s} \quad (6)$$

where W_x is the weight of the unknown element, W_s is the weight of the same element in the standard, and R_x and R_s are their respective counting rates. When a large number of elements are to be determined in a sample, a single comparator can be used so that individual standards are not required for each of the elements (4).

There are errors in activation analysis, quite characteristic of the method itself, which arise from different activation rates of the sample and standard. Error will occur if both sample and standard are not placed within the same small volume of a reactor since the neutron flux is not constant throughout the reactor. Another source of error is self-shielding. This occurs when the sample matrix has a high neutron cross section causing a depression of the flux within the sample which the standard does not experience. A further source of error is due to interfering nuclear reactions, which may be classified as primary and second order interferences. Primary interferences are caused by reactions of the irradiating particles with elements, other than the element sought, which produce the radionuclide of interest. Second

order reactions are induced in transformation products by the irradiating particles, either increasing or decreasing the yield of the radionuclide of interest. The most obvious uncertainty in activation analysis arises from the statistical nature of radioactive decay. When the half-life of a nuclide is much greater than the counting interval, as is usually the case in reactor irradiations, the standard deviation (σ) of the number of counts observed over the time interval Δt is given by

$$\sigma = (\text{counts})^{\frac{1}{2}}/\Delta t \quad (7)$$

A minimum of 10^4 counts is usually observed during a measurement, and since the minimum time interval is usually one minute, the maximum standard deviation of the count rate is 1%. Activation analysis is also subject to those errors which may be classified as processing errors, e.g., contamination of the sample from the irradiation container, existence of different isotopic ratios in the samples and standards, and occurrence of the trace and carrier in different chemical forms.

As with all methods which provide information about a chemical system, activation analysis has its advantages and disadvantages. On the credit side is the often wide availability of methods by which an element can be determined. In addition to the differences in chemistry among elements, methods of analysis are provided by the various nuclear reactions that can be induced in different isotopes of the same element and by the different half-lives, modes, and energies of decay of the respective transformation products. Activation analysis is seldom biased by reagent contamination since a sample usually requires no chemical treatment before irradiation and only activities are measured after irradiation. Another advantage is being able to use

semi-quantitative separations when a known amount of carrier has been added and the chemical yield determined. A disadvantage is the need of a nuclear reactor or accelerator to obtain a high sensitivity in the determination of many elements. In addition, activation analysis measures only the total weight of a constituent and does not account for its different states of chemical combination.

Books and reports on the fundamentals and techniques of activation analysis and compilations of nuclear data important to the field have appeared in recent years. The texts by Bowen and Gibbons (5) and by Lyon (3) complement one another well, the former giving greater attention to examples with the latter favoring fundamentals. Also available are the texts by Taylor (6) and by Lenihan and Thompson (7), the latter including a discussion of computer applications to activation analysis. A report by Brooksbank (8) presents the basics of activation analysis along with data from several experimental determinations. A handbook of activation analysis by Koch (9) references many analyses by thermal and fast neutron and charged particles reactions in addition to providing nuclear data, threshold energies for reactions, sensitivities, and possible interfering nuclear reactions. A literature search has been reported by Raleigh (10). Heath (11, 12) and Crouthamel (13) have discussed gamma-ray spectrometry and have presented various tables listing isotopes by their half-lives and gamma-ray energies. Each has also made available extensive catalogs of gamma-ray spectra. A comprehensive study of neutron cross sections as a function of neutron energy has been made by Hughes and Harvey (14). Detailed nuclear energy levels and decay schemes of the nuclides, and other nuclear data are

available in "Nuclear Data Sheets" (15) which is now published as the periodical "Nuclear Data" (16). Of the many nuclide charts available, the "Chart of the Nuclides", General Electric Company, Educational Relations, Schenectady, N. Y., is very useful and is periodically revised.

Rare Earths

The term "rare earths" is the classical name given to the group of elements from lanthanum through lutetium, in addition to yttrium, whereas the term "lanthanides" refers to the series of elements from cerium through lutetium. The lanthanide series arises from the filling of the 4f subshell with increasing atomic number. Since the 4f electrons are effectively screened by the filled 5s5p subshells, they are not directly involved in chemical bonding. All the rare earths have three electrons in their valency shells, and since the valence electrons of an atom are responsible for most chemical properties, the rare earths are nearly chemically identical. The ground-state "outermost" electronic configurations of the yttrium ion, $4s^2 4p^6$, and the lanthanum ion, $5s^2 5p^6$, are similar to the electronic configurations of the lanthanide(III) ions, $4f^{1-14} 5s^2 5p^6$, resulting in the "rare-earth" classification. The ionic radii of the tripositive rare-earth ions range from 0.848-1.061 Å.

As knowledge concerning the rare-earth field advances it becomes necessary to know the type and quantity of impurities present in the rare-earth metals and their compounds. The most common impurities found in a rare-earth matrix are those rare earths adjacent to it in the periodic table. Direct chemical methods can not be used to analyze

for such impurities because they are present in trace quantities and are highly similar chemically to one another and to the matrix. Therefore, one must resort to an analytical method that makes use of the atomic or nuclear properties of the rare earths.

Although the 4f electrons play a negligible role in determining the chemical properties of the rare earths, they play a leading role in establishing energy states within the atomic system. However optical absorption, optical fluorescence, and x-ray fluorescence spectra can not be used for trace rare-earth analysis for one or more reasons (17-20). At present, optical emission spectroscopy is the main method of analysis for rare earths at either the trace or major constituent level. Although the probability of line interference is high, the method is able to achieve sensitivities of about 1-500 ppm, depending on the matrix analyzed (21-22).

Mass spectrometry has been used with some success for trace analysis of the rare earths. Guthrie (23) has found as high as fifty impurities in a single sample when analyzing Ce, Er, and Lu metals from unknown sources. The sensitivities for the rare-earth impurities ranged from 0.1-10 ppm. Guthrie states that although the method is semi-quantitative, it has potential for greater accuracy.

Purpose

The purpose of this investigation was to develop a general method, using thermal neutron activation analysis, to determine sub-ppm quantities of rare-earth impurities in rare-earth matrices. Although

activation analysis has been used in the past, as described below, the methods have been quite specific for several rare-earth matrices and not easily adapted to others.

REVIEW OF LITERATURE

I. Curie and F. Joliet produced the first recognized activation of elements in 1933 by bombarding light metals with alpha particles from polonium. This event, and the discovery of the neutron by J. Chadwick in 1932, soon led to the application of induced radioactivity to analytical problems.

Hevesy and Levi (24) announced the first activation analysis in 1936 after detecting dysprosium in purified Y_2O_3 . In 1938 they reported (25) the determination of 10 mg. amounts of europium in Gd_2O_3 . One year later, Goldschmidt and Dyourkovitch (26) showed that irradiation with a constant source of neutrons and measurement of the intensity of activation is a satisfactory method for determining the dysprosium content in a mixture of yttrium-group oxides. Until the latter part of the 1940's, activation analyses of the rare earths stood at a near standstill until appreciable quantities of these elements were available in pure form and until higher neutron fluxes and more elaborate radiation detection equipment were at hand.

With the development of nuclear reactors and advances in proportional and scintillation counting, non-destructive activation analysis became more exact. Using decay curve resolution, Kohn and Tompkins (27) determined samarium in Ce_2O_3 , dysprosium in Y_2O_3 , while Phillips and Cornish (28) determined dysprosium in Ho_2O_3 . Meinke and Anderson (29), making use of a low flux radium-beryllium source, estimated that dysprosium and europium could be measured to $1\mu g.$ at a flux of 10^7 n/cm^2 sec and that activation analysis was superior to spectrophotometric

procedures in many cases. Born, et al. (30), have described specific procedures for determining europium in samarium, dysprosium in yttrium earths, with or without gadolinium, samarium in cerium earths free of europium, and gadolinium in yttrium earths low in europium.

In the 1960's M. Okada published a series of papers (31-36) describing the non-destructive activation analysis of Sc, Y, Dy, Er, and Yb in various minerals, ores, and rare-earth oxides. Using a fast delivery system from a reactor to a multichannel pulse-height analyzer, he measured the activities of the short-lived meta-stable isomers which were produced. The first application of fast neutrons to rare-earth activation analysis was made by Tada and Fujii (37) in the determination of praseodymium in mixtures of lanthanum and neodymium. Cuypers and Menon (38, 39) have also used 14-Mev neutrons to determine Ce, Pr, and Y in minerals. Kawashima (40) subjected pure rare-earth oxides to a flux of 3×10^{11} n/cm² sec. His results compared favorably to those of emission spectroscopy, except that the values for dysprosium and yttrium differed by a factor of about five. Kawashima (41) has also determined dysprosium in Y₂O₃ using the latter as an internal standard.

Separation of the rare earths by ion exchange led to a more sensitive and less specific means of analysis of rare-earth impurities in a rare-earth matrix by providing a destructive method of analysis. In 1947 Kettle and Boyd (42), after exhaustively purifying Er₂O₃ by ion exchange, subjected the sample to neutron bombardment and subsequent separation by ion exchange with citric acid and Dowex-50 resin. In addition to detecting Lu and Yb, they determined 10 ppm thulium. Six

years later, Cornish (43) determined sub-microgram amounts of rare earths in spec-pure Sm_2O_3 by using Zeokarb-225 as an ion exchanger. Minczewski and Dybczynski (44) have found a detection limit of less than 10 ppm for the rare earths in spec-pure Er_2O_3 using an EDTA separation technique after activation. Bildstein, et al. (45), have determined Eu in Gd, Pr in Nd, and Lu in Yb at the 100-1000 ppm level using a Dowex 50W column with α -hydroxyisobutyrate or lactate solutions. Lévêque (46) non-destructively determined 10-100 ng. of Sm, Eu, or Dy in the presence of the other two with an error of $\pm 20-30\%$, but found that a destructive method provided better results. Leddicotte, et al. (47), in a published list of activation analyses done at Oak Ridge National Laboratory, reported the determination of 1-10 ppm samarium in cerium using a radio-chemical separation. By 1959 many ion-exchange methods for separating the rare earths had appeared in the literature and at this time Powell and Spedding (48) published a review on the use of chelating agents for such separations. Since then Powell (49-50) has made available more detailed reviews. Fujii (51-52) determined individual rare-earth elements in their ores after activation and ion exchange but made the final analysis spectrophotometrically rather than utilizing the available radioactivities of the elements. Ryabchikov and Ryabukhin (53) have determined 8 ppm Tm and 1 ppm Ho in 0.25 mg. samples of spec-pure Er_2O_3 using citric acid as chelating agent. Using a micro-ion exchange column, Grosse-Ruyken and Rommel (54) determined 10 ppm Sm, 5 ppm Eu, and 1000 ppm Gd and Y in 100 g. samples of Y_2O_3 and Sm_2O_3 . Rengan and Meinke (55) have determined Dy and Eu in monazite and Y_2O_3 30 minutes after activation. Their use of small Dowex-50 columns and α -hydroxyiso-

butyric acid did not allow for complete separation when the rare earths were less than three apart. Yakovlev and Dogadkin (56) have detected dysprosium in Y_2O_3 with a sensitivity of 10 ppb after a one hour separation of Dy^{165} on an anion-exchange resin using EDTA. The activation required a five minute irradiation at a flux of 10^{13} n/cm² sec.

Reversed-phase partition chromatography provides a faster and more complete separation of the rare earths than that obtained with ion-exchange resins. In general, an organo-phosphorus compound is absorbed on an inert powder which is used as the solid support in a column. The rare-earth sample is loaded on the column and eluted with a mineral acid.

In 1958 Winchester (57) separated radiotracers of Nd, Pm, and Eu by elution with dilute HCl on a column of alumina using di-(2-ethylhexyl) phosphonic acid, HDEHP¹, as the liquid phase. He observed that column behavior was similar to solvent extraction in which separation factors for adjacent rare earths had a mean value of 2.5. Fidelis and Siekierski separated microgram quantities of the light rare earths (58) and the heavy rare earths (59) by using a liquid phase of tributyl phosphate, TBP, on a solid support of silanized kieselguhr² with HNO₃ or HCl as eluant. Separation factors³ for adjacent rare earths were about 2.0. Although

¹Also known as di-(2-ethylhexyl) orthophosphoric acid, di-(2-ethylhexyl) hydrogen phosphate, or as any of the above names with bis- in place of di-, and also abbreviated as D2EPA and DEP.

²Kieselguhr, a diatomaceous earth, is silanized by treating it with vapors of dichlorodimethylsilane which react with surface Si-OH groups rendering the kieselguhr inert.

³A separation factor is defined as the ratio of the positions, measured from zero eluant volume, of two peak maxima on an elution curve.

the mean separation factor for TBP is less than that of HDEHP, the silanized kieselguhr column provided better separations because the height equivalent to a theoretical plate, HETP, is very small, 0.2 mm. Cerrai, Testa, and Triulzi (60-61a) used HDEHP on unsilanized cellulose columns and found a mean separation factor of 2.5 with HCl. However, the HETP value varied from 4 mm. at 45° C. to 1 mm. at 75° C. Pierce and Peck (61b, 61c) used HDEHP on a solid support of Corvic, a poly-(vinyl-chloride/vinylactate) copolymer, and separated microgram amounts of the rare earths at 69° C. using a gradient elution with HClO_4 . Also, however, the HETP values they found were 2 mm., twice that found by Siekierski and Fidelis (58-59). Pierce and Hobbs (62) have made a study of the behavior of column materials using HDEHP on Corvic, and Pierce, Peck, and Hobbs (63) have determined rare-earth separation factors in HClO_4 . Cerrai and Testa (64) have studied separations using HDEHP on Kel-F, a poly-trichlorofluoroethylene powder, and found a relatively high HETP value. They have also published (64) an informative paper on rare-earth separations on filter paper impregnated with HDEHP in which R_f values are given.

Winchester (66) in 1963, coupled the high separation factors of HDEHP with the small HETP of silanized kieselguhr columns to obtain good separations of all the rare earths using a gradient elution technique. Previous methods have given incomplete separations of the adjacent rare earths Ce-Pr-Nd, Eu-Gd, Dy-Ho, and Yb-Lu. Sochacka and Siekierski made rare-earth separations by reversed-phase partition chromatography practical with publication of two papers in 1964. The first (67) provided a method of preparing a solid support with a HETP value of 0.3 mm. In addition to providing separation conditions and separation factors

in HCl and HNO₃, a study of HEHP values as a function of HDEHP concentration and a study of separating micro-amounts of Tb from macro-amounts of Er was presented. The second paper (68) involved a study of the effect of eluting acid, flow rate, and temperature on the HEHP values for individual rare earths. Still more complete separations have been obtained by Fidelis and Siekierski (69) by using 2-ethylhexyl phenylphosphonic acid, HEHP, which has a mean separation factor of 2.8 compared to 2.5 for HDEHP.

Since trace level determinations in rare earths require a destructive means of analysis, activation analysis coupled with reversed-phase partition chromatography provides a sensitive method. Nascutiu (70) has quantitatively studied the possibility of determining thorium and the rare earths by activation on paper after a prior chromatographic separation. For sub-microgram amounts the errors were $\leq \pm 12\%$. Grosse-Ruyken and Bosholm (71) have determined 0.1 ppm Ho in Dy and 1 ppm Lu in Yb with a variance of $\pm 15\%$. The trace rare earth was separated from the matrix before activation by elution on a HDEHP-silica gel column. Prior separation is required because the trace impurity would be formed from the matrix during irradiation through neutron capture and beta decay. This type of procedure, however, removes one of the advantages of activation analysis, in that trace quantities of the element in question may be introduced into the sample prior to activation.

Grosse-Ruyken, et al. (72), have purified dysprosium and gadolinium using a HDEHP-silica gel column so that terbium and europium impurities were no longer detectable by activation analysis. Under their experi-

mental conditions the detection limits were 1 ppb terbium and 0.001 ppb europium.

PART I. SEPARATION BY ION-EXCHANGE CHROMATOGRAPHY

EXPERIMENTAL

Equipment and Materials

Ion-exchange columns, 55 cm. long, were constructed from 10 mm. inside diameter Pyrex glass tubing. One end of the column was fitted with a 9 mm. Snaptite glass joint and the other with a fritted glass disk, followed by a stopcock. A drawing is shown in Figure 1.

An automatic fraction collector from the E. H. Sargent and Co., Chicago, Illinois, was used to collect the ion-exchange column effluent. The collector consisted of a photoelectric drop counter which indexed a turntable, holding 400 test tubes, after a preset number of drops.

All counting was done using one of the following gamma-ray scintillation spectrometers. One of the counting systems used was a single channel analyzer built in the Ames Laboratory incorporating a R. C. L. Decade Scaler and a lead shielded 2x2" NaI(Tl) well-type scintillation crystal. Integral counting of Tm-170 was performed with the lower discriminator set at the minimum of the valley between the 24 Kev escape peak and the 52 Kev Yb X ray. The other counting system was composed of R. I. D. L. transistorized components, a Model 34-12B 400 channel analyzer, Model 30-19 linear amplifier, Model 33-10-001 pulse-height analyzer, Model 54-7 timer, and Model 49-28 scaler. Differential counting of the Tm-170 activity was performed in the 5-100 Kev energy range using a lead shielded 4x4" NaI(Tl) well-type scintillation crystal with a Model 10-17 preamplifier.

Quartz tubing used to contain rare-earth samples was CFQ Standard 204 tubing from the General Electric Company.

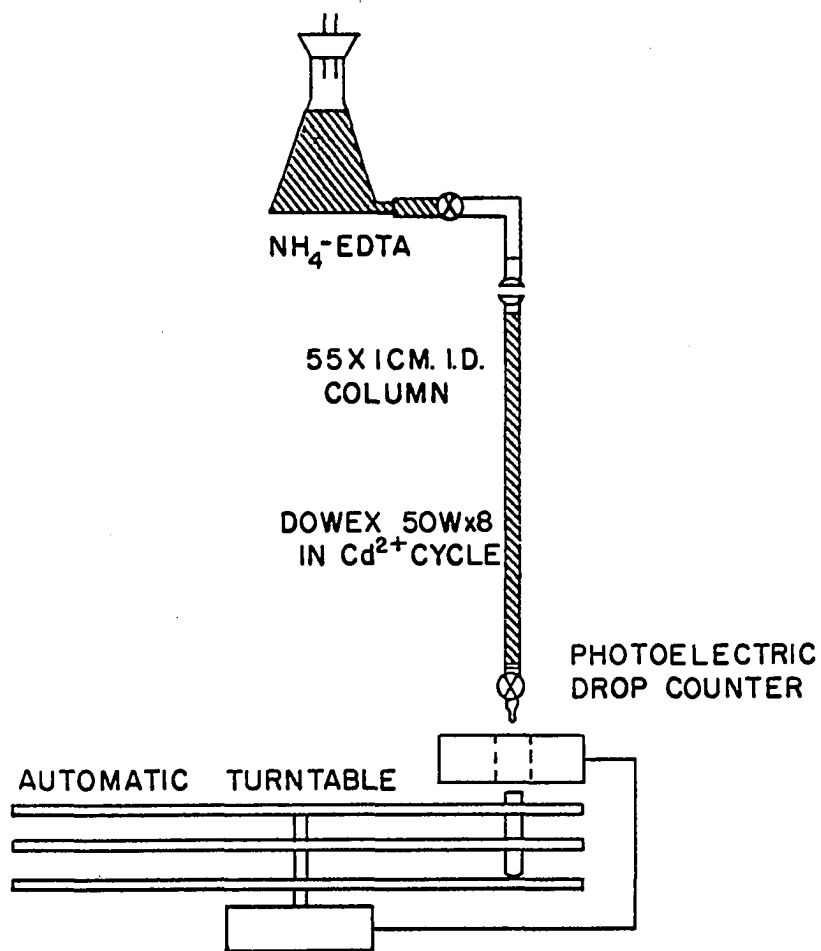


Figure 1. Elution and collection system

The rare-earth oxides used in the analyses were obtained from the Ames Laboratory, Iowa State University. The emission spectrographic analyses of the oxides appear in Table 1.

Table 1. Emission spectrographic analyses of rare-earth oxides

Sample	Impurity (ppm)
Ho_2O_3	<400 Dy, <70 Er, <100 Tm, <50 Y
Tm_2O_3	≤ 400 Ho, ≤ 50 Er, 50 Yb, <30 Lu, $\overset{d}{\leq 200}$ Y, no Th

All other chemicals used in the analyses were of reagent grade quality.

Samples and Standards

A main standard solution of thulium was prepared by dissolving a known amount of dry Tm_2O_3 in 3N HCl and diluting it to volume. Other standard solutions of thulium were prepared by dilution of the main standard solution. Standard samples of thulium were prepared for irradiation by pipetting 100 λ aliquots of the standard solutions, followed by three washings, into half sealed quartz tubes, 50x5 mm. inside diameter. The standards were evaporated to incipient dryness at 98° C., followed by complete drying at 110° C. The quartz tubes were then completely sealed and wrapped with aluminum foil to prevent contamination during irradiation. The 100 λ pipettes had been standardized with triply cleaned mercury. The quartz tubes had been cleaned with sulfuric acid/dichromate solution, washed with distilled water, and dried.

Holmium oxide samples containing predetermined amounts of thulium were prepared for irradiation by dissolving known amounts of dry Ho_2O_3 in crucibles with 3N HCl. Aliquots of standard thulium solutions were added and the resulting solutions were carefully evaporated to dryness on a hot plate. The rare-earth chlorides were then converted to the oxides in a muffle furnace at 800°C . The final samples were prepared by weighing known amounts of the doped Ho_2O_3 into quartz tubes, which were then sealed and wrapped with aluminum foil.

Spec-pure Ho_2O_3 samples were prepared by directly weighing the nontreated oxide in tared quartz tubes.

In order to remove the samples and standards from their quartz tubes after irradiation, the quartz tubes must undergo the same chemical treatment as the oxides. Hence, as an added precaution to prevent contaminating their surfaces, the quartz tubes containing the samples and standards were all sealed in a large quartz tube.

Irradiation and Analysis

All activated samples were irradiated in the CP-5 Reactor at Argonne National Laboratory. Samples containing 100 ppm thulium were irradiated for one day at a thermal neutron flux of 5×10^{12} n/cm² sec (nvt= 4.32×10^{17}), those containing 10 ppm for seven days at 6×10^{12} n/cm²-sec (nvt= 3.63×10^{18}), and those containing 1 ppm for seven days at 5×10^{13} n/cm² sec (nvt= 3.02×10^{19}). The spec-pure Ho_2O_3 samples were irradiated for eight days at 5×10^{12} n/cm² sec (nvt= 3.46×10^{18}). Since a large amount of Ho-166 activity was produced during irradiation, the samples were not treated until the Ho-166 activity had fallen below the 10 mc. level.

Microcurie amounts of Ho-166m are produced during long irradiations calling for caution to be taken in handling the samples. Nuclear data for holmium and thulium are presented in Table 2.

Table 2. Selected rare-earth nuclear data^a

Nuclear Reaction	% Abundance of Target	Thermal Neutron Cross Section (barns)	Half-life of Product
$Y^{89}(n,\gamma)Y^{90}$	100	1.3	64.2 h.
$Sm^{152}(n,\gamma)Sm^{153}$	26.72	210	46.7 h.
$Eu^{151}(n,\gamma)Eu^{152m2}$	47.82	2800	9.3 h.
$Eu^{151}(n,\gamma)Eu^{152}$	47.82	5900	12.4 y.
$Eu^{153}(n,\gamma)Eu^{154}$	52.18	320	16 y.
$Gd^{152}(n,\gamma)Gd^{153}$	0.20	<180	240 d.
$Tb^{159}(n,\gamma)Tb^{160}$	100	46	72 d.
$Dy^{164}(n,\gamma)Dy^{165}$	28.18	700	2.35 h.
$Dy^{165}(n,\gamma)Dy^{166}$	0	4700	82 h.
$Ho^{165}(n,\gamma)Ho^{166m}$	100	1	1200 y.
$Ho^{165}(n,\gamma)Ho^{166}$	100	64	27.2 h.
$Tm^{169}(n,\gamma)Tm^{170}$	100	125	125 d.
$Yb^{168}(n,\gamma)Yb^{169}$	0.135	11000	32 d.
$Yb^{174}(n,\gamma)Yb^{175}$	31.84	9	4.2 d.
$Yb^{176}(n,\gamma)Yb^{177}$	12.73	7	1.9 h.
$Lu^{176}(n,\gamma)Lu^{177}$	2.59	2100	6.8 d.

^aNuclear data taken from "Chart of the Nuclides", eighth edition

The samples were removed from the large quartz tube by breaking it under water with a sample breaker. The quartz tubes containing thulium standards were broken open, individually, under a solution of $3N$ HNO_3 containing about 100 mg. of dissolved Tm_2O_3 . Upon dissolution, the solutions were quantitatively transferred to 100 ml. volumetric flasks and diluted to volume. The samples containing doped Ho_2O_3 were treated similarly, except that after dissolution, the solutions were twice evaporated to incipient dryness to remove excess acid in order to prevent precipitation of EDTA on the ion-exchange resin during separation.

The separation of thulium from holmium involved the use of elution chromatography. In this type of chromatography the ion initially sorbed on the resin and the eluent ion are usually the same, with the eluent ion always having less affinity for the resin than the ions being separated. Hence, the eluent ions displace the sorbed ions inefficiently and overrun them. Since the sorbed ions have different affinities for the resin, they travel down the column at different rates under the influence of the eluent. In the case of the rare earths, separation is due primarily to the differences in the affinity of the chelating eluent for the sorbed ions rather than that of the rare earths for the resin. In this work the ion initially sorbed on the resin was the Cd^{2+} ion and the eluent ion was the NH_4^+ ion. Cadmium has an "effective stability constant" with EDTA of 19.0 (73) that falls between the stability constants of thulium, 19.3, and holmium, 18.7. Although cadmium has much less affinity for the resin than the rare earths, its EDTA stability constant of 16.4 is also less than that of the rare earths causing cadmium to have a desirable "effective stability constant" for the separation of thulium

from holmium. Since the order of the metal-EDTA stability constants is $Tm > Cd > Ho$, when the rare earths are loaded on the resin and eluted, thulium overruns cadmium while holmium lags behind. Cadmium acts as a wedge shoving the two rare earths apart.

A 50 cm. resin bed was prepared by twice backwashing a column of Dowex 50W-X8 (100-200 mesh) resin with distilled water to remove the "fines". The resin was converted to the cadmium cycle by passing a filtered solution of 2M. $Cd(NO_3)_2$ through the column. Excess $Cd(NO_3)_2$ was removed with distilled water and the resin was backwashed once more to give a uniform bed.

The activated rare-earth sample was loaded on the column with water at a flow rate of 0.5 ml/min. Before elution of the sample was begun, the column was thoroughly washed with distilled water to remove anionic activity. Elution was carried out with a filtered NH_4 -EDTA solution which had been prepared by adjusting the pH of a 0.015 M. solution of EDTA, ethylenediaminetetraacetic acid, to 8.45 with NH_4OH . For the doped Ho_2O_3 samples, the column effluent was collected in a 1000 ml. volumetric flask until the valley between the thulium and holmium peaks occurred, at which time the separation was completed by fractional collection of three milliliter portions. All Tm-170 activity was diluted to volume. In the case of spec-pure Ho_2O_3 samples, the effluent was entirely collected by fractionation.

The determination of the Tm-170 activity in each sample also involved the measurement of the activity of the corresponding thulium standard. An aliquot of four or eight milliliters, depending on the size of the sample holder, was withdrawn from a volumetric flask, delivered to a test tube

and counted in one of the systems described previously. A total of at least 10,000 counts were accumulated and background corrections were made for each measurement.

RESULTS AND DISCUSSION

All separations of doped Ho_2O_3 samples were, or were nearly, complete as shown by a typical elution curve in Figure 2. Flow rates varied from 0.4 to 0.6 ml/min. giving separations between 21 hr. with 710 ml. and 36 hr. with 880 ml. of NH_4 -EDTA.

The weights of the samples and standards and their corresponding activities appear in Table 3. The results for the thulium analyses of doped Ho_2O_3 are presented in Table 4.

Table 3. Sample and standard weights and activities

Number	<u>Samples</u>			<u>Standards</u>		
	mg. Ho	$\mu\text{g. Tm}$	Tm-170 Activity (C/M) ^a	Number	$\mu\text{g. Tm}$	Tm-170 Activity (C/M) ^b
1	106.5	10.71	1268	1	10.07	1203
2	100.1	10.07	1181	1	10.07	1203
3	99.26	9.984	1205	1	10.07	1214
4	117.9	1.175	1679	2	1.007	1349
5	107.7	1.073	1430	2	1.007	1349
6	107.6	1.072	1448	2	1.007	1349

^aAll counting rates were accumulated over 60 minutes, except Sample 8 which was for 38.3 minutes.

^bAll counting rates were accumulated over 60 minutes, except Standard 3 which was for 6 minutes.

Table 3. (Continued)

<u>Samples</u>				<u>Standards</u>		
Number	mg. Ho	$\mu\text{g. Tm}$	Tm-170 Activity (C/M) ^a	Number	$\mu\text{g. Tm}$	Tm-170 Activity (C/M)
7	108.5	0.1086	2934	3	0.1009	1178
8	116.9	0.1170	2781	3	0.1009	1178

Table 4. Results for thulium analyses of doped Ho₂O₃

Sample No.	Tm added (ppm atomic)	Tm found (ppm atomic)	Average Tm found (ppm atomic)	Average % error
1	100.6 \pm 0.3	99.62 \pm 0.76		
2	100.6 \pm 0.3	98.76 \pm 0.77		
3	100.6 \pm 0.3	100.6 \pm 0.8	99.66 \pm 0.92	-0.9 \pm 0.9
4	9.965 \pm 0.039	10.63 \pm 0.08		
5	9.965 \pm 0.039	9.907 \pm 0.075		
6	9.965 \pm 0.039	10.05 \pm 0.07	10.20 \pm 0.38	+2.3 \pm 3.8
7	1.001 \pm 0.004	2.316 \pm 0.044		
8	1.001 \pm 0.004	2.038 \pm 0.042	2.18 \pm 0.20	+118

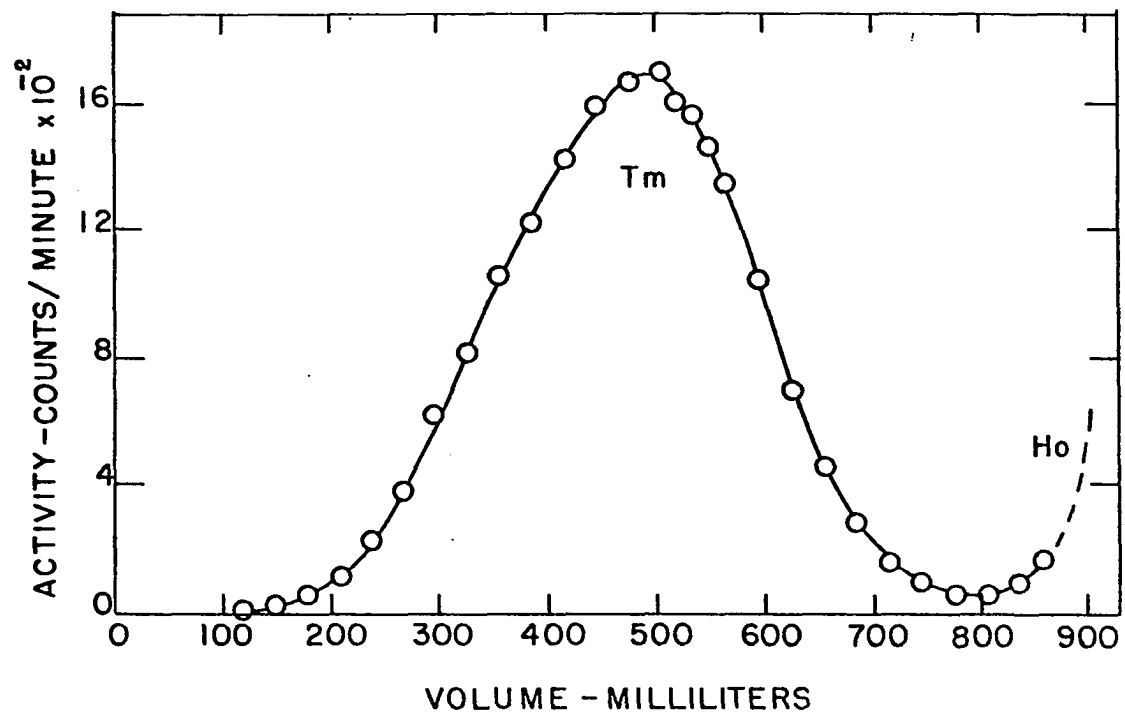


Figure 2. Elution curve for the separation of thulium from doped Ho₂O₃

In Table 4, the standard deviations of the amounts of thulium added and found were calculated from the errors occurring in the individual analyses, as more fully described below. The standard deviation of the average amount of thulium found was calculated from the differences between the average and the individual analyses. For Samples 1-3 and 4-6, the experimentally determined amounts of thulium compare favorably with the amounts added. The accuracy and precision of the analyses are indicated by the average percent error and by the standard deviation of the average amounts of thulium found, respectively. For Samples 7 and 8, the amount of thulium analyzed is more than twice the amount added, suggesting that the level of thulium present in the nondoped Ho_2O_3 is on the order of the amount of thulium added. The difference between the amount of thulium found and the amount added does not give an exact analysis of the thulium present in the nondoped Ho_2O_3 , however, because of the presence of ytterbium activity, as shown below in the analysis of a spec-pure Ho_2O_3 sample.

Six sources of error that can affect a thulium analysis are listed below:

1. Measurement of sample and standard weights.
2. Measurement of solution volumes.
3. Neutron self-shielding during irradiation.
4. Estimation of a separation that is not complete.
5. Sample geometry during counting.
6. Counting statistics.

The first two sources of error can be measured. The third source would not be expected to be large from consideration of sample size and cross

sections of the irradiated materials, as the results tend to verify. Estimating where to stop a separation that is not complete introduces little error because of the small counting rate in the valley between the thulium and holmium peaks compared to the total activity in the thulium peak itself. The fifth source of error is small because an essentially constant sample geometry is obtained by counting a liquid sample in a well-type crystal. In this work counting statistics were the greatest source of error. Because of the small counting rates shown in Table 3, longer than usual counting times were used. The standard deviation of each thulium analysis given in Table 4 included the standard deviation of weight, volume, and counting measurements. The size of the error introduced by the counting rate is shown by comparison of the standard deviation of the thulium analysis of Sample 1, $\sigma = \pm 0.76$, to the standard deviation if only the counting rate is considered, $\sigma = \pm 0.53$.

The separations of spec-pure Ho_2O_3 samples did not allow a determination of thulium to be made. Figure 3 shows the separation obtained for a 120 mg. spec-pure Ho_2O_3 sample to which 100 mg. of Tm_2O_3 had been added as carrier after irradiation. The amount of ytterbium present in the sample caused an ytterbium activity to be produced that is of the same order of magnitude as the thulium activity. The Yb/Tm ratio of this particular Ho_2O_3 sample would allow a separation of ytterbium and thulium to be made if a longer column were used. However, if the Yb/Tm ratio were much greater, the extra length of column needed to effect the separation would be impractically long. No interference of the type found for ytterbium was found for erbium because the only erbium

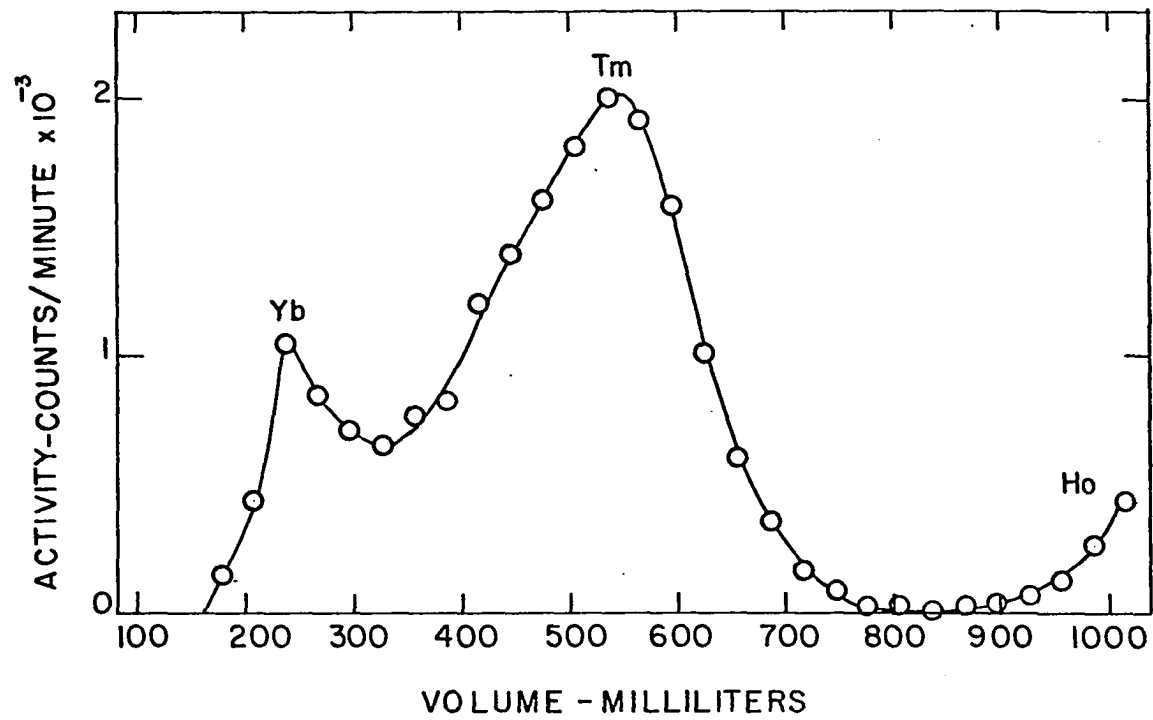


Figure 3. Elution curve for the separation of thulium from spec-pure Ho_2O_3

isotope measurable under the detection conditions employed was 7.5 hour Er-171 which had decayed before analysis.

The limitations of the above type of elution chromatography are obvious upon examination of Table 5. Although the table shows many ions that can be used as a wedge to separate a pair of rare earths, the cost of using a rare-earth ion as a wedge can be prohibitive when a column of Dowex 50 must be saturated with it. Depending on the closeness of two rare-earth stability constants, a divalent ion wedge may not provide separation on a reasonable size column in a reasonable time. Further limitations of this method are demonstrated by the Tm-Ho separation above. When approximately equal amounts of thulium and ytterbium are present in a holmium matrix, thulium can not be accurately determined because of its incomplete separation from ytterbium.

The wedge-method of elution chromatography as applied to trace analysis by neutron activation analyses is not a general method but is applicable to specific cases. If, for example, a holmium sample has a relatively high trace quantity of ytterbium in comparison to Tm and Lu, a determination of ytterbium can be easily performed. Analyses other than those suggested by Table 5 are possible when the pH of the eluent is changed. Increasing the pH from 8.45 to 8.65 does not change the elution sequence (74). However, decreasing the pH to 8.0 changes the elution sequence to Yb^{3+} , Tm^{3+} , Zn^{2+} , Er^{3+} , Co^{2+} , Ho^{3+} , Cd^{2+} , Dy^{3+} . With this sequence it is now possible to use cadmium as a wedge between holmium and dysprosium.

Table 5. Elution sequence and stability constants with $\text{NH}_4\text{-EDTA}$ at $\text{pH} = 8.45$ (73)

Ion	$\text{Log } K_{MY}^{M+n(n-4)}$ ^a	Ion	$\text{Log } K_{MY}^{M+n(n-4)}$
Sc^{3+}	23.1	Ho^{3+}	18.7
Cu^{2+}	23.3	Dy^{3+}	18.3
Ni^{2+}	23.1	Y^{3+}	18.1
Th^{4+}	23.2	Tb^{3+}	18.1
Pb^{2+}	22.6	Gd^{3+}	17.9
Lu^{3+}	19.9	Sm^{3+}	17.1
Yb^{3+}	19.8	Fe^{2+}	16.9
Zn^{2+}	19.1	Nd^{3+}	16.6
Tm^{3+}	19.3	Pr^{3+}	16.4
Co^{2+}	18.9	Mn^{2+}	16.6
Er^{3+}	18.9	Ce^{3+}	16.0
Cd^{2+}	19.0	La^{3+}	15.5
Al^{3+}	16.1		

^aThe arbitrary number 2.6 has been added to the actual values of the logarithms of the stability constants for all divalent ions so that the logarithms most nearly follow the same sequence as the elution order of all the above ions from a Dowex 50 column. The value

is defined as

$$K_{MY}^{M+n(n-4)} = \frac{[MY^{(n-4)}]}{[M^{+n}][Y^{4-}]}$$

in which Y^{4-} is the ethylenediaminetetracetate ion.

SUMMARY

A sensitive method of destructively determining thulium in a Ho_2O_3 matrix has been developed which is accurate to better than $\pm 4\%$ at a concentration of 10 ppm or higher. The procedure consists of a comparator method of neutron activation analysis with separation of the activated sample by NH_4 -EDTA on a cation exchange resin in the cadmium cycle. The counting rates of aqueous samples were determined with a gamma-ray scintillation spectrometer.

The trace amount of ytterbium present in the spec-pure Ho_2O_3 used did not allow a determination of thulium to be made in the one ppm range or lower due to incomplete separation of ytterbium and thulium. In the absence of ytterbium, thulium could be determined in the sub-ppm range.

The method that has been developed can be extended to determine rare-earth impurities, other than thulium, in different holmium matrices as well as in other rare-earth matrices. When extending the method to other analyses, one must consider the nuclear constants of the rare earth being analyzed, possible interfering activities produced in other rare-earth impurities, and the existence of a divalent ion that can be used as a wedge between the matrix ion and the ion of the rare earth being analyzed.

Part II. SEPARATION BY REVERSED-PHASE PARTITION CHROMATOGRAPHY

EXPERIMENTAL

Equipment and Materials

The column and collection system used for rare-earth separations by reversed-phase partition chromatography was similar to that described in Part I. Since the solid support is firmly packed in the column, a pressure system, as shown in Figure 4, was required to force the eluent through the column. A maximum flow rate of 1.2 ml/min. was obtained with a pressure of 6 psig. on the system. A rubber stopper in the eluent reservoir served as a pressure safety valve for the system.

A single channel gamma-ray scintillation spectrometer was used to measure the counting rates of all samples and standards. A lead shielded 2x2" well-type NaI(Tl) scintillation crystal and photomultiplier tube were used with the following transistorized R.I.D.L. components: Model 40-12B high voltage supply, Model 10-17 preamplifier, Model 30-19 linear amplifier, Model 33-10B pulse-height analyzer, and Model 49-25 scaler and timer. Integral counting was performed with the low energy pulse-height discriminator at 35 Kev. The dead time of the above system was 1.5 μ sec.

Gamma-ray spectra of samples and standards were recorded for comparison using a 4x4" well-type NaI(Tl) crystal in conjunction with a R.I.D.L. Model 34-12B multichannel analyzer. Read-out was a Frieden adding machine.

Quartz tubing used as ampoules for rare-earth samples was either CFQ Standard 204 tubing from the General Electric Company or Suprasil quartz tubing from Amersil, Incorporated.

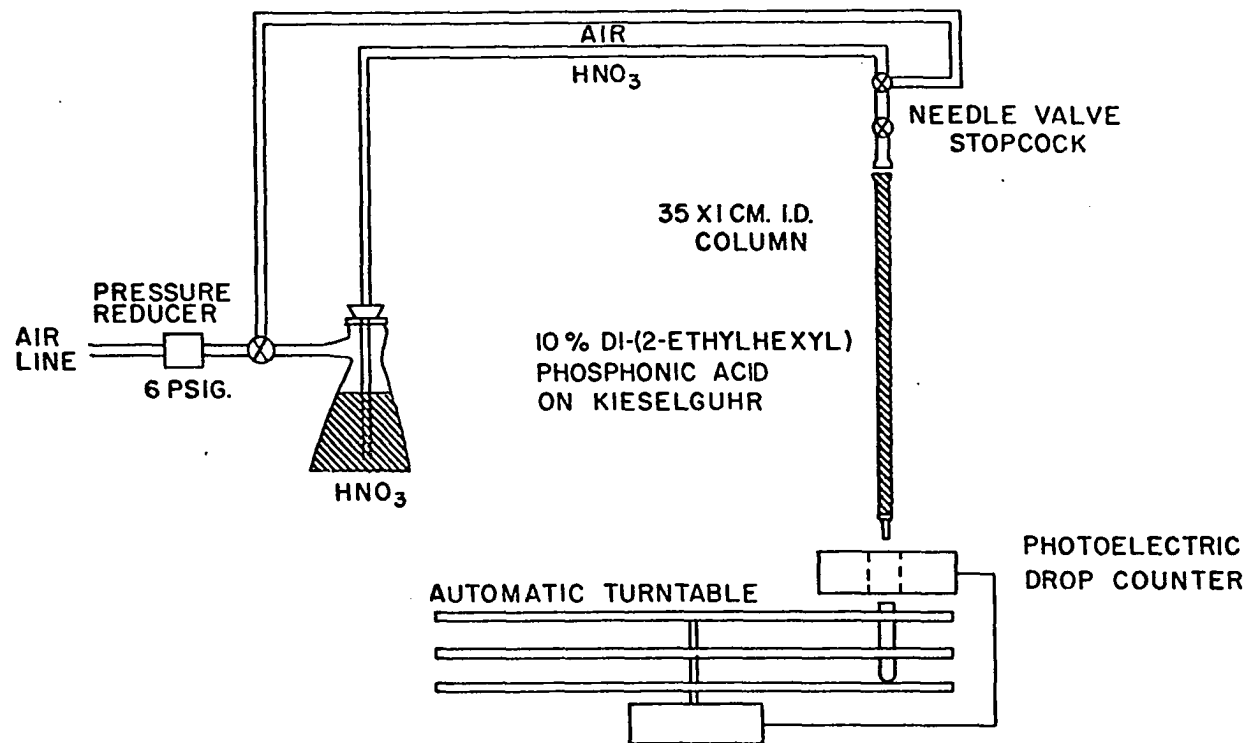


Figure 4. Elution and collection system

Rare-earth oxides used in the analyses were obtained from Ames Laboratory, Iowa State University. The emission spectrographic analyses of the oxides appear in Table 6.

Table 6. Emission spectrographic analyses of rare-earth oxides

Sample	Impurity (ppm)
Sm_2O_3	≤ 200 Nd, ≤ 100 Eu, < 200 Gd, < 100 Y, ≤ 100 Ca, ≤ 60 Si, ≤ 60 Fe
Eu_2O_3	< 250 Sm, < 250 Gd
Gd_2O_3	≤ 500 Sm, ≤ 200 Eu, ≤ 100 Tb, ≤ 1000 Y
Tb_4O_7	< 100 Dy, < 50 Y
Ho_2O_3	< 400 Dy, < 70 Er, < 100 Tm, < 50 Y
Tm_2O_3	< 400 Ho, < 50 Er, ≤ 30 Yb, < 30 Lu, ≤ 100 Y, no Th
Yb_2O_3	≤ 50 Er, ≤ 20 Tm, ≤ 30 Lu, ≤ 200 Th, ~ 500 Ca, ~ 8 Fe
Lu_2O_3	< 5 Yb, < 5 Ca

Kieselguhr, a diatomaceous earth marketed under the trade name Infusorial Earth by the Fisher Scientific Company, was used as a solid support for di-(2-ethylhexyl) phosphonic acid (HDEHP). The HDEHP obtained from Union Carbide Corporation was reputed to be $\geq 98\%$ pure. Since appreciable amounts of the mono-ester derivative (the dibasic acid, H_2EHP) can decrease the separation factors of the rare earths by forming strong and unselective complexes with them (66), the HDEHP was analyzed according to Baes, et al., (75). A pH titration was performed on HDEHP in a 75% ethanol-25% water solution using 0.2N NaOH as titrant. From

a Δ pH plot against Δ ml., the first inflection point, due to HDEHP + H₂EHP, and the second inflection point, due to H₂EHP alone, showed that the compound contained 99.1% HDEHP and 0.4% H₂EHP. The remaining impurities were attributed to 2-ethylhexanol and tri-(2-ethylhexyl) phosphate (75).

Other chemicals used in the analyses were of reagent grade quality.

Solid Support and Column Preparation

The separation of rare earths by reversed-phase partition chromatography is due to the exchange reaction of the rare-earth ions with the hydrogen ion of HDEHP. Since kieselguhr is used only as a solid support for liquid HDEHP, the kieselguhr must be completely inert so that it will not influence the exchange reaction. To ensure inertness, the diatomaceous earth is silanized to remove any surface Si-OH groups which may be present. Kieselghur was prepared for silanization by fractionating the original material. This was accomplished by collecting the fraction of kieselguhr which settled in a beaker within ten minutes after slurring it with water. The fractionated product was dried and silanized by exposing it to vapors of dichlorodimethylsilane in a closed dessicator for two days. The silanized material was dried for approximately ten hours at 160° C. Column material, containing 10% HDEHP, was prepared by adding HDEHP in hexane to a slurry of the silanized kieselguhr in hexane. The hexane was slowly removed under reduced pressure in a rotating flash evaporator. This material was used as column packing.

Small portions of column packing were firmly pressed and tamped into the column described above. The column packing varied in height from 30-31 cm., corresponding to 14-15 g. of material. The free volume

of the packing material was found to be 8.5% by elution of NaI^{131} through the column with water. Columns remained quite stable upon use, with only slight changes in separating ability being noticed after 4-7 l. of HNO_3 had been passed through.

Samples and Standards

Samples and standards were prepared similarly to those discussed in Part I. The samples of Ho_2O_3 contained in General Electric quartz tubing were weighed by difference on a microbalance. The weight of a holmium sample contained in Suprasil quartz tubing was determined by pipetting a 100 μ aliquot of a 100 mg/ml. solution of Ho_2O_3 , in nitric acid, into a quartz tube followed by three washings of the pipette. All standards were prepared by dissolving a known weight of about one gram of each rare-earth oxide in nitric acid followed by dilution of the solutions to 100 ng/ml. Ten nanograms of a solution was transferred by pipette to a quartz tube of the type used for the corresponding holmium sample. Samples and standards were dried, sealed, and wrapped in aluminum foil as described in Part I. All quartz tubing had been cleaned in hot concentrated nitric acid for one hour and then flushed with distilled water.

Irradiation and Analysis

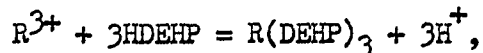
Irradiations were performed in the Ames Laboratory Research Reactor for 5-7 days at an integrated flux of 1.5×10^{19} n/cm². Samples and standards were received shortly after irradiation and were removed from the irradiation can in a "hot" cell with master-slave manipulators due to the high activity of Ho-166. The rare-earth standards were separated

immediately while the holmium samples were allowed to decay for approximately one week.

The standards were separated in order to prevent possible contamination from unknown activities. Individual standards were prepared for separation by breaking the quartz ampoule containing the standard under water. Nitric acid was added to aid dissolution and 10 μ g. of the same rare earth as the standard was added as carrier. The solution was evaporated to approximately 10 ml. and then decanted through glass wool to remove fine quartz particles. The major portion of the broken quartz ampoule was washed three times with hot 3N HNO₃, each portion being decanted through the glass wool. The decanted solution was evaporated to about 5 ml., transferred to a 40 ml. pyrex centrifuge tube, and evaporated to dryness in a water bath. The standard was dissolved in nitric acid of the same concentration used initially for the separation and transferred, with washings, to the column.

Holmium samples were prepared for separation as described above, except that no carrier was added.

The rare earths were separated by elution with nitric acid. Since the exchange reaction between rare-earth ions in solution and the HDEHP on the solid support is represented (65) by



the elution rates of the rare earths were controlled by adjusting the hydrogen ion concentration using a stepwise gradient elution technique. The eluent was fractionally collected in 2.6 ml. portions. The fractions of eluent making up each rare-earth elution peak were combined, evaporated to a small volume, and transferred to a test tube suitable

in size for counting in a well-type scintillation crystal. When two or more rare earths were not completely separated, the fractions that included the elution peaks were combined, evaporated to a small volume, transferred to a 40 ml. centrifuge tube, and evaporated to dryness. The rare earths were then dissolved, loaded on the column and re-separated.

The final comparator measurement of a rare earth with its standard was made by counting the solutions in identical test tubes. The liquid levels in the test tubes were the same height in order to reduce any error due to different counting geometries.

RESULTS AND DISCUSSION

The reversed-phase partition chromatographic separation of nanogram quantities of rare-earth impurities from a 10-20 mg. sample of holmium could not be obtained by one pass of the sample through a column. The lighter rare earths, which precede holmium in elution sequence, trailed as they were eluted from the column, although this effect did not occur for the rare earths heavier than holmium. Trailing of the lighter rare-earth impurities in the original sample can be attributed, therefore, to the difficulty of separating the impurities from the chemically similar environment of holmium which is approximately six orders of magnitude more abundant.

Complete separation of the rare-earth impurities from holmium involved two passes of the sample through a column. In the first separation, as shown in Figure 5, the rare earths lighter than holmium were separated as a group while the heavier rare earths were separated individually. The normality of the HNO_3 used as eluent appears at the top of the figure. The lighter group of rare earths, with a small portion of the leading edge of the holmium elution peak, to ensure obtaining all the lighter rare earths, was then individually separated on another column as shown in Figure 6. The elution peaks marked with a question mark could not be identified. Elutions were performed at a flow rate of 0.6-1.2 ml/min., depending on the rare earths being separated, and took approximately five hours to complete.

The weights of the samples and standards sealed in General Electric quartz tubing are presented in Table 7. The activities of the impurities

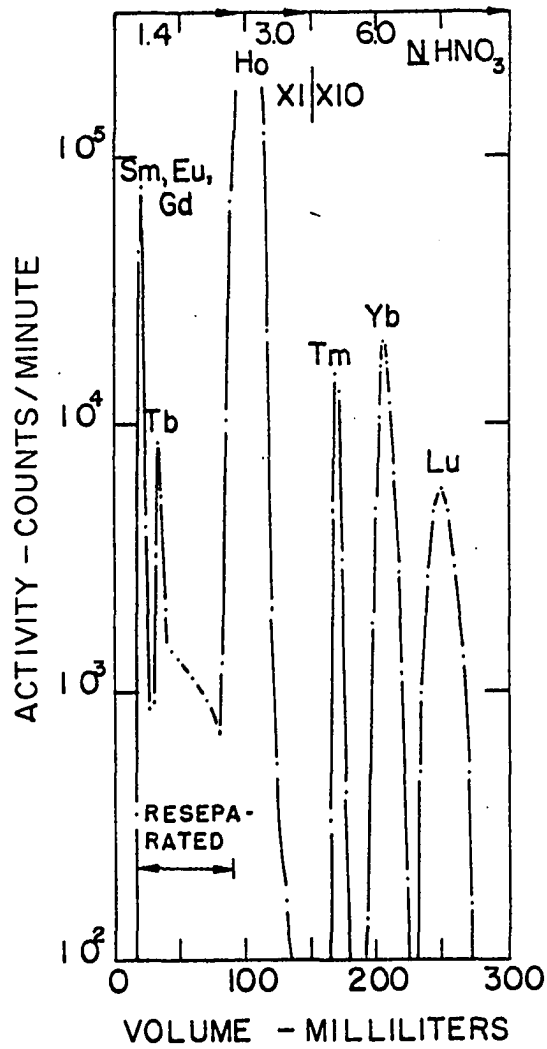


Figure 5. Elution curve for the separation of heavy rare earths from spec-pure Ho_2O_3

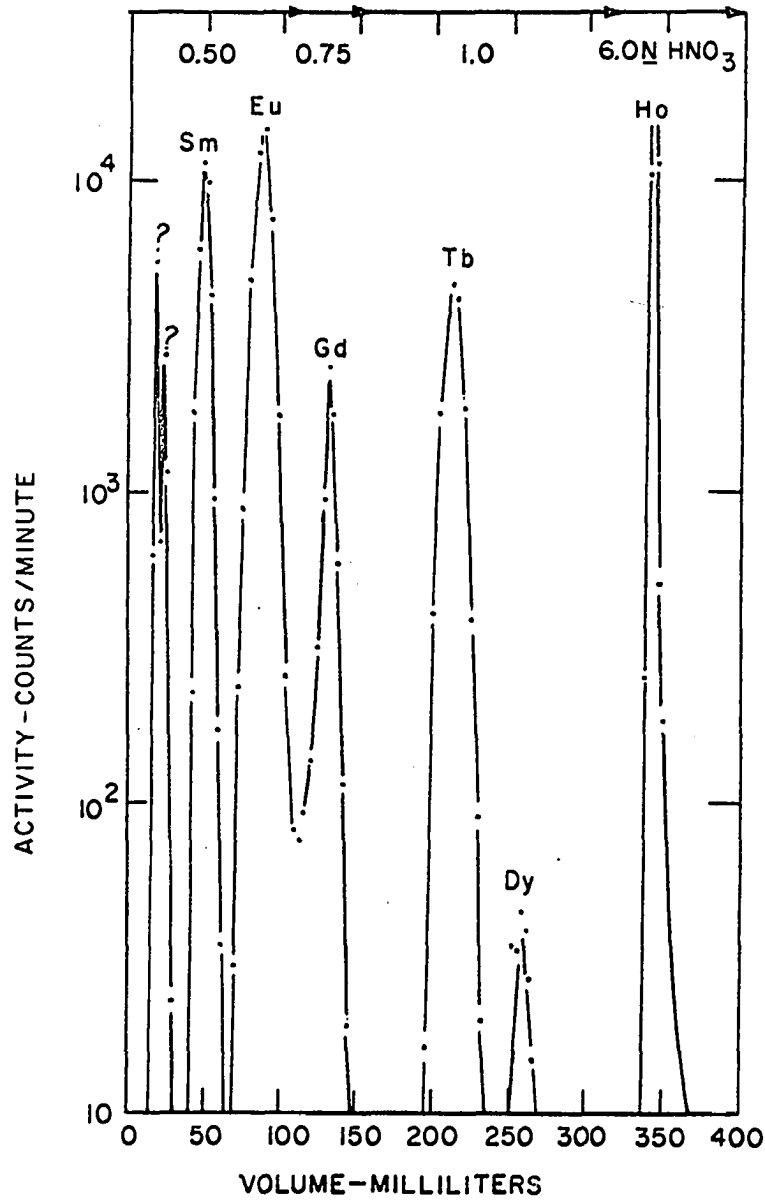


Figure 6. Elution curve for the separation of light rare earths from spec-pure Ho_2O_3

Table 7. Weights of samples and standards sealed in General Electric quartz tubing

<u>Standards</u>		<u>Samples</u>	
Rare earth	ng. metal	Number	mg. Ho
Eu	9.0511	1	11.073
Tb	10.001	2	13.800
Tm	9.9970	3	19.196
Yb	10.016	4	16.405
Lu	10.029		

in the holmium samples and the activities of the corresponding standards, after chromatographic separation, appear in Table 8. Listed in Table 9 are the analyses of the holmium samples for Eu, Tb, Tm, Yb, and Lu.

The precision of the data presented in Table 9 is indicated by the standard deviations of the average analyses which are, respectively, ± 1.8 , ± 13 , ± 23 , ± 25 , and $\pm 15\%$ for Eu, Tb, Tm, Yb, and Lu.

Although the precision of the data is fair for europium, it is poor for the other rare earths. The high precision of the europium analyses in comparison to the analyses of the other rare earths indicates that sample inhomogeneity is not the major factor causing poor precision.

Due to the low precision of the data above, a piece of General Electric quartz tubing was irradiated under the same conditions and analyzed. The elution curve, four days after irradiation, for the quartz tubing is shown in Figure 7. The Sm, Eu, and Gd in Figure 7

Table 8. Activities of rare-earth impurities and standards sealed in General Electric quartz tubing

Holmium Sample	<u>Activities (C/M)^a</u>									
	Eu impurity	Eu standard	Tb impurity	Tb standard	Tm impurity	Tm standard	Yb impurity	Yb standard	Lu impurity	Lu standard
1	62979	22457	14733	20301	1553	4924	4708	7597	2368	11085
2	80832	22140	25032	22247	2671	5036	14520	11777	9732	25543
3	111280	22319	25514	19608	3323	4930	9037	7154	4076	8311
4	94874	22435	29640	21006	4102	5081	15688	9867	7894	18689

^aMinimum of 10^4 counts were accumulated per measurement.

Table 9. Analyses of Ho₂O₃ sealed in General Electric quartz tubing

Holmium Sample	<u>Impurity (ppb, atomic)</u>				
	Eu	Tb	Tm	Yb	Lu
1	2292 ± 18 ^a	655.5 ± 5.1	284.7 ± 3.8	560.6 ± 6.8	193.5 ± 2.8
2	2395 ± 18	815.4 ± 7.5	384.2 ± 5.8	895. ± 10	276.9 ± 2.7
3	2351 ± 17	678.0 ± 6.4	351.0 ± 4.8	659.1 ± 7.6	256.2 ± 2.5
4	2333 ± 17	860.2 ± 7.7	492.0 ± 7.0	971. ± 10	258.2 ± 2.8
Average	2343 ± 43 ^b	752.3 ± 100.9	378.0 ± 86.5	771.4 ± 193.4	246.2 ± 36.3

^aThe standard deviation of an analysis was calculated from counting rates only.

^bThe standard deviation was calculated from the differences between the average and the individual analyses.

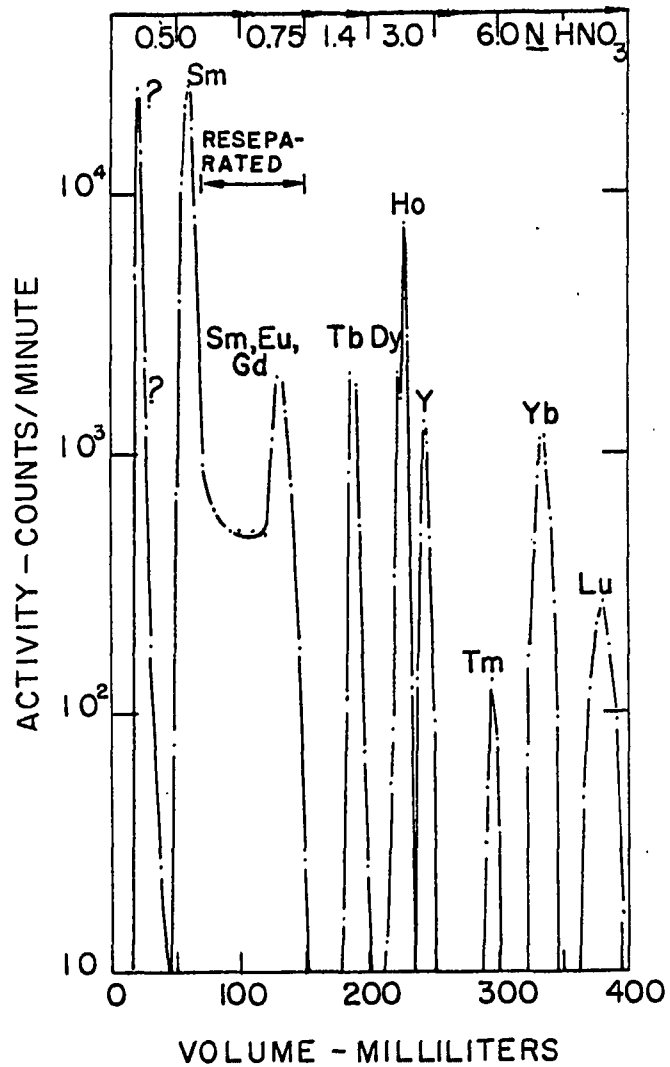


Figure 7. Elution curve for the separation of rare earths from General Electric quartz tubing

were re-separated as shown in Figure 8. The tubing, although containing no added rare earths, was treated as if it contained a rare-earth sample. In Figure 9 is presented the elution curve, two days after irradiation, for the europium standard used in the previous Ho_2O_3 analyses. The similarities of Figures 7 and 8 to Figure 9 indicates that the General Electric quartz tubing contained quantities of rare earths that were of the same order of magnitude as the amounts of rare-earth impurities in the Ho_2O_3 samples. The rare earths were displaced from the quartz by an ion-exchange reaction (76) between the hydrogen ions in solution and the rare-earth ions on the newly exposed quartz surfaces of the broken ampoule. Since each broken quartz ampoule has a different amount of fresh surface area exposed, different quantities of rare earths are displaced from the ampoules resulting in low precision for the analyses of the rare earths in the Ho_2O_3 samples.

The data presented in Table 8 were corrected for the counting rates due to impurities from the quartz tubing analysis. The errors introduced into the rare-earth analyses in Table 9 were calculated for the lowest and highest weight Ho_2O_3 samples and were, respectively, Eu: -2.6 and -3.0%; Tb: 9.7 and -4.5%; Tm: 19 and 3.7%; Yb: 32 and -7.5%; and Lu: 21 and 2.8%. These errors are only approximate because the ampoule used for the quartz tubing analysis most likely had a different freshly exposed surface area than those ampoules containing Ho_2O_3 samples. Although the above errors due to the quartz impurities are only approximate, they do account for the precision of the average analyses as expressed in Table 9. For example, the high precision of the average

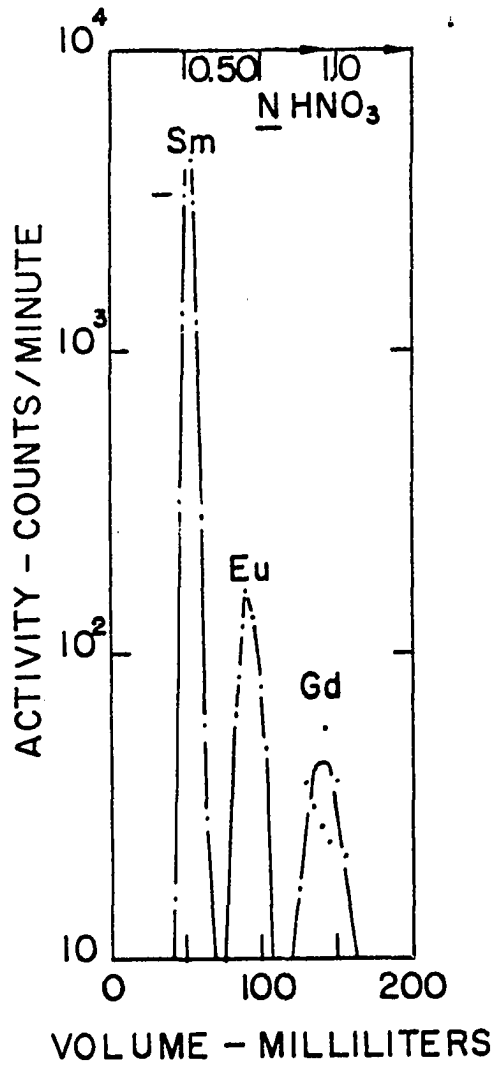


Figure 8. Elution curve for the re-separation of Sm, Eu and Gd from General Electric quartz tubing

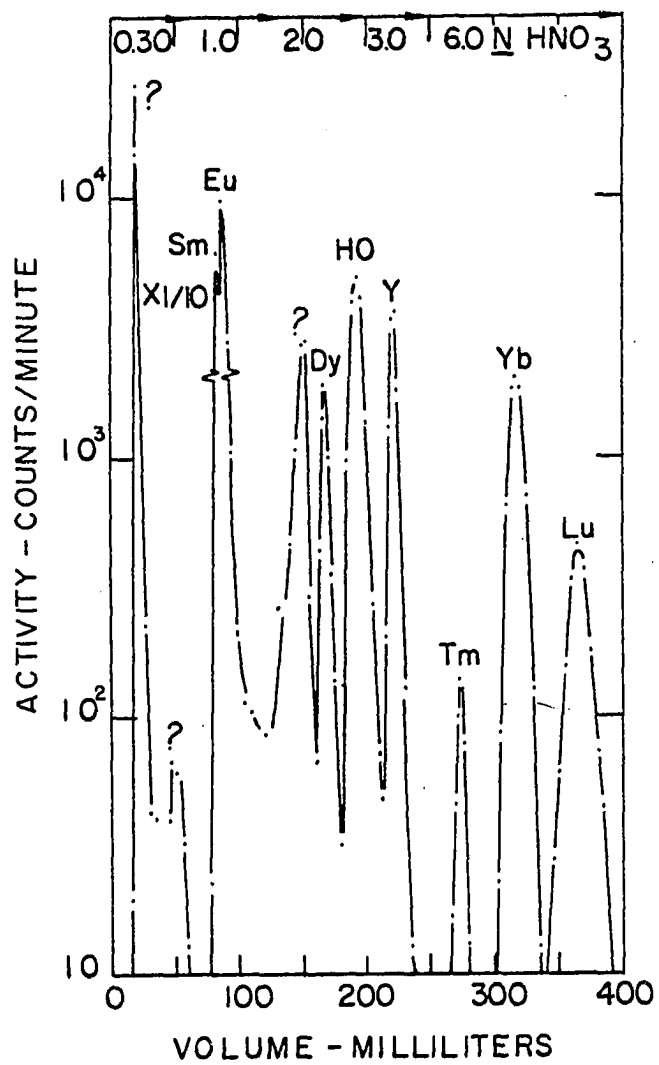


Figure 9. Elution curve for the separation of the europium standard

europium analysis is due to the small amount of europium impurity from the quartz as compared to the amount of europium from the Ho_2O_3 samples, themselves.

Suprasil, a synthetic quartz tubing, was also used as an ampoules for the rare-earth samples and standards because of the high purity of the quartz reported by Shedlovsky and Mott (77) and by Gleit, et al. (78). Analysis of a piece of Suprasil containing no added rare earths showed only the presence of sodium, which moves off the column with the eluent front, and samarium. The samarium impurity, however, was only 0.1% of the total samarium activity from the standard and 0.5% of the total samarium activities from the Ho_2O_3 samples.

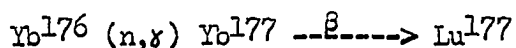
The weights of the samples and standards sealed in Suprasil appear in Table 10. After irradiation the samples were separated as described

Table 10. Weights of samples and standards sealed in Suprasil quartz tubing

<u>Standards</u>		<u>Samples</u>	
Rare earth	ng. metal	Number	mg. Ho
Sm	10.179	1	10.004
Eu	9.0511	2	10.004
Gd	10.086	3	10.004
Tb	10.001		
Tm	9.9970		
Yb	10.016		
Lu	10.029		

previously except that 1.2N HNO₃ was used to completely separate the Sm-Eu-Gd-Tb fraction from Ho, see Figure 5, and that 0.45N HNO₃ was used to completely separate Eu from Gd, see Figure 6. The activities of the impurities in the Ho₂O₃ samples and the activities of the corresponding standards are presented in Table 11. Listed in Table 12 are the analyses of the holmium samples for Eu, Gd, Tb, Tm, Yb, and Lu.

The precision of the data in Table 12 is indicated by the standard deviations of the average analyses, which are respectively ± 1.8 , ± 0.97 , ± 0.73 , ± 2.2 , ± 1.3 , and $\pm 1.0\%$. The average standard deviations per analysis based on counting rates are, respectively, ± 0.77 , ± 1.7 , ± 1.2 , ± 1.5 , ± 1.3 , and $\pm 1.3\%$. The accuracy of the data is inferred from its high precision as well as from the accuracy of the thulium analyses from the previously described ion-exchange work. The lutetium analysis is expected to be slightly high due to the reaction



Calculation of the amount of lutetium produced from ytterbium indicates that the error in the lutetium analysis is about 2%.

The results on the terbium content were found to decrease with increasing time when the counting technique previously described was used. Gamma-ray spectra of the standard samples were those due to Tb¹⁶⁰ except for the presence in the sample of additional gamma rays with energies below approximately 200 Kev. The samples were also observed to decay with a shorter half-life than that of the standard which showed the 72 hour half-life characteristic of Tb¹⁶⁰. The activity due to 6.9 day Tb¹⁶¹, produced by a double neutron capture reaction, was negligibly small. The presence in the samples of an active isotope which was not

Table 11. Activities of rare-earth impurities and standards sealed in Suprasil quartz tubing

Holmium Sample	<u>Activities (C/k)^a</u>											
	Eu Impu- rity	Eu Stand- ard	Gd Impu- rity	Gd Stand- ard	Tb Impu- rity	Tb Stand- ard	Tm Impu- rity	Tm Stand- ard	Yb Impu- rity	Yb Stand- ard	Lu Impu- rity	Lu Stand- ard
1	58277	23648	4454	469.7	3281	4018	1497	3667	5399	11194	4590	14368
2	57860	23576	4550	485.3	3272	4018	1476	3738	6143	12473	5751	17960
3	59183	23595	4510	471.8	3236	4018	1513	3675	4824	9773	3853	11839

^aA minimum of 10⁴ counts were accumulated per measurement.

Table 12. Analyses of Ho_2O_3 sealed in Suprasil quartz tubing

Holmium Sample	<u>Impurity (ppb atomic)</u>					
	Eu	Gd	Tb	Tm	Yb	Lu
1	2230 ± 17^a	9560 ± 164	816.3 ± 10.6	408.0 ± 6.9	482.9 ± 6.8	320.3 ± 3.9
2	2220 ± 17	9452 ± 167	814.1 ± 10.7	394.6 ± 6.1	493.1 ± 6.5	321.0 ± 4.0
3	2269 ± 18	9637 ± 151	805.1 ± 10.5	411.4 ± 6.0	494.2 ± 5.8	326.3 ± 4.5
Average	2240 ± 26^b	9550 ± 93	811.8 ± 5.9	407.7 ± 8.9	490.1 ± 6.2	322.5 ± 3.3

^aThe standard deviation of an analysis was calculated from counting rates only.

^bThe standard deviation was calculated from the differences between the average and the individual analyses.

present in the standard could be due to the elution of an activated non-rare-earth impurity from the column with terbium. The additional activity could also be attributed to a terbium isotope, other than Tb^{160} , that was produced from a nuclear reaction in a rare-earth impurity or in the matrix itself. Interference in the terbium analyses was eliminated by counting only the portion of the Tb^{160} gamma-ray spectrum above 350 Kev.

The samarium analyses were also found to decrease when the standard and samples were counted at different times. A counting technique similar to that used for terbium was not used for samarium due to the low activity and short half-life of the predominant Sm^{153} isotope. The amount of samarium present in the Ho_2O_3 samples was estimated to be 3 ppm.

Rare earths lighter than samarium were not observed in the Ho_2O_3 samples analyzed. Dysprosium and yttrium were found in the samples but were not quantitatively determined. Erbium, the only heavy rare earth not observed, is difficult to detect because the isotopes produced either have short half-lives or low gamma-ray energies.

The time required to perform these analyses depends to a large extent on the activity induced in the rare-earth matrix and on the number of rare-earth impurities to be separated. For example, five days were required to irradiate a 10 mg. Ho_2O_3 sample, and ten days were required for the holmium activity to decay to a safe level for handling. Remote control handling of the samples can be used, however. After decay, the separation and complete analysis of seven rare-earth impurities in a Ho_2O_3 sample took about twenty hours. Rare-earth standards required approximately three hours apiece to prepare and could be worked with immediately after irradiation while the samples were decaying.

Activation analysis followed by separation using reversed-phase partition chromatography should be adaptable to determining rare-earth impurities in rare-earth matrices other than holmium. The problem of neutron self-shielding, which was not observed in this work, is probable in matrices of Sm, Eu, Gd, and Dy due to their high thermal neutron cross sections.

SUMMARY

A method has been devised for the analysis of trace rare-earth impurities in a spectrographically-pure Ho_2O_3 matrix. Europium, gadolinium, terbium, thulium, ytterbium, and lutetium were determined in the 0.3-10 ppm range with a precision of approximately $\pm 2\%$. The procedure consisted of a comparator method of neutron activation analysis involving separation of the activated sample by reversed-phase partition chromatography. The counting rates of the rare earths in aqueous solution were determined with a gamma-ray scintillation spectrometer. The purity of each rare earth was determined by comparison of its gamma-ray spectrum with that of the standard for that element.

The use of standard quartz tubing to contain rare-earth samples and standards was found to lead to erroneous results because of the rare-earth impurities in the tubing. Errors due to rare-earth impurities from synthetic quartz tubing were found to be within the experimental errors of the analyses.

The method developed is general enough to be easily adaptable to the determination of rare-earth impurities in rare-earth matrices other than holmium.

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