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INSTRUMENTAL ACTIVATION ANALYSIS
OF RARE EARTH MIXTURES

by

Duane Ernest Becknell

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INTRODUCTION

Activation Analysis

Activation analysis is a technique by which qualitative as well as quantitative determinations can be made of a component by measuring the radiation emitted from a nuclide which was produced from the component by a selected nuclear transformation. If each different induced radioactivity can be distinguished or separated from all others produced, the amount of each radioactivity is a measure of the quantity of the parent nuclide present in the material. During recent years activation analysis, particularily neutron activation analysis, has enjoyed continued and advancing success with the development of multichannel analyzers, solid state and scintillation radiation detectors, and computer hardware and software. The method is in general fast, economical, nondestructive and highly sensitive.

The activation of a sample can be accomplished in one of several ways. Irradiating particles might include fast and thermal neutrons, photons, and a variety of heavy atoms. During the bombardment, atoms of the sample are transformed into other nuclides either of the same or of different elements. If the isotopes produced from one or more constituents is radioactive and if its radioactivity can be distinguished or separated from other activities present, the amount of this radioactivity is a measure of the parent isotope and, hence, of the parent element in the original sample. As an example, the thermal neutron activation of holmium proceeds as follows: holmium which is 100 percent holmium-165 captures a thermal neutron to produce holmium-166 which is unstable and emits a beta particle producing stable erbium-166. In addition to the beta particle, gamma rays are emitted which arise from the de-excitation of upper energy levels in erbium-166. Thus either the beta particles or the gamma rays could be measured. If at all possible gamma rays are used because of their characteristic energies.

Of the possible irradiating particles which are available the one most frequently used is the neutron at thermal energies (0.025 ev), the characteristic energy of moderated reactor neutrons. The advantages of using thermal neutrons include the lack of an energy threshold for the bombarding neutrons as well as the availability of these neutrons. Typically thermal neutron fluxes on the order of 10^{12}-10^{13} n/cm^2-sec are easily obtained in a nuclear reactor. The reaction most frequently observed with thermal neutrons is the (n, γ) reaction. Here, as in the above example, a neutron is added to the nucleus and gamma rays are emitted within approximately 10^{-9} seconds. These "prompt" gamma rays range in energy from 10^3 to greater than 10^6 electron volts. Neutrons of other energies are also used. Neutrons directly from fission have average energies of one to two million electron volts and can induce some reactions in addition to the (n, γ) capture process. High energy (14 Mev) neutrons can readily be produced in simple accelerators by the D + T reaction but the fluxes are much lower (10^8 - 10^9 n/cm^2-sec). These higher energy neutrons can induce a greater variety of reactions such as (n, p), (n, α), and (n, 2n). Greater opportunity for varied reactions exist with the use of charged particles where reactions such as (d, p), (d, n), (d, α), (α, n) and (α, p) are possible.

The rate of production of a given species during a thermal neutron irradiation is given by the equation

$$R_{Growth} = \frac{dN}{dt} = n\sigma\phi = \frac{N_a\sigma\phi wf}{M} \qquad (1)$$

where N is the number of atoms of the product nuclide at time t, N_a is Avogadro's number, σ is the neutron capture cross section in cm^2, ϕ is the flux in n/cm^2, w the weight of the element being determined, f the fractional abundance of the isotope responsible for the nuclear reaction, and M is its molecular weight. At the end of the period of irradiation the rate of decay of a particular species is given by

$$R_{Decay} = -\frac{dN}{dt} = \lambda N \qquad (2)$$

where N is the number of atoms of the species and λ is its decay constant. Activation analysis is concerned with the number of atoms of a given nuclide which are present at some specified time after the end of an irradiation. At the end of an irradiation the overall rate of the formation of a given nuclide is its formation rate minus its decay rate, i.e.,

$$\frac{dN}{dt} = R_{Growth} - R_{Decay} \tag{3}$$

$$= \frac{N_a \sigma \phi wf}{M} - \lambda N \tag{4}$$

which upon integration yields

$$\frac{dN}{dt} = \frac{\sigma \phi N_a wf}{M} (1 - e^{-\lambda t}) \tag{5}$$

At any time, T, after the end of an irradiation the activity, A, of the species is

$$A = \frac{\sigma \phi N_a wf}{M} (1 - e^{-\lambda t})(e^{-\lambda T})$$

The detection of the gamma rays produced during the radioactive decay process can be performed in any one of several ways. Perhaps the simplest method of observation is a visual one in which light can be seen when emitted after gamma rays have been allowed to impinge on scintillators. A much more exact count can be obtained by allowing electronic instruments to count these light impulses. This is the basis for the scintillation detection systems which have enjoyed wide popularity during the past two decades. In recent years improvements over these scintillation detectors have been available with the perfection of solid state detectors. In particular, lithium-drifted germanium-detectors which operate on an ion chamber principle allow greater resolution of gamma rays. Under proper conditions gamma rays as close as 4 kev apart in energy can be resolved with these detectors. There are certain problems which arise when using either the scintillation or solid state gamma ray detection systems. The problem of resolution, although greatly improved in the solid state system, must always be anticipated. The effects of the Compton continuum adding unusually large numbers of background gamma rays must also be considered. This effect reduces the relative size of gamma ray peaks whose energies fall within the Compton background energy range. In turn, the area calculated under a peak which has a large Compton background will not represent purely photoelectric events.

Once data have been removed from the instrumental system there are several methods by which the analysis can be performed. First, and perhaps the least desirable, is the absolute method. This method uses Equation 6.

$$W = \frac{AM}{N_a \sigma \phi f(1 - e^{-\lambda t_1})} \tag{6}$$

which is obtained from a rearrangement of Equation 5. By inserting the values of all of the quantities in Equation 6 the weight of the species of interest in the sample can be determined. There are, however, several difficulties with this method. Specifically, cross sections and fluxes are seldom known with sufficient accuracy for quantitative analysis. In order to obtain the exact value for the flux, ϕ, a flux monitor must be measured along with the sample. Due to the fact that it is physically impossible for both the sample and flux monitor to occupy the same position in the irradiation facility there will be differences in the flux received by the two specimens. There will thus be an error induced into the analysis.

A second method of data handling is the comparator or external standard method. Here the amount of a component in an unknown, W_u, is determined from the activity of the component in that unknown, A_u the activity, A_s, due to the same component in a standard and the known amount of the element in the standard, W_s. The equation relating these is

$$W_u = \frac{W_s A_u}{A_s} \qquad (7)$$

The primary disadvantage in the external standard method lies in its limitation to a relatively small number of components in a mixture. The method can, under certain conditions, be used for up to 10 or 15 elements. A second problem arises from the limitation of physical space in the irradiation facility. Although it is assumed that the flux received by each sample is the same this may not be true. Fluxes vary widely depending upon position in an irradiating facility. In an attempt to minimize any flux differences, samples are irradiated simultaneously and in as close proximity as possible.

A third method of data handling is the internal standard method. In this method the activity of a certain radionuclide in an unknown sample is compared to the activity of another radionuclide in the same sample. This yields a ratio of the areas under two gamma ray peaks which is then compared to the ratio of the same two gamma ray peaks in a standard spectrum. From this third ratio, the internal standard ratio, the amount of a given component can be determined since the divisor used in calculating the first two ratios is the same for both spectra or is known to represent a certain added amount of that component in each spectrum. In addition, the amount of the species of interest in the standard spectrum is known and therefore the only unknown is the amount of that species in the spectrum of the sample of unknown composition. For example, in a two component system containing Tb and Ho where the Ho 1380 kev gamma ray is the internal standard peak, the area under each Tb gamma ray peak is divided by the area under the Ho 1380 kev peak in the same spectrum. For a set of n samples, n ratios are generated. One of the samples is then chosen to be the standard and the Tb/Ho ratio for that sample is divided into the Tb/Ho ratios for each of the remaining samples thus generating n-1 internal standard ratios. Knowing the amount of Ho in each sample as well as in the designated standard and the amount of Tb in the standard, the amount of Tb in the samples of unknown composition can be determined by

$$Tb_{unk} = (ISR)\left(\frac{Ho_{unk}}{Ho_{std}}\right)(Tb_{std}) \tag{8}$$

where Tb_{unk} is the amount of Tb in the sample of unknown composition, Tb_{std} the amount of Tb in the standard, Ho_{unk} and Ho_{std} the amount of Ho in the unknown and standard respectively and ISR is the calculated internal standard ratio. In general, the amount of Ho in the unknown and standard samples will be the same and thus $Ho_{unk}/Ho_{std} = 1$.

As in any chemical analysis there are errors which are inherent in a radioactivation method. Systematic errors comprise such items as contamination of compounds used for targets or of the irradiation capsule. Due to the high sensitivity of activation analysis and the size limitations during irradiation, smaller samples are usually used in activation studies than in wet chemical methods. For this reason any inhomogeneity in the sample is important and relative contamination is greater than with other methods.

The problems imposed by differences in isotopic ratios are also important in activation analysis and care must be taken to assure that differences in this ratio in the standards and in the unknowns do not exist. As has previously been mentioned, the flux at various points in an irradiating facility will in general not be uniform. Care must be taken to minimize any differences in flux received by unknown and standard samples. It is possible, however, to circumvent this particular difficulty by using the internal standard method of data reduction.

Another problem which must be considered is the self-shielding phenomenon which occurs in the irradiation of high neutron cross section nuclides. This reduces the flux as neutrons pass through a sample and the center might not receive the same number of neutrons as the surface. Thus as the weight of a sample increases its specific activity decreases.

Errors which are charactertistic of the counting system also exist. Specifically, the geometry under which specimens are counted must be matched as closely as possible from sample to sample. Variations in the configuration of counting might cause erroneous results if not properly handled. This problem is usually minimized by imposing physical restraints so that each sample is maintained in exactly the same geometry.

A very important source of error in activation analysis arises from the possible existence of interfering gamma rays, i.e., gamma rays from impurity elements or of matrix elements which have energies close enough to the energy of the gamma ray of interest that resolution is impossible. This problem can sometimes be circumvented by allowing samples to decay so that the interference no longer exists. This is possible, of course, only when the half-life of the interfering activity is significantly different from that of the species of interest. If this is not the case the technique of spectrum stripping is sometimes helpful. In this method a spectrum of the interfering substance is collected and a point-for-point subtraction of this spectrum from the composite spectrum effects the removal of the interference. The technique is in general extremely difficult to use due to the necessity of exactly reproduced geometries as well as the prevention of gain shifts which will move the gamma ray peaks from one position in a given spectrum to a slightly different place in another spectrum. In either case, a point-for-point subtraction will invariably yield erroneous results.

In addition to problems which originate from irradation, counting and interfering gamma rays, the question of interfering reactions must also be considered in any activation analysis procedure. This involves the production or loss of the nuclide of interest in one of two ways. One type of interfering reaction involves the production of the species of interest from the irradiating particles and other nuclides which are present. For example, the (n, γ) reaction on a nuclide with atomic number Z and mass number A could produce the same product as the (n, p) reaction on a nuclide with atomic number $Z + 1$ and mass number $A + 1$. This type of an interfering reaction is referred to as a primary interference. A secondary interference produces an increase or decrease in the yield of the species of interest through a subsequent transformation of a nuclide which has previously been produced by the irradiating particles.

One of the most important, and yet often overlooked, errors in activation analysis arises from the statistical nature of the radioactive decay process. When the half-life of a radionuclide is much greater than the counting interval, which is usually the case, the relative standard deviation, σ_R, of the number of counts observed over the time interval Δt is given by

$$\sigma_R = \frac{(\text{counts})^{1/2}}{(\Delta t)(\text{counts})} \times 100 \tag{9}$$

Assuming a minimum of ten thousand counts over the counting interval, the maximum standard deviation of the count rate will be one percent. Obviously as the counting interval increases the standard deviation expressed as a percentage decreases and the analysis becomes more reliable.

Activation analysis, as with any other analysis method, has its inherent advantages and disadvantages. Advantages include a wide variety of methods of activation which allow selection of the method most applicable to a given problem. The differences in half-life, mode of decay, and energy of decay of the respective transformation products make optimization of the analytical method possible. In addition there is often no need for a chemical work-up or any post irradiation wet chemical handling. On the negative side is the expense of obtaining and operating highly sophisticated equipment such as reactor or accelerator, detectors and associated electronic gear. An often overlooked disadvantage is that activation analysis yields no information as to the chemical form, structure, or states of a species which is present. The method measures only the total amount of a nuclide which is contained in a sample.

There are many books and reports available which collectively discuss all aspects of activation analysis. Among them Bowen and Gibbons (1) present many examples while fundamentals are covered by Lyon (2) and Brooksbank (3), the latter also including sections on experimental determinations. Other books include Taylor (4) and Lenihan and Thompson (5) the latter extensively treating computer applications to activation analysis. A handbook has been written by Koch (6) which includes references for analyses by thermal neutrons, fast neutrons and charged particles plus selected nuclear data, threshold energies, sensitivities and possible interfering nuclear reactions. A literature search has been reported by Raleigh (7) and an activation analysis bibliography published by the National Bureau of Standards and edited by Lutz, Boreni, Maddock and Meinke (8). The latter contains a listing of papers and an author bibliography, as well as listings by element determined, matrix analyzed and technique used. General aspects of gamma-spectrometry have been discussed by Heath (9, 10) and Crouthamel (11). Information such as tables of nuclides by their gamma ray energy and catalogs of gamma ray spectra can also be found in these sources. Hughes and Harvey (12) have written a text in which neutron capture cross sections as a function of neutrons energy can be found. Nuclear information is compiled and can be found in Nuclear Data (13) where detailed nuclear energy levels and decay schemes plus other data are presented. Nuclear energy level diagrams can also be found in Lederer, Hollander and Perlman (14); the chart of the nuclides (15) published for the USAEC contains a wide variety of recent data. Many examples of the application of activation analysis to various problems can be found in reports from the three International Conferences on Modern Trends in Activation Analysis (16, 17, 18).

Rare Earths

The rare earth or lanthanide elements are the 14 elements following lanthanum in the periodic chart where the 4f electrons are added to the lanthanum electronic configuration. The 4f electrons of the rare earths are deeply buried in the atoms and ions. Electrons occupying these orbitals are screened from the surroundings by overlying 5s and 5p electrons and thus reciprocal interactions between the 4f electrons and their environment are of little chemical significance. This, in turn, forces the rare earths to be similar in their chemical properties. The largest M^{3+} ion is La^{3+} with a radius of 1.061 Å and the radii range downward to Lu^{3+} at 0.848 Å. The chemistry of the M^{3+} species is determined largely by their ionic character and by the size of the M^{3+} ion (19).

Yttrium which is above La in transition group III has a similar +3 ion with a noble gas core. It has atomic and ionic radii similar in size to Tb and Dy and is therefore generally included with the rare earths. It occurs naturally with them and Y(III) resembles Tb(III) and Dy(III) in its compounds. The lightest group III A element, scandium, also has a +3 valence state but possesses a much smaller ionic radius than the rare earths and is generally not considered to be a rare earth.

Major deposits of rare earth ores exist in Scandinavia, India, Soviet Union and the United States. Of the many minerals the most important is monazite which is a lanthanide orthophosphate with up to 30 percent thorium. Ninety percent of the rare earths found in minerals are the lighter elements La, Ce, Pr and Nd while Y and the heavier elements compose the other 10 percent. Europium is generally of low concentration partially due to its +2 oxidation state which allows it to concentrate in the calcium group minerals. Promethium is not a naturally occurring lanthanide since its most stable isotope has a short half-life, 18 years. Selected nuclear data for other rare earths can be found in Table 1.

Prior to the use of ion exchange techniques for the separation of rare earths fractional crystallization, precipitation or decomposition were required to separate them. The use of ion exchange and chromatographic techniques allowed relatively pure rare earth elements and compounds to be prepared. These improved preparation techniques have led to a need for a fast and accurate method for analysis of rare earths when present in macro and trace quantities. The development of a method by which rare earth elements can be analyzed without the need for pre-irradiation wet chemistry or post-irradiation chemical separation was the purpose of this research project.

Table 1. Selected rare earth nuclear data[a]

Nuclear reaction	% Abundance of target	Thermal neutron cross section (barns)	Half-life of product
$^{144}\mathrm{Sm}(n, \gamma)^{145}\mathrm{Sm}$	3.16	0.7	340 d
$^{147}\mathrm{Sm}(n, \gamma)^{148}\mathrm{Sm}$	15.07	90	1.2×10^{13} y
$^{152}\mathrm{Sm}(n, \gamma)^{153}\mathrm{Sm}$	26.63	210	46.8 h
$^{154}\mathrm{Sm}(n, \gamma)^{155}\mathrm{Sm}$	22.53	5	23.5 m
$^{151}\mathrm{Eu}(n, \gamma)^{152}\mathrm{Eu}$	47.77	5,900	12.7 y
$^{151}\mathrm{Eu}(n, \gamma)^{152m}\mathrm{Eu}$	47.77	2,800	9.3 h
$^{153}\mathrm{Eu}(n, \gamma)^{154}\mathrm{Eu}$	53.23	320	16 y
$^{152}\mathrm{Gd}(n, \gamma)^{153}\mathrm{Gd}$	0.2	180	242 d
$^{158}\mathrm{Gd}(n, \gamma)^{159}\mathrm{Gd}$	24.9	3.4	18.0 h
$^{160}\mathrm{Gd}(n, \gamma)^{161}\mathrm{Gd}$	21.9	0.8	3.6 m
$^{159}\mathrm{Tb}(n, \gamma)^{160}\mathrm{Tb}$	100	46	72.1 d
$^{156}\mathrm{Dy}(n, \gamma)^{157}\mathrm{Dy}$	0.05	3	8.1 h

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[a] Nuclear data taken from "Table of Isotopes" sixth edition.

Table 1. (Continued)

Nuclear reaction	% Abundance of target	Thermal neutron cross section (barns)	Half-life of product
$^{158}\mathrm{Dy}(n, \gamma)^{159}\mathrm{Dy}$	0.09	100	144 d
$^{164}\mathrm{Dy}(n, \gamma)^{165}\mathrm{Dy}$	28.18	800	139.2 m
$^{165}\mathrm{Ho}(n, \gamma)^{166}\mathrm{Ho}$	100	64	26.9 h
$^{162}\mathrm{Er}(n, \gamma)^{163}\mathrm{Er}$	0.14	2	75.1 m
$^{164}\mathrm{Er}(n, \gamma)^{165}\mathrm{Er}$	1.58	1.7	10.3 h
$^{167}\mathrm{Er}(n, \gamma)^{168}\mathrm{Er}$	22.94	700	stable
$^{168}\mathrm{Er}(n, \gamma)^{169}\mathrm{Er}$	27.07	2	9.6 d
$^{170}\mathrm{Er}(n, \gamma)^{171}\mathrm{Er}$	14.88	9	7.52 h
$^{169}\mathrm{Tm}(n, \gamma)^{170}\mathrm{Tm}$	100	125	134 d
$^{168}\mathrm{Yb}(n, \gamma)^{169}\mathrm{Yb}$	0.14	11,000	31.8 d
$^{174}\mathrm{Yb}(n, \gamma)^{175}\mathrm{Yb}$	31.84	9	101 h
$^{176}\mathrm{Yb}(n, \gamma)^{177}\mathrm{Yb}$	12.73	7	1.9 h
$^{175}\mathrm{Lu}(n, \gamma)^{176}\mathrm{Lu}$	97.4	5	10^{10} y
$^{176}\mathrm{Lu}(n, \gamma)^{177}\mathrm{Lu}$	2.6	2,100	6.74 d

REVIEW OF LITERATURE

In 1933 I. Curie and F. Juliet produced the first recognizable activation by bombarding light metals with alpha particles from polonium. This event, coupled with the discovery of the neutron by J. Chadwick in 1932, led to the application of neutron activation analysis to analytical problems.

The first activation analysis was reported by Hevesy and Levi (20) in 1936 in which they reported the detection of Dy in Y_2O_3. Again in 1938, Hevesy and Levi (21) reported the detection of 10 mg amounts of Eu in Gd_2O_3. One year later, Goldschmidt and Djourkovitch (22) irradiated samples with a constant source of neutrons and measured the intensity of activation to determined Dy in Y-group oxides. It was not until the late 1940's that pure rare earth elements were available. In addition the availability of higher neutron fluxes and improved detection equipment led to the application of these advances to the analysis of rare earth elements in minerals, biological samples and matrices of other rare earths.

After the development of high flux reactors and proportional as well as scintillation counters decay curve resolution became a popular method of rare earth activation analysis. Kohn and Tompkins (23) analyzed Sm in Ce_2O_3 and Dy in Y_2O_3 by this method. In addition, Phillips and

Cornish (24) used it to determine Dy in Ho_2O_3. Meinke and Anderson (25) used a low flux Ra-Be source to determine Dy and Eu to 1 μg at fluxes of 10^7 n/cm^2-sec and activation analysis was often used as a supplement to spectrophotometric procedures. Born _et al_. (26) analyzed Eu in Sm, Dy in Y earths, Sm in Ce earths free of Eu and Gd in Y earths of low Eu content.

In the early 1960's, M. Okada (27-32) reported a non-destructive activation analysis for Sc, Y, Dy, Er and Yb in minerals, ores and rare earth oxides through the measurement of short-lived meta-stable isomers produced in a reactor. The first use of fast neutrons for rare earth activation was reported by Tada _et al_. (33) in which a method for the analysis of Pr in La and Nd was described. Cuypers and Menon (34, 35) used 14 mev neutrons for Ce, Pr and Y in minerals. Kawashima (36) irradiated rare earth oxides with a neutron flux of 3 x 10^{11} n/cm^2-sec and obtained results which were competitive with emission spectrographic analysis except for Dy and Y which differed by a factor of five. Later Kawashima (37) reported an analysis for Dy in Y_2O_3 using Y as an internal standard.

The papers which have appeared in the mid- and late 1960's fall generally into two classes. The first group which contains by far the largest number of papers contain reports of the analysis of only a few rare earths as a supplement to the analysis of biological or mineral samples as well as trace components in purified metals. In 1963 Ross (38) reported finding Dy and Eu in samples of highly purified Be, Al and Fe after irradiating 1 g samples for 20 minutes at a flux of 6 x 10^{13} n/cm^2-sec followed by NaI(Tl) gamma ray spectrometry. Yule (39) reported finding all of the heavy rare earths in samples of whole blood, urine, milk, tap water and polyethylene vials although not necessarily all rare earths in any one of these samples. Here again, gamma ray counting was performed on NaI(Tl) crystals. Steinnes (40) reported an instrumental activation analysis method for detecting Sm, Eu and Dy in apatites using NaI(Tl) crystals to count the complex x-ray peak at about 40 kev. The results obtained were accurate to ± 10 percent and were calculated using an external standard method of data reduction. Kline and Brar (41) reported determinations of Eu and Sm in irradiated soils using NaI(Tl) spectrometry.

Several papers have appeared which describe the analysis of rare earth elements by a group separation followed by gamma ray counting of the partially or completely separated components. Haskin *et al.* (42) reported an analysis for rare earths in rocks and minerals in which powdered rocks were dissolved, in the presence of carriers, using Na_2O_2 fusion. Following separation of the rare earth group from silicate residues the individual rare earths in irradiated samples and standards were separated by ion exchange and radioassay was performed by beta or gamma counting. Although the average precision was ± 4 percent mean deviation the method was long and tedious. Other investigators including Massart and Hoste (43) and Neirinckx *et al.* (44) have reported similar procedures for the determination of rare earth content in rare earth ores and titanium compounds respectively.

During the second half of the 1960's papers began to appear which reported the use of Ge(Li) detectors in activation analysis. Girardi *et al.* (45) performed experiments using Ge(Li) detectors of various dimensions and enumerate in their paper techniques for the rapid characterization of the detectors, including evaluation of efficiency and resolution as a function of gamma ray energy. In addition, sections on qualitative and quantitative analysis of activated biological products lead to the conclusion that even with the low efficiency of Ge(Li) detectors their applicability to activation problems is eminent.

One of the first papers in which the application of Ge(Li) detectors to the activation analysis of rare earths was authored by Cosgrove *et al.* (46) in which detection limits for thermal and 14 mev neutron irradiations followed by gamma ray counting are listed. In 1967 Cobb (47) reported the analysis of Sm, Eu, Dy, Yb, and Lu in various rock samples. Fleishman and Lukens (48) reported a technique by which all of the rare earths from Sm through Lu could be analyzed with the single exception of Tm. The analysis required nine days to complete and samples were counted at periods of 2, 7, 24, 48 and 216 hours after the end of the irradiation and the results obtained were poor for Gd and Tb.

The most recent papers can again be divided into two groups. Lukens _et_ _al_. (49) have reported an activation analysis of all 14 rare earth elements with group separation and Ge(Li) spectrometry applying their method to rocks and minerals. Onuma and Hamaguchi (50) also used group separations and reported finding Sm, Eu, Gd, Tb, Tm, Yb and Lu in rock samples. After a rather elaborate wet chemical separation, Marsh and Allie (51) reported a successful analysis for Gd and CaF_2 using Sm as an internal standard. Anion exchange has been used by Brunfelt and Steinnes (52) to effect an analysis of Lu, Yb and Tb in rocks while Higuchi, Tomura and Hamaguchi (53) used a cation exchange method for rare earths in rocks.

Among the papers which have reported activation analysis of rare earths without employing group separations, Lukens _et_ _al_. (54) discussed a method for the analysis of Eu in monazite and tungsten ores. Using a TRIGA Mark I reactor as a neutron source, 0.1 g ore samples are irradiated for 30 minutes and Eu is determined via the ^{152}Eu activity. Lombard and Isenhour (55) analyzed for Sm and Gd in four of the most common rare earth ores. Following a 10 minute live time irradiation the data from samples of 10 to 100 mg of each ore were fitted by a weighted least squares method and a calibration curve relating the amount of the individual rare earth to the observed count rate was constructed from which the analysis of subsequent samples could be ascertained.

An additional paper reporting the use of epithermal neutrons in instrumental activation analysis was authored in 1969 by Brunfelt and Steinnes (56) in which the determination of Sm, Yb, Tb and Eu in silicate rocks was reported. The theoretical aspects of epithermal neutron activation were previously discussed by Högdahl (57) and Prouza and Rakovic (58). Brunfelt and Steinnes in the current paper describe an analysis in which rock samples were irradiated in small Cd boxes and gamma ray counting was performed by a Ge(Li) detector. In addition to five rock samples a standard was simultaneously irradiated for each rare earth element determined and the analysis of the rocks was achieved by a comparator method. The only conclusions offered are that Sm and Tb could be better analyzed by epithermal neutrons while in the case of Yb and Eu no advantage of epithermal over thermal neutron activation was noted.

Several authors during the 1968-1969 period reported the application of gamma-gamma coincidence and anti-coincidence spectrometry to rare earth activation analysis. Two of these, Michelsen and Steinnes (59) and Perkins et al. (60), were reported at the 1968 International Conference on Modern Trends in Activation Analysis; the former authors using coincidence while the latter using anti-coincidence spectrometry. Both of these authors analyzed Sm, Eu, Tb, Yb and Lu in rock samples and Michelsen and Steinnes were also able to detect Dy. An additional communication by Michelson and Steinnes (61) in 1969 reported refinements of their method and its extension to include Ho.

EXPERIMENTAL

Irradiation Facilities and Detection Equipment

All rare earth mixtures were irradiated at the Ames Laboratory Research Reactor (ALRR), a heavy water moderated and cooled steady state reactor which operates at five megawatts thermal power output.

Irradiations at the reactor facility were performed in the "R-5" and "V-3" pneumatic transfer systems. In both cases one inch diameter "rabbits" were used to contain the samples. The R-5 irradiation position is 17-1/2 inches from the reactor's vertical center line and 14 inches from the horizontal center line and has a thermal neutron flux of 3.5×10^{13} n/cm^2-sec. V-3 is a vertical thimble in which a neutron flux converter assembly (62) was installed. With the converter assembly installed a fast neutron flux of 2.7×10^{12} n/cm^2-sec with $E > 1$ mev was recorded.

The detector system consisted of a lead shielded lithium-drifted germanium detector [Ge(Li)] having a trapezoidal active area of 11 cm^2 and drifted depth of 1.1 cm. The relative peak efficiency at 1.33 mev is 3.5 percent and the resolution of the system at 1.33 mev FWHM is 3.48 kev. The Ge(Li) detector was coupled through a preamplifier and amplifier to a RIDL 1600 channel pulse height analyzer, Model 24-3. The analyzer sorts and stores the detector output pulses in one of a series of storage units or channels, each channel representing a predetermined energy range.

Rare Earth Mixtures

Rare earth oxides were obtained through the courtesy of Dr. F. H. Spedding and Dr. J. E. Powell of the Ames Laboratory. The spectrographic analysis of the various oxides used are contained in Appendix A . In all cases the rare earth mixtures were prepared by weighing the appropriate amount of the rare earth oxide using an analytical balance. The oxides were quantitatively transferred to previously calibrated volumetric flasks and dissolved in nitric acid. The solution was subsequently diluted to volume with distilled water.

During the work on one-to-one rare earth mixtures the samples were prepared by pipetting the required amount of the rare earths from standard rare earth solutions. For the gadolinite simulation all of the rare earths were weighed and dissolved in a single volumetric flask and only one pipetting was necessary to prepare samples for irradiation. The addition of Y to the gadolinite simulation was accomplished by pipetting from a standard Y solution directly into the irradiation capsules.

The samples were prepared for analysis by pipetting the required volume of rare earth or rare earth mixtures into one inch polyethylene irradiation capsules which were placed in a drying oven to evaporate all of the liquid. The lids of the capsules were heat sealed to the body and the capsules were washed in nitric acid to remove any exterior contamination. The samples were then arranged so that the bottoms of the capsules were in as close proximity as possible. This maintains the samples in as uniform a flux as possible. After irradiation the samples were placed in pyrex test tubes and put into the constant geometry sample holder. The samples were then counted eight inches above the Ge(Li) detector system; generally they were counted from 45 to 75 minutes live time. The spectra were removed from analyzer storage on punch tape and the data were subsequently transferred to IBM cards through the use of the computer program PRESTO. From IBM cards data reduction was accomplished by the ICPEAX program or by a hand calculation of the areas under the particular gamma ray peaks. In addition, a plot of the data was produced by ICPEAX. Once the area under each gamma ray peak was obtained the rare earth composition in samples of unknown composition was calculated by both internal and external standard methods. Here, again, the calculations were performed by hand or by using the computer program HRATIO. Detailed descriptions of PRESTO, ICPEAX and HRATIO are contained in Appendices C, D, and E respectively.

One-to-One Holmium-Terbium Mixtures

Preliminary work was done on a Ho and Tb mixture which contained 0.5 mg of each of these rare earths. Eight samples were irradiated for 10.0 minutes in the R-5 facility at the ALRR. After a 4 hour "cooling" period the gamma ray spectra of these samples were accumulated using the Ge(Li) detector. In a representative spectrum (Figure 1) the ^{160}Tb gamma ray peaks are found at 216, 299, 879 and 1178 kev while the 1380 kev peak is due to ^{166}Ho. From the areas under these peaks subsequent data reduction led to the results in Table 2. An examination of this table reveals that the analysis for Tb ranged from 0.8 percent to 3.3 percent above the expected value.

The standard deviations as shown in Table 2 were calculated as deviations in the mean using the standard formula

$$\sigma_m = \left[\frac{\sum_i (x_i - \bar{x})^2}{n(n - 1)} \right]^{1/2} \tag{10}$$

where x_i is the value of the individual measurement, $\bar{x}$ the average of all measurements and n the number of measurements taken.

An equal weight of a third component, Yb, was added to the 1:1 Ho-Tb mixture. Irradiation of five samples under the conditions previously described led to spectra (Figure 2) with two gamma rays in addition to those in Figure 1. These gamma ray peaks at 282 and 396 kev are due to ^{175}Yb.

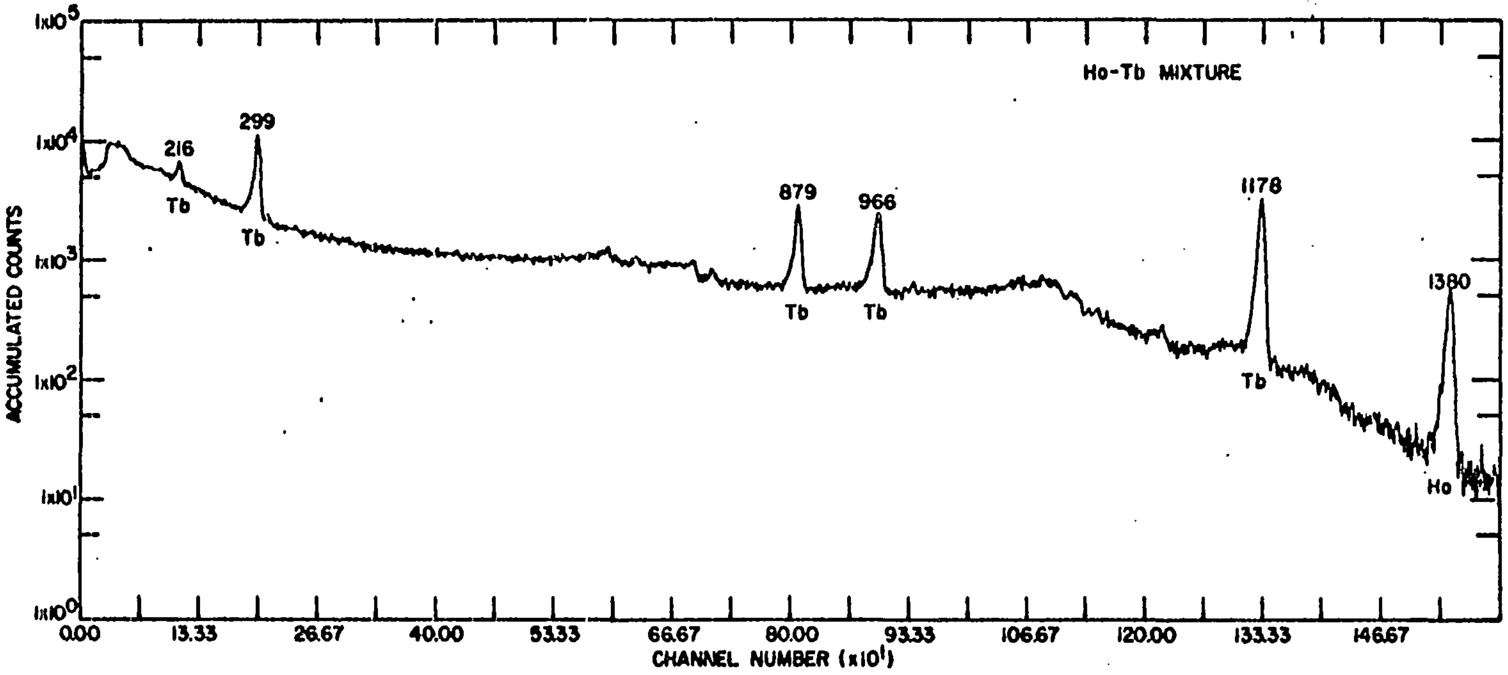

Figure 1. Gamma ray spectrum of equal weight Ho-Tb mixture

Table 2. Analysis of 1:1 Ho-Tb mixture using 216 kev Tb peak, 1380 kev Ho peak

	External	Standard	Internal	Standard
Sample	Area	$\frac{\text{Sample}}{\text{Standard}}$	Tb/Ho	$\frac{(\text{Tb/Ho})_n}{(\text{Tb/Ho})_1}$
Standard	73550			
1	57770	0.785	1.241	
2	97060	1.320	1.364	1.099
3	77850	1.058	1.352	1.089
4	69220	0.941	1.202	0.969
5	74970	1.019	1.302	1.049
6	74280	1.010	1.290	1.039
7	68060	0.925	1.182	0.952
Average		1.008 ± 0.062		1.033 ± 0.025
Weight Tb (mg)		0.504 ± 0.031		0.516 ± 0.012

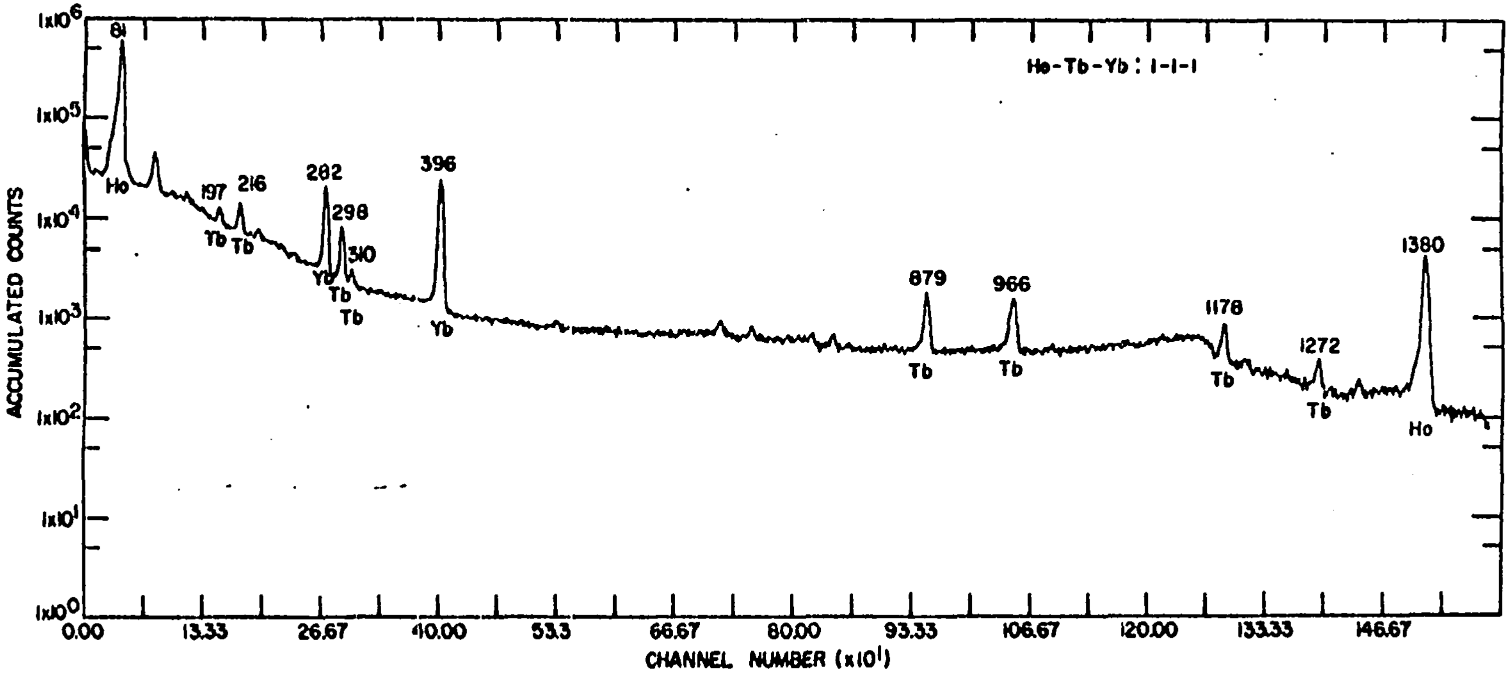

Figure 2. Gamma ray spectrum of equal weight Ho-Tb-Yb mixture

Data from the analysis for Yb and Tb in the presence of an equal amount of Ho are shown in Table 3. Errors in the Tb analysis ranged from 0.1 to 2.7 percent high and those for Yb ranged from a 0.61 percent low to 0.3 percent high.

Subsequent addition of Lu and Gd gave a five component system an analysis of which is shown in Table 4. The next rare earth to be added to the five component system was Eu, again in 1:1 correspondence with the other rare earths. Comparison of the sample spectrum in Figure 3 with the pure Eu spectrum in Appendix B shows very little difference. This can be explained with the data in Table 5 in which the product of isotopic abundance and cross section, fσ, are

Table 3. Analysis of Ho-Tb-Yb 1:1:1. Expected value = 1.00

Isotope	Gamma ray energy (kev)	Internal standard ratio
^{160}Tb	299	1.020 ± 0.031
	879	1.001 ± 0.009
	1178	1.027 ± 0.063
^{175}Yb	282	0.9939 ± 0.009
	396	1.003 ± 0.006

Table 4. Analysis of Ho-Tb-Yb-Lu-Gd. Expected value = 1.00

Isotope	Gamma ray energy (kev)	Internal standard ratio
^{159}Gd	363	0.9722 ± 0.0139
^{160}Tb	299	0.9945 ± 0.0309
	879	0.9692 ± 0.0142
	1178	1.037 ± 0.029
^{175}Yb	282	0.9970 ± 0.0122
	396	0.9989 ± 0.0163
^{177}Lu	113	0.9748 ± 0.0177
	208	1.010 ± 0.011

listed for the six rare earths in these samples. The sum of these products is 5098.3 barns with Eu contributing 4155.9 or 81.5 percent of the total. Thus Eu will absorb 81.5 percent of the available thermal neutrons. Attempts to correct for the large amount of Eu produced through the use of a spectrum stripping technique failed. The magnitude of the gain shift between Eu standard and rare earth mixture spectra moved peak positions significantly and the subtraction method proved inadequate. It was thus decided to

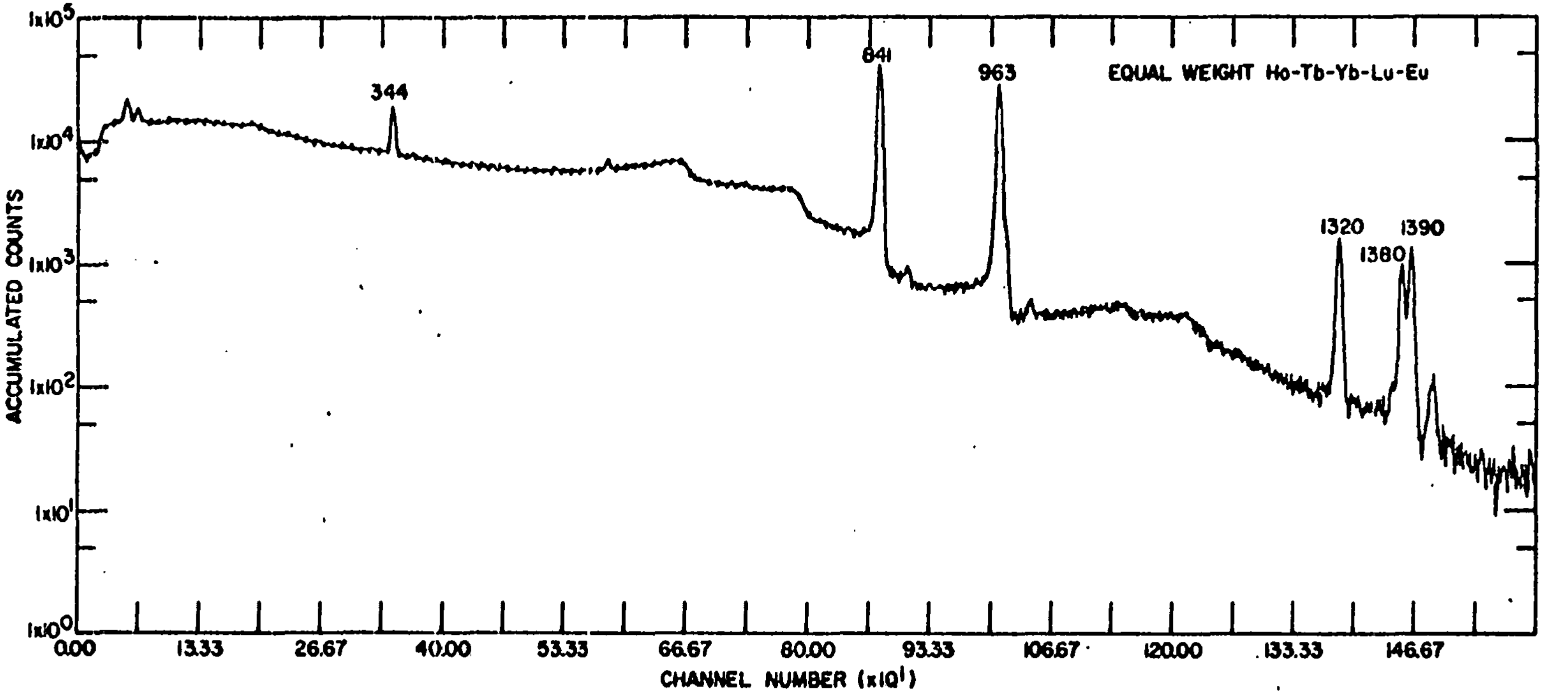

Figure 3. Gamma ray spectrum of equal weight Ho-Tb-Yb-Lu-Eu mixture

Table 5. fσ products for rare earths

Isotope	Abundance (f)	Cross section (σ)	fσ	Relative fσ
^{144}Sm	3.16	0.7	0.022	0
^{147}Sm	15.07	90	13.56	0.003
^{152}Sm	26.63	210	55.92	0.010
^{154}Sm	22.53	5	1.13	.0002
^{151}Eu	47.77	5,900 (to ^{152}Eu)	2818.4	.553
		2,800 (to ^{152m_1}Eu)	1337.5	.262
^{153}Eu	53.23	320	170.3	0.033
^{152}Gd	0.2	180	0.36	0
^{158}Gd	24.9	3.4	0.85	0.0001
^{160}Gd	21.9	0.8	0.18	0
^{159}Tb	100	46	46	0.0017
^{156}Dy	0.05	3	0.002	0
^{158}Dy	0.09	100	0.09	0
^{164}Dy	28.18	800	225.4	0.0442
^{165}Ho	100	64	64	0.0125
^{162}Er	0.14	2	0.003	0
^{164}Er	1.56	1.7	0.27	0
^{167}Er	22.94	700	160.6	0.0315
^{168}Er	27.07	2	0.54	0
^{170}Er	14.88	9	1.34	0.0003
^{169}Tm	100	125	125	0.0245

Table 5. (Continued)

Isotope	Abundance (f)	Cross section (σ)	fσ	Relative fσ
^{168}Yb	0.14	11,000	15.4	0.003
^{174}Yb	31.84	9	2.87	0.0006
^{176}Yb	12.73	7	0.89	0
^{175}Lu	97.4	5	4.87	0.0010
^{176}Lu	2.6	2,100	54.6	0.011
			$\Sigma = 5098.3$	

decrease the relative amount of Eu to 1/10 that of the other rare earths. In view of the +2 valence state exhibited by Eu it is not generally present in large amounts in rare earth minerals and such a reduction in the relative amount of Eu was felt to be justified. A spectrum of the rare earths Ho-Tb-Yb-Gd-Lu in 1:1 ratios and Eu in 1/10 that amount is shown in Figure 4. The corresponding analysis is given in Table 6.

The addition of rare earth elements to the mixture was continued until the mixture contained equal weights of all of the rare earths from Sm through Lu except for Eu which was at 0.1 this weight. A spectrum of this 10 component mixture is shown in Figure 5. All of the gamma ray peaks in this spectrum are fairly intense with the exception of the ^{159}Gd gamma ray at 363 kev. Due to the large Compton background from higher energy gamma rays, especially the 396 kev peak of ^{175}Yb, the Gd peak has rather low intensity and does not have a true Gaussian shape. This has led to the rather poor results for ^{159}Gd as shown in Table 7.

In an attempt to reduce the large Compton contribution from the high energy gamma rays in the ten component system the experimental method was changed. A check of the capture cross sections for the rare earths as a function of neutron energy indicated a possibility of reducing the amount of ^{152m}Eu and ^{175}Yb produced by irradiating with

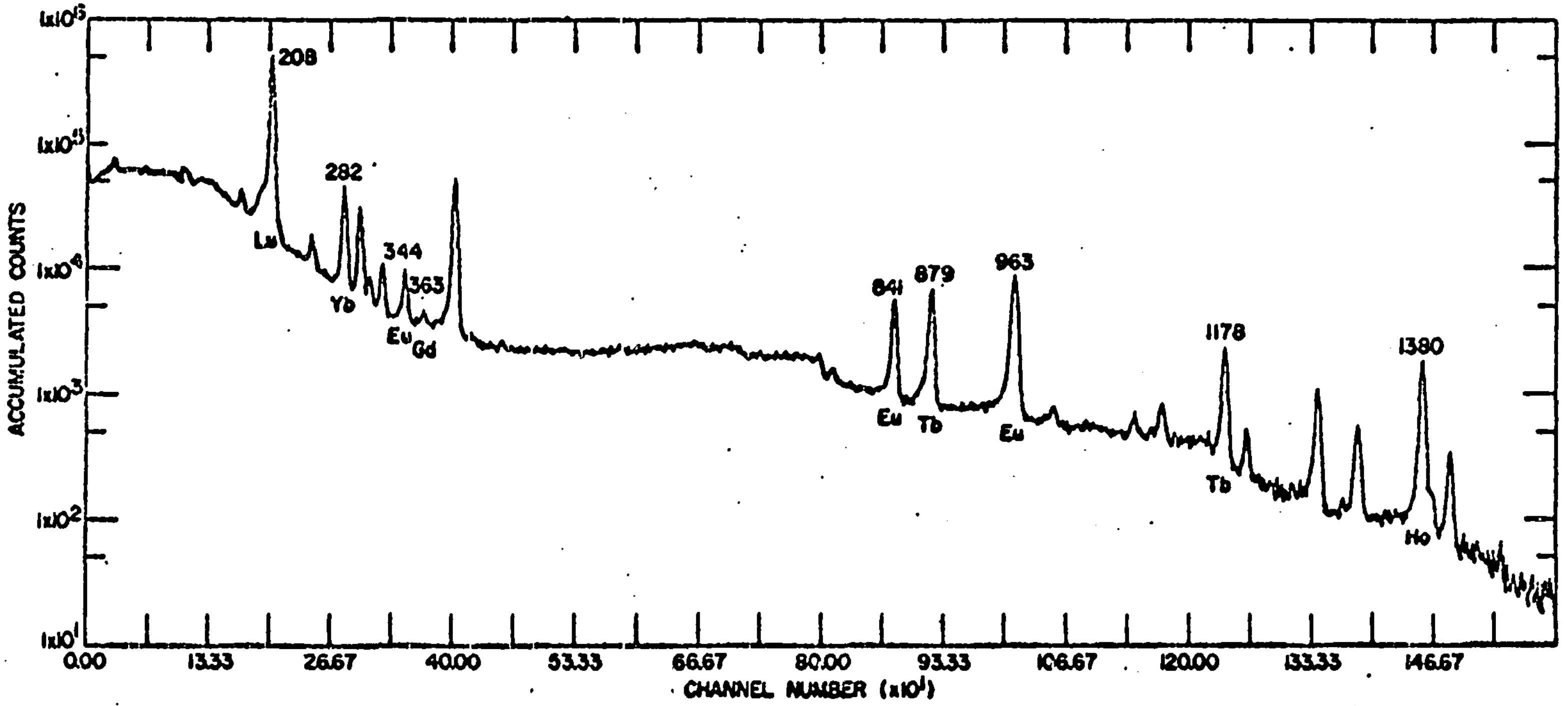

Figure 4. Gamma ray spectrum of equal weight Ho, Tb, Yb, Lu, Gd with 1/10 Eu

Table 6. Analysis of Ho-Tb-Yb-Lu-Gd in 1:1 ratios plus Eu in 1/10 ratio

Isotope	Gamma ray energy (kev)	Internal standard ratio
^{152m}Eu	344	0.1033 ± 0.004
	841	0.0996 ± 0.002
	963	0.1004 ± 0.003
^{159}Gd	363	1.056 ± 0.017
^{160}Tb	299	1.016 ± 0.010
	879	1.016 ± 0.017
^{175}Yb	282	1.006 ± 0.016
	396	0.9968 ± 0.021
^{177}Lu	113	0.9935 ± 0.028
	208	1.012 ± 0.017

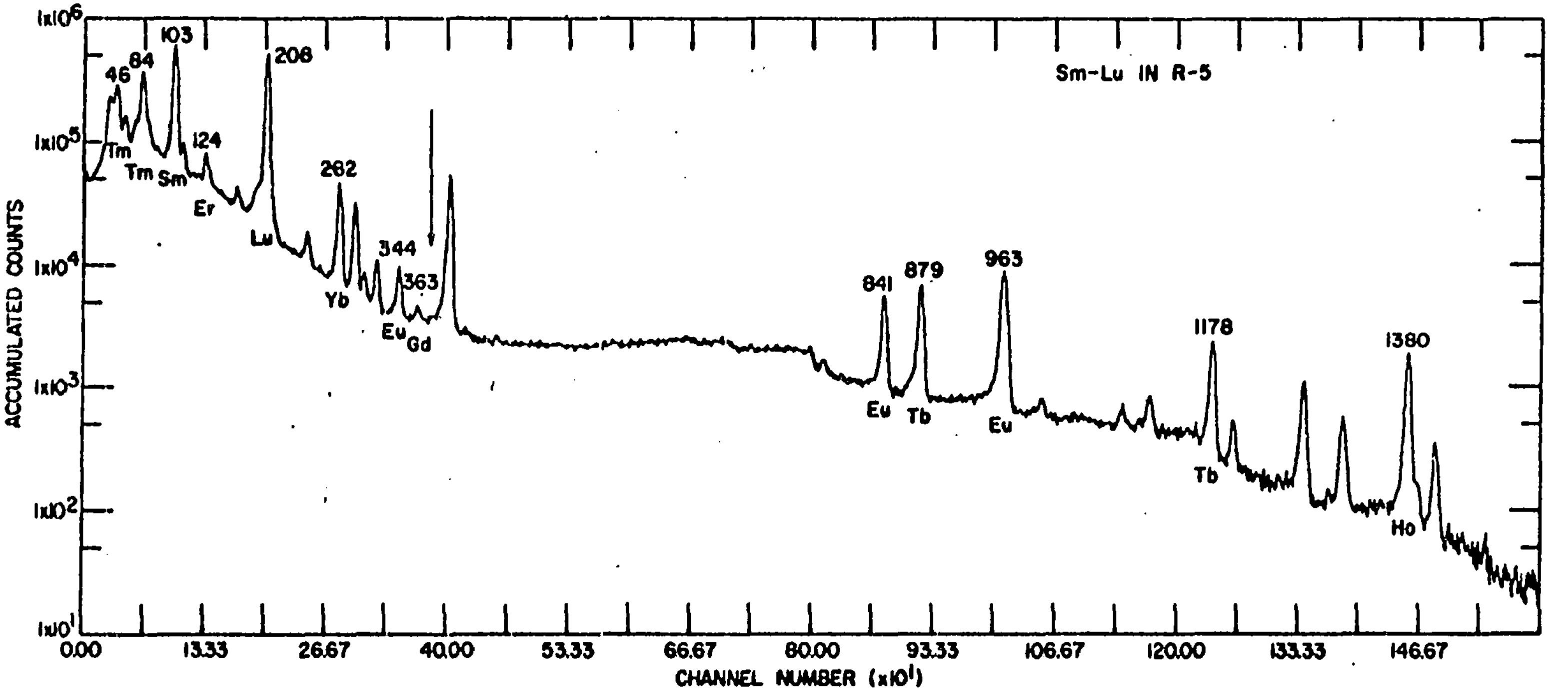

Figure 5. Gamma ray spectrum of equal weight Sm, Gd-Lu and 1/10 Eu in R-5

Table 7. Analysis of Sm-Lu. Expected value Sm, Gd-Lu = 1.00, Eu = 0.100

Isotope	Gamma ray energy (kev)	Internal standard ratio
^{153}Sm	103	0.9917 ± 0.0243
^{152m}Eu	841	0.0964 ± 0.003
	963	0.0958 ± 0.003
^{159}Gd	363	0.8959 ± 0.0430
^{160}Tb	299	0.9653 ± 0.0274
	879	0.9802 ± 0.0049
^{165}Dy	277	1.020 ± 0.066
	719	1.016 ± 0.066
	995	1.023 ± 0.074
^{170}Tm	46	1.033 ± 0.056
	68	0.9371 ± 0.035
^{171}Er	124	0.9708 ± 0.0236
^{175}Yb	282	0.9859 ± 0.0152
^{177}Lu	208	0.9894 ± 0.0120

epithermal rather than thermal neutrons. The spectrum obtained when the same ten component mixture was irradiated with epithermal neutrons in the neutron converter facility (V-3) at the A.L.R.R. is shown in Figure 6. Comparison of this spectrum with Figure 5 reveals several important differences. The height of the ^{175}Yb 396 kev gamma ray has been reduced which greatly decreases the Compton background in the vicinity of the ^{159}Gd 363 kev peak. In addition there has been a slight intensification of the Gd gamma ray. These two factors have improved the shape of this peak remarkably. Also, in the irradiation with epithermal neutrons the background in the 300 to 400 kev region has been reduced from 2000 to 800 counts per channel. In order to check the accuracy of the analysis using epithermal neutrons samples were irradiated for 10.0 minutes in V-3 at the A.L.R.R. and allowed to cool for 30 hours prior to spectra accumulation. The data reduction results are in Table 8 and the results were, with the exception of those for Dy, as accurate as in the thermal neutron irradiations and the results for Gd were far superior.

The problem with the ^{165}Dy isotope was circumvented by reirradiating the samples in the thermal neutron facility and counting the gamma rays 12 hours after the end of the irradiation. This approach led to the Dy analysis at the bottom of Table 8. In view of the improved results for Gd

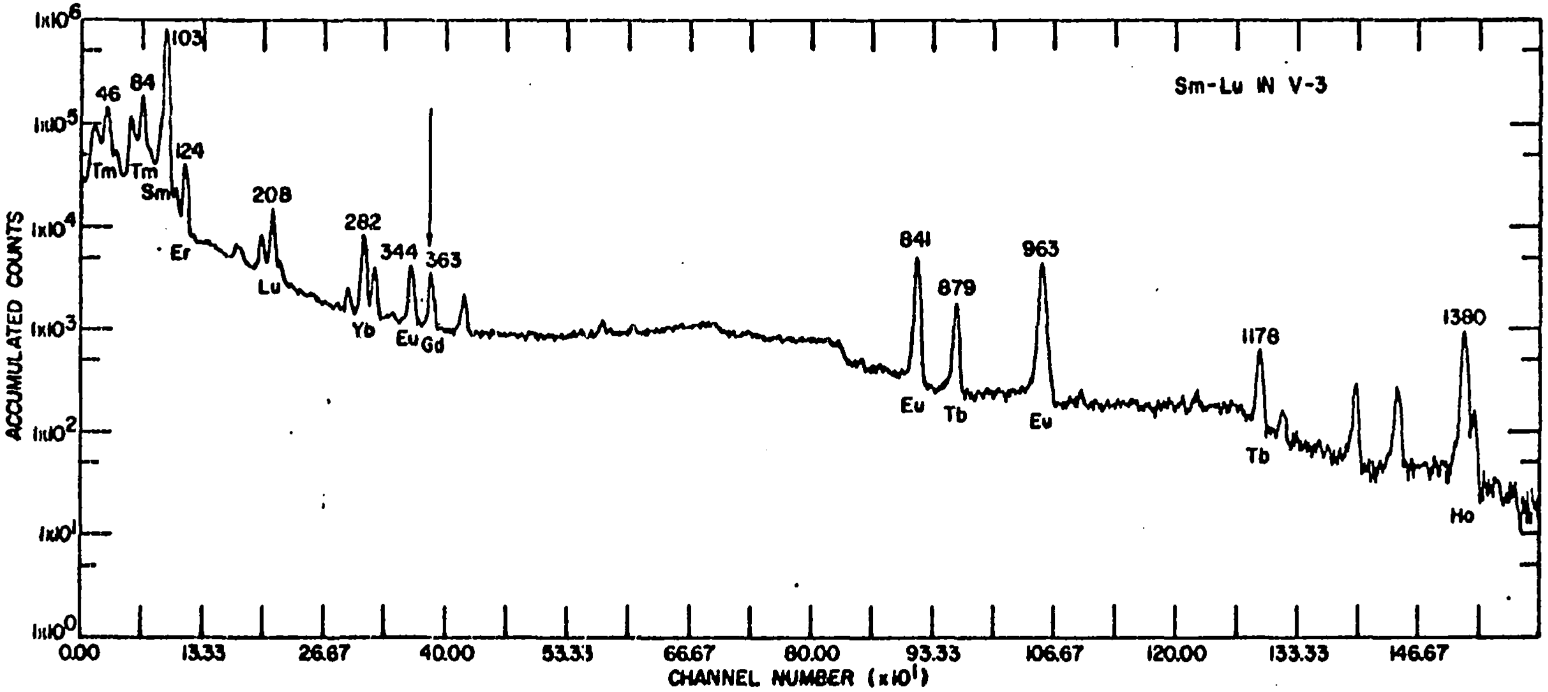

Figure 6. Gamma ray spectrum of equal weight Sm, Gd-Lu and 1/10 Eu in V-3

Table 8. Analysis of Sm-Lu using epithermal neutrons. Expected value Sm, Gd-Lu = 1.00, Eu = 0.100

Isotope	Gamma ray energy (kev)	Internal standard ratio
^{153}Sm	103	0.9917 ± 0.0246
^{152m}Eu	841	0.0983 ± 0.004
	963	0.0968 ± 0.005
^{159}Gd	363	0.9830 ± 0.0215
^{160}Tb	879	0.9650 ± 0.0147
	1,178	0.9819 ± 0.0225
^{165}Dy	277	1.012 ± 0.024
	719	0.9890 ± 0.012
	995	0.9891 ± 0.035
^{170}Tm	46	0.9642 ± 0.0317
	68	0.9618 ± 0.0229
	78	0.9709 ± 0.0810
^{171}Er	124	0.9732 ± 0.0153
^{175}Yb	282	1.014 ± 0.044
^{177}Lu	208	0.9989 ± 0.0505

the following method was adopted for all subsequent analyses:

1. Irradiation of the samples for 10.0 minutes in epithermal neutrons.
2. Thirty hour cooling followed by gamma ray counting and data reduction to determine all of the rare earths except Dy.
3. Reirradiation of the same samples for 10.0 minutes in thermal neutrons.
4. Twelve hour cooling followed by gamma ray counting and data reduction for the determination of Dy.

Analysis of a Rare Earth Ore

Although the results obtained with the one-to-one rare earth mixtures were extremely good, the practicality of applying activation analysis to such a system is questionable. Rarely, if ever, will rare earth mixtures be of interest in which the composition of the rare earths is in a one-to-one relationship. To apply the method to a more practical system the ore gadolinite was studied. The relative composition of the rare earth oxides which comprise gadolinite are listed in Table 9. Rather than using an ore which would require exact analysis a simulation of gadolinite was prepared. Initially only the heavy rare earths were considered even though gadolinite is actually 60 percent Y_2O_3. The exact amount of each rare earth in the gadolinite simulation is shown in Table 10.

Table 9. Composition of the rare earth ore gadolinite

Rare earth oxide	% by weight	Relative percentage heavy rare earths
Lu_2O_3	0.6	2.25
Yb_2O_3	5.7	21.35
Tm_2O_3	0.8	3.00
Er_2O_3	5.7	21.35
Ho_2O_3	1.7	6.37
Dy_2O_3	7.3	27.34
Y_2O_3	60.0	-
Tb_2O_3	0.9	3.37
Gd_2O_3	2.7	10.11
Eu_2O_3	0.1	0.375
Sm_2O_3	1.2	4.49
Nd_2O_3	2.8	-
Pr_2O_3	0.8	-
Ce_2O_3	4.3	-
La_2O_3	3.1	-

Table 10. Composition of gadolinite simulation

Rare earth	Weight (mg)
Sm	0.2502
Eu	0.0018
Gd	0.5052
Tb	0.1704
Dy	1.3679
Ho	0.3195
Tm	0.1498
Er	1.0671
Yb	1.0568
Lu	0.1121

Samples of the gadolinite simulation were irradiated and analyzed by the methods previously described. The results are shown in Table 11 and a spectrum is shown in Figure 7. The results using both internal and external standard techniques are quite good ranging from 2.5 percent low to slightly over 3 percent high. The 68 and 78 kev peaks in ^{170}Tm were the poorest of any results at 8 to 10 percent above the expected value. This is not surprising due to the relatively poor resolution of these two low energy gamma rays and the large amount of Compton background which

Table 11. Analysis of gadolinite simulation (without Y)

Isotope	Gamma ray energy (kev)	Internal standard method	External standard method
^{153}Sm	103	0.2586 ± 0.0043	0.2606 ± 0.0045
^{152m}Eu	841	0.00186 ± 0.00003	0.00183 ± 0.00003
	963	0.00184 ± 0.00003	0.00185 ± 0.00003
^{159}Gd	363	0.5010 ± 0.0118	0.5045 ± 0.0152
^{160}Tb	879	0.1660 ± 0.0032	0.1702 ± 0.0032
	1,178	0.1674 ± 0.0113	0.1677 ± 0.0128
^{165}Dy	277	1.386 ± 0.031	1.421 ± 0.015
	719	1.421 ± 0.025	1.327 ± 0.015
	995	1.418 ± 0.032	1.323 ± 0.016
^{166}Ho	1,380	-	0.3220 ± 0.0032
^{170}Tm	46	0.1516 ± 0.0060	0.1529 ± 0.0077
	68	0.1643 ± 0.0026	0.1656 ± 0.0024
	78	0.1624 ± 0.0054	0.1638 ± 0.0054
^{171}Er	124	1.070 ± 0.031	1.076 ± 0.034
^{175}Yb	282	1.035 ± 0.041	1.033 ± 0.022
^{177}Lu	208	0.1145 ± 0.0032	0.1179 ± 0.0036

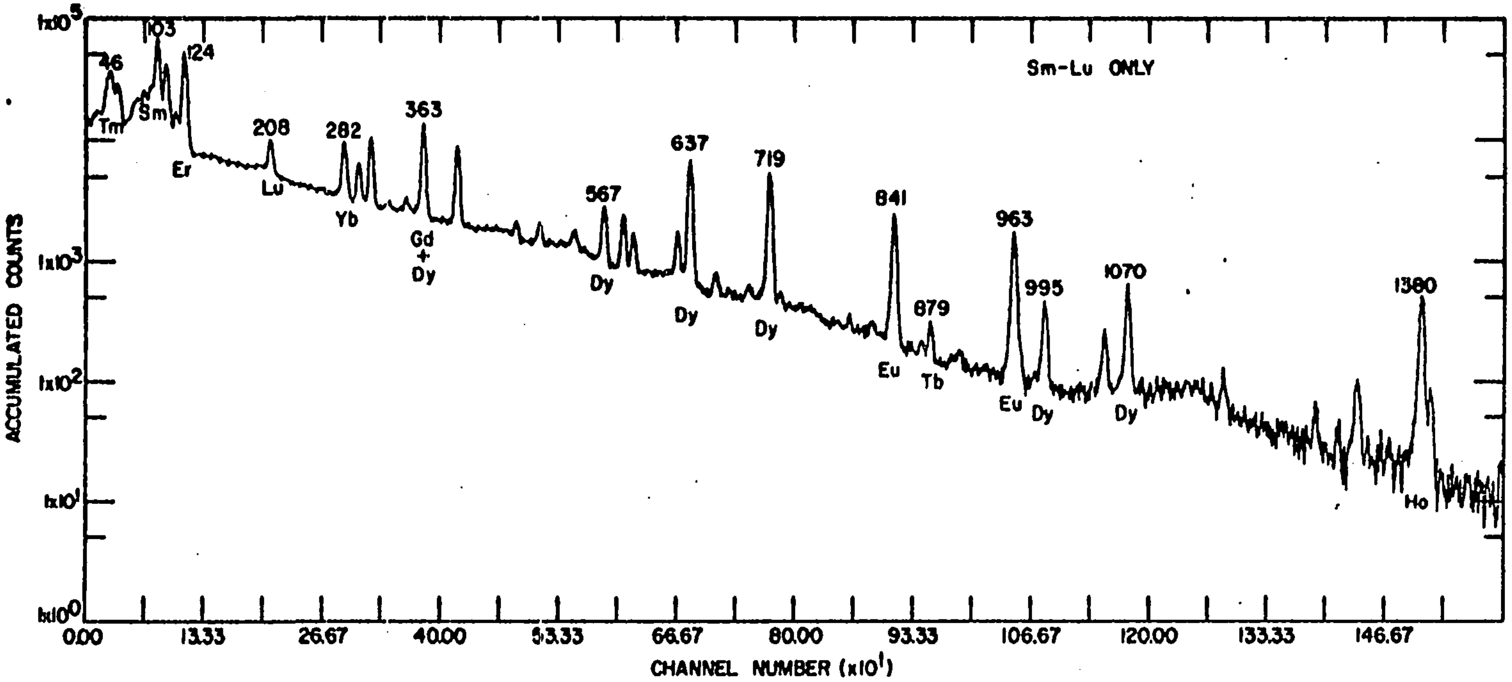

Figure 7. Gamma ray spectrum of gadolinite simulation without Y

when subtracted leads to poor accuracy. Tm can, however, be analyzed for through the use of the 46 kev peak. This peak also has a large background but does not have the doublet problem of the 68 and 78 kev peaks. The difference in these two situations can be seen by an examination of the spectrum in Figure 7.

As indicated in Table 9, gadolinite is 60 percent Y_2O_3. The effects of this relatively large amount of Y on the analysis were studied by adding 60 percent Y_2O_3 to the gadolinite simulation. The irradiation and data reduction gave the results as contained in Table 12; a representative spectrum is shown in Figure 8. An examination of both Table 12 and Figure 8 reveals that the addition of Y_2O_3 to the system has had no effect on the spectrum or the accuracy of the results obtained.

Self-Shielding Studies

An activation analysis study cannot be considered complete until the extent of neutron self-shielding has been established. Among the rare earths isotopes of three elements, Gd, Eu and Sm have neutron capture cross sections which are sufficiently large to warrant a self-shielding study. The abundances and cross sections of these isotopes are listed in Table 1.

To study the neutron self-shielding in the rare earth systems used in this investigation a method reported by

Table 12. Analysis of gadolinite simulation (Y added)

Isotope	Gamma ray energy (kev)	Internal standard method	External standard method
$^{153}\mathrm{Sm}$	103	0.2419 ± 0.0043	0.2404 ± 0.0045
$^{152m}\mathrm{Eu}$	841	0.00185 ± 0.00006	0.00185 ± 0.00006
	963	0.00174 ± 0.00007	0.00173 ± 0.00005
$^{159}\mathrm{Gd}$	363	0.5176 ± 0.0128	0.5230 ± 0.0203
$^{160}\mathrm{Tb}$	879	0.1728 ± 0.0131	0.1757 ± 0.0154
	1,178	0.1743 ± 0.0064	0.1746 ± 0.0020
$^{165}\mathrm{Dy}$	277	1.379 ± 0.016	1.373 ± 0.005
	719	1.330 ± 0.016	1.329 ± 0.021
	995	1.421 ± 0.065	1.417 ± 0.060
$^{166}\mathrm{Ho}$	1,380	-	0.3266 ± 0.0036
$^{170}\mathrm{Tm}$	46	0.1523 ± 0.0034	0.1502 ± 0.0068
	68	0.1607 ± 0.0055	0.1417 ± 0.0042
	78	0.1398 ± 0.0020	0.1465 ± 0.0028
$^{171}\mathrm{Er}$	124	1.059 ± 0.018	1.042 ± 0.020
$^{175}\mathrm{Yb}$	282	1.080 ± 0.061	1.091 ± 0.044
$^{177}\mathrm{Lu}$	208	0.1144 ± 0.0543	0.1159 ± 0.0045

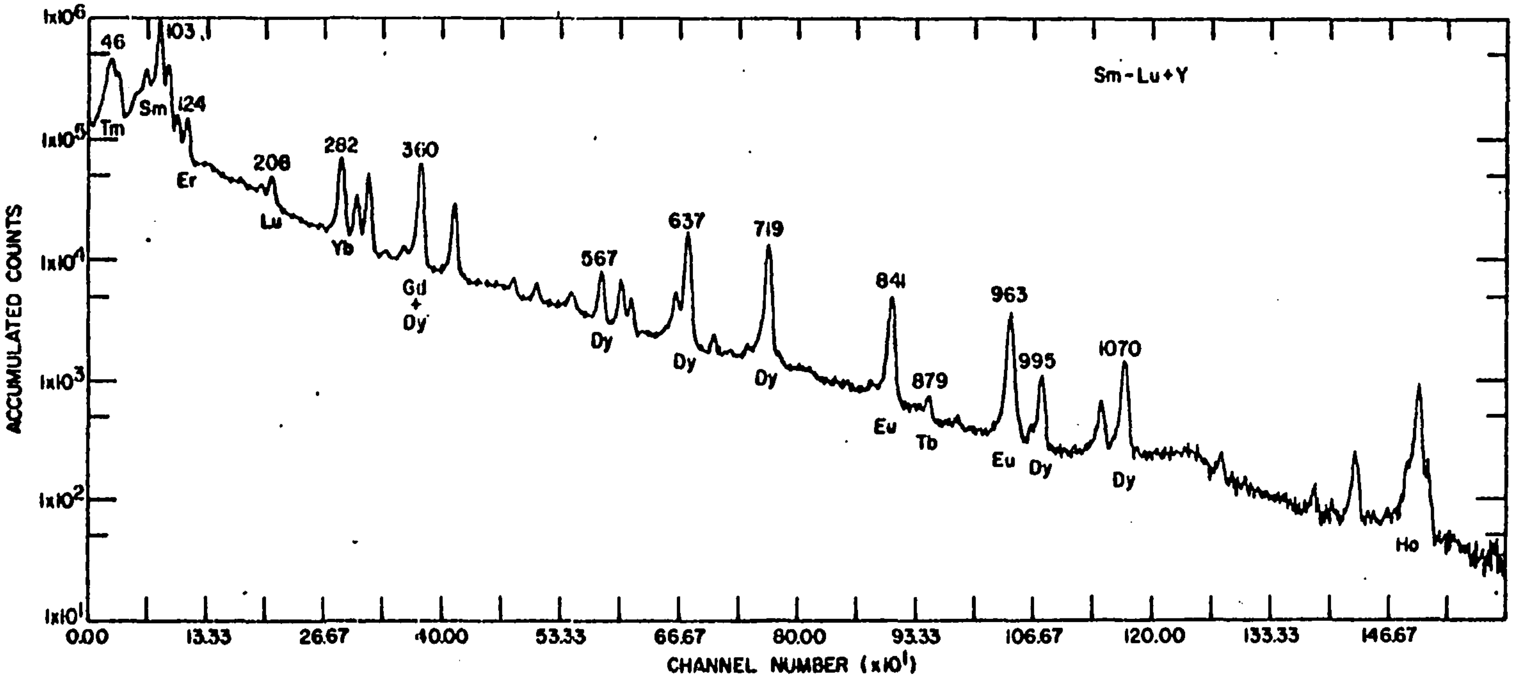

Figure 8. Gamma ray spectrum of gadolinite simulation with Y

Michelsen and Steinnes (63) was adopted. Samples were prepared by adding various amounts of the rare earth whose self-shielding was being studied to the gadolinite simulation previously described. The samples were irradiated in accordance with the method used during previous experiments. Following data reduction, the sample which contained only the gadolinite simulation was used as a standard to determine the amount of the particular rare earth present in the remaining samples. Plots were then made of the determined amount as a function of the amount added, which is known. In the absence of any self-shielding this plot will be a straight line at a 45 degree angle passing through the origin. For each of the rare earths samples were used with up to 20 times the amount of the element in the gadolinite simulation. In addition, to determine whether any combined effects existed, the Sm experiments were performed with the maximum amount of Gd added and the Eu samples contained the maximum amount of Gd and Sm previously studied. The data obtained during the self-shielding studies are listed in Appendix F and the graphs are reproduced in Figures 9 through 14. The straight lines for the plots of Gd in V-3 and Eu in V-3 and R-5 imply that self-shielding due to these elements will not interfere with an analysis for these rare earths in the concentration range studied. For Gd under thermal neutron (R-5) irradiation the self-shielding effect is substantial but since Gd is

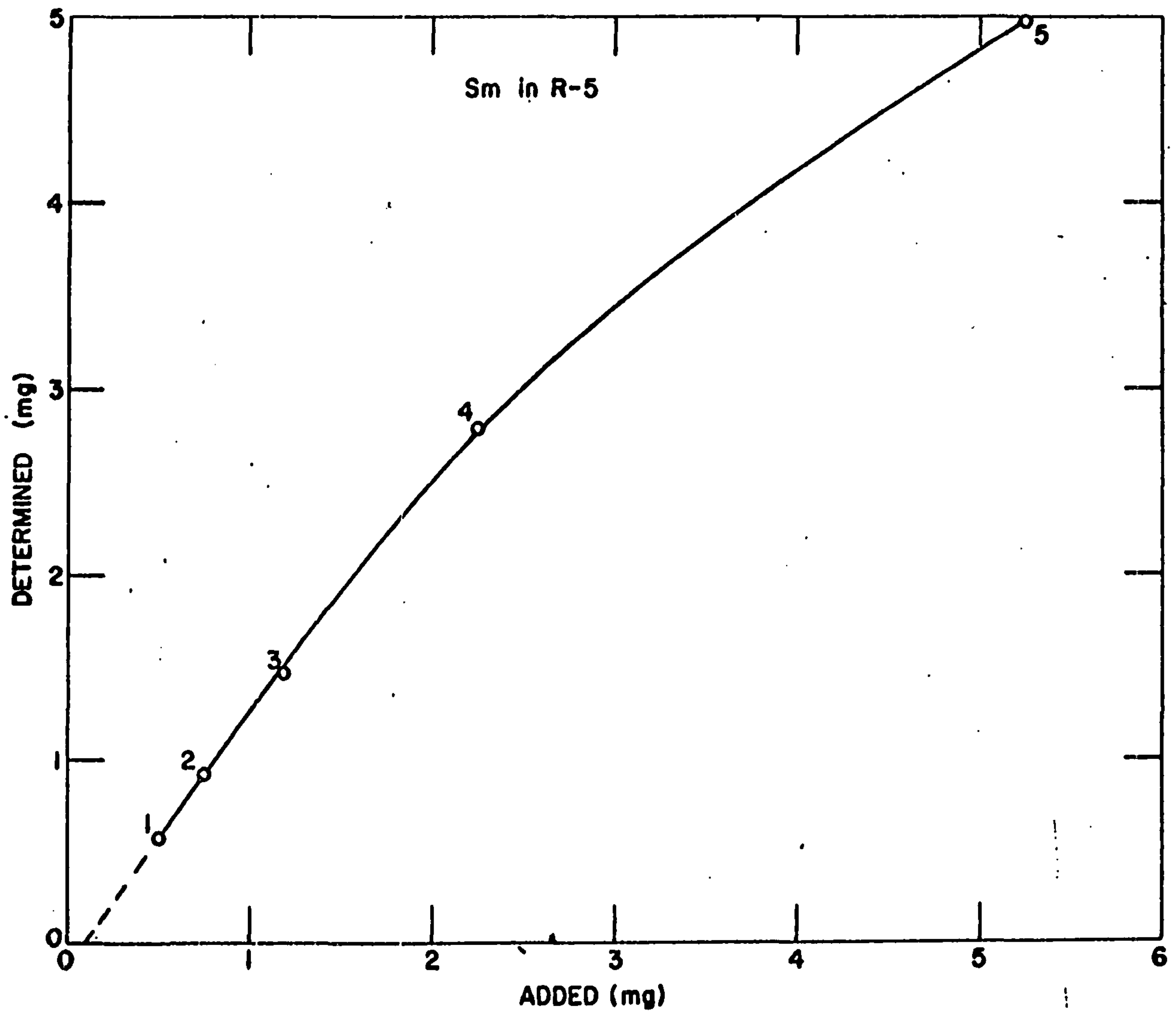

Figure 9. Self-shielding due to Sm in R-5

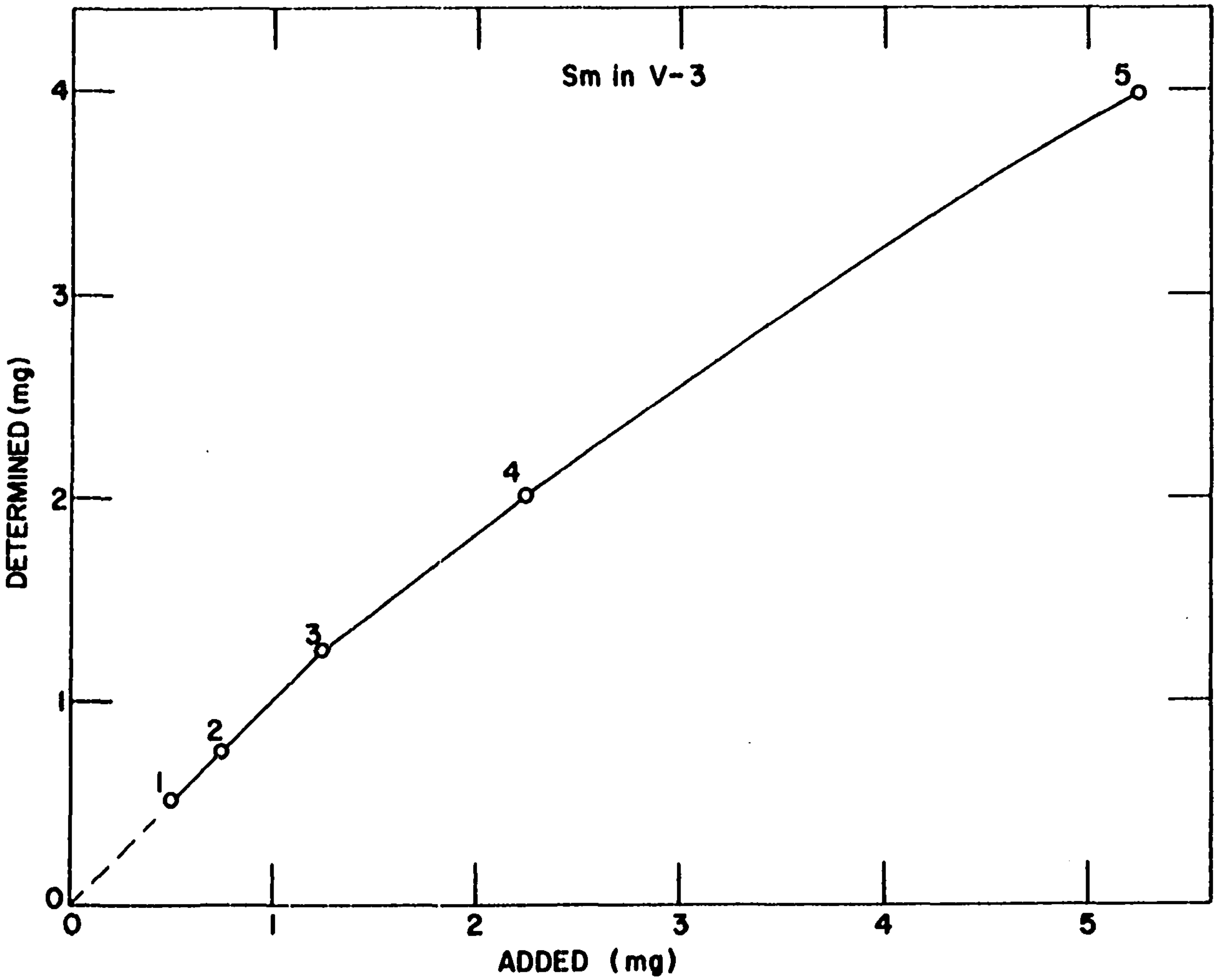

Figure 10. Self-shielding due to Sm in V-3

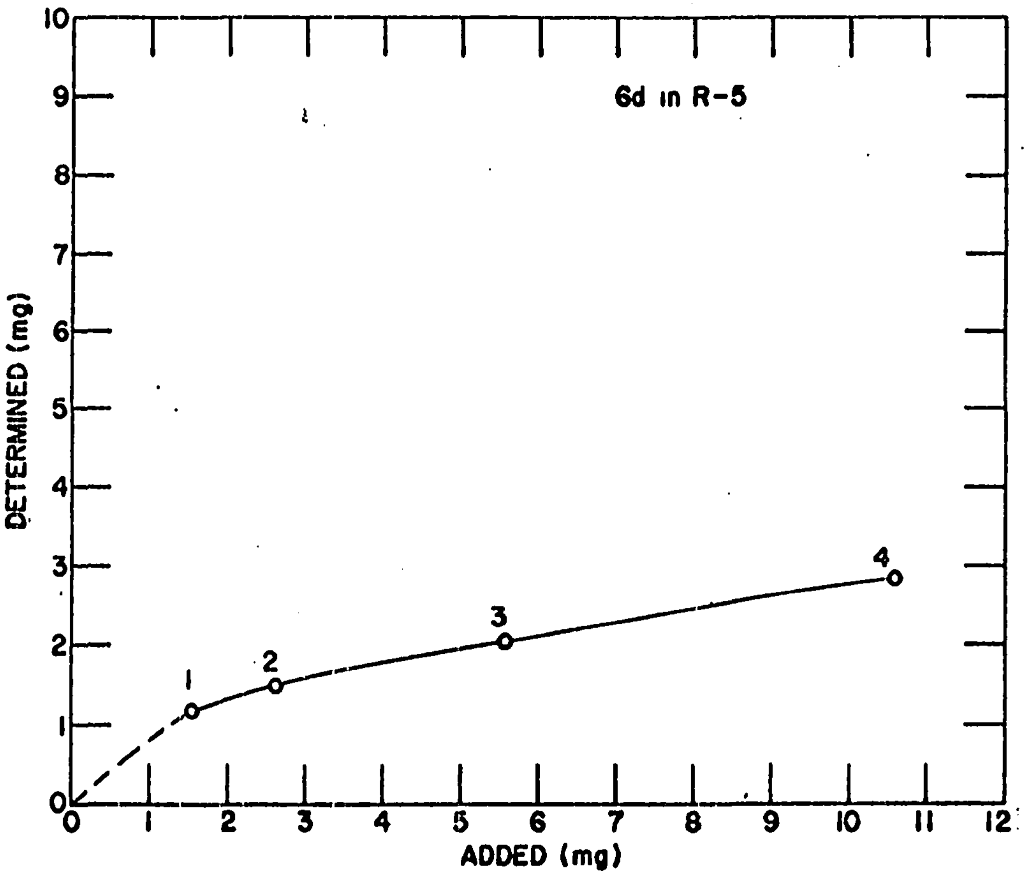

Figure 11. Self-shielding due to Gd in R-5

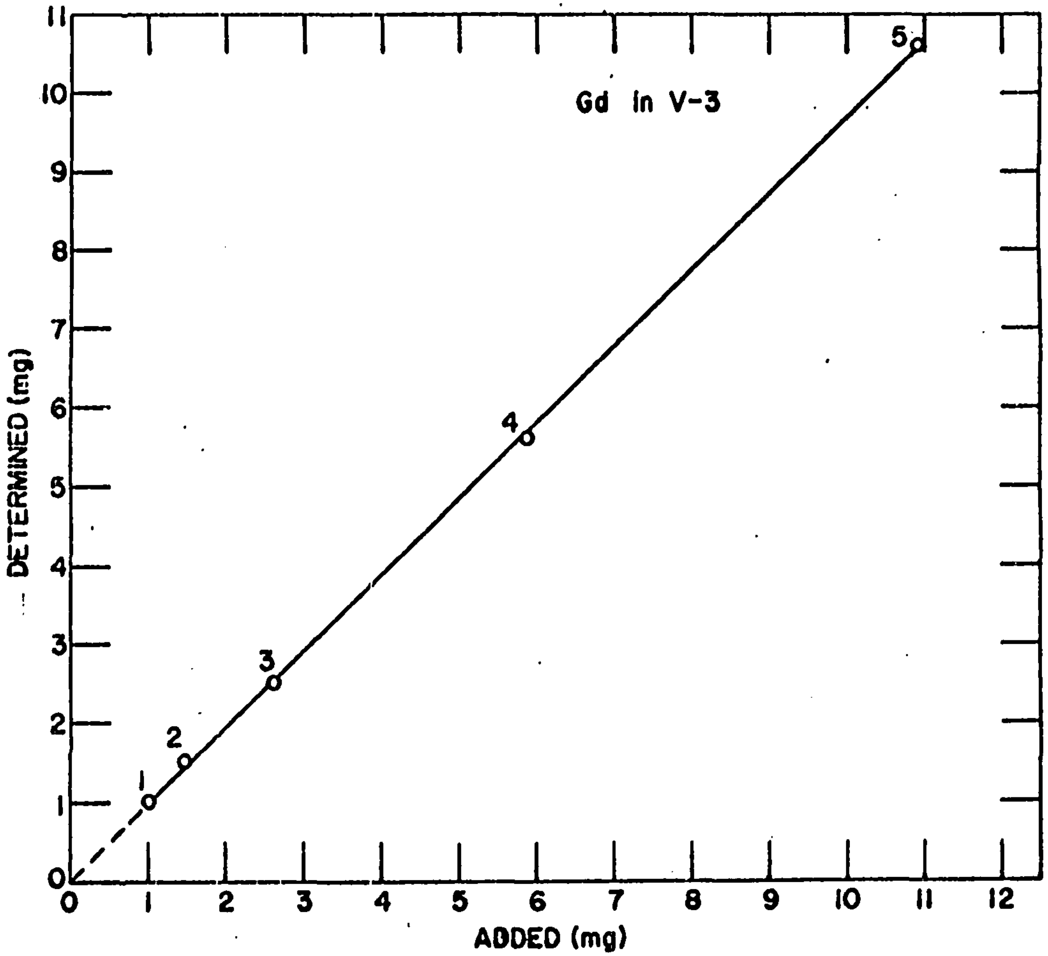

Figure 12. Self-shielding due to Gd in V-3

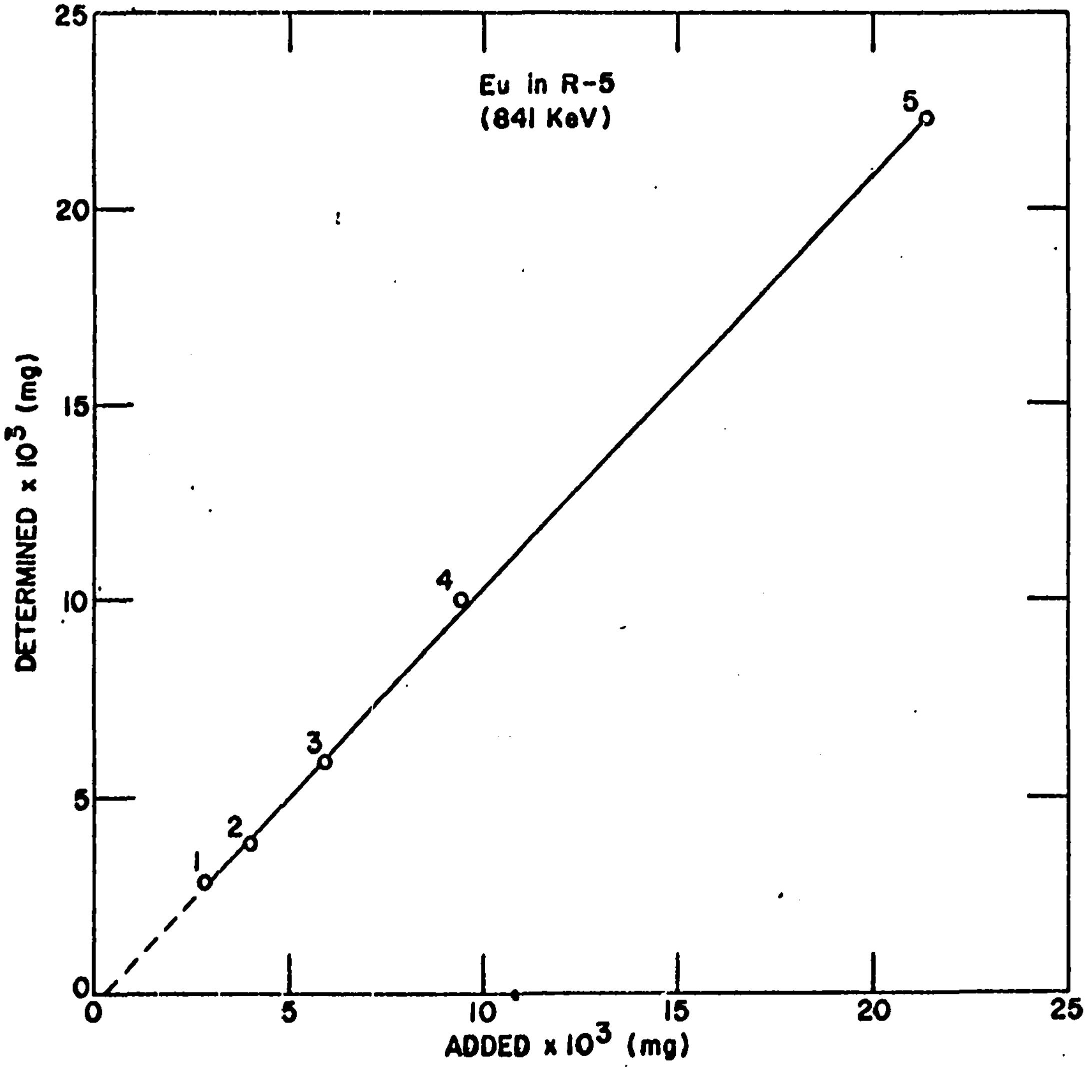

Figure 13. Self-shielding due to Eu in R-5

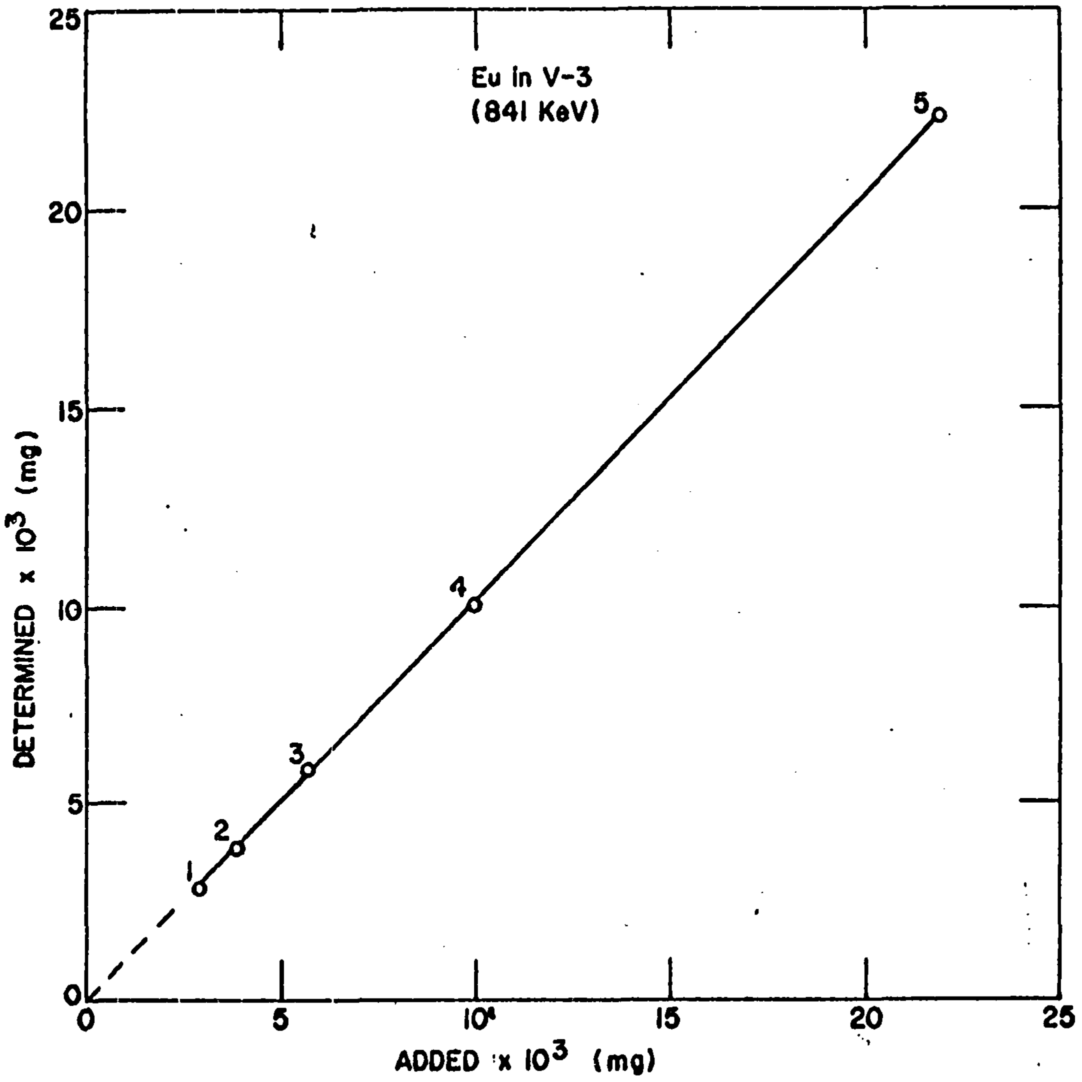

Figure 14. Self-shielding due to Eu in V-3

detected using epithermal neutrons the analysis does not suffer because of the strong Gd self-shielding in the thermal facility. It is important to attempt to match the amount of Gd in the standard fairly closely to the amount in unknown samples to eliminate the possibility of a reduction of the number of neutrons received by the other rare earths due to the large neutron absorption of Gd.

Self-shielding effects due to Sm are found to exist in both the V-3 and R-5 irradiations but only becomes important in samples containing above 2.25 mg of Sm. The samples used in this investigation contained 0.5 mg or less of Sm and the ultimate goal would be to apply the method developed to samples of decreasing size. Sm self-shielding need not be considered here or as long as the total Sm content is less than 2.25 mg.

Analysis of Rare Earth "Unknowns"

In order to demonstrate the applicability of the method as developed to systems in which the rare earth composition is not known and thus where a standard must be used to analyze the mixture, two "unknowns" were analyzed. These "unknowns" were prepared by weighing out arbitrary, but accurately measured amounts of rare earth oxides. These were dissolved in nitric acid and diluted to volume in previously calibrated volumetric flasks. The composition of these "unknowns" is listed in Table 13 and the standard used for

Table 13. Composition of rare earth "unknowns" 1 and 2

Rare earth	Amount in unknown 1 (mg)	Amount in unknown 2 (mg)
Sm	0.1286	0.2095
Eu	0.0056	0.0150
Gd	0.2046	0.6285
Tb	0.1062	0.3995
Dy	0.4630	0.8088
Ho	0.3192	0.3202
Er	0.3802	0.7932
Tm	0.1050	0.2465
Yb	0.3728	1.1922
Lu	0.0888	0.0735

the analysis was the gadolinite simulation (see Table 10). Five "unknowns" and one standard were prepared by pipetting with the same 250 λ pipette for all samples. After evaporation to dryness the samples were packed in one inch "rabbits" so that the solid material was in as close proximity as possible. The irradiation and data collection then proceeded as in all previous experiments.

The analysis of the two "unknowns" are listed in Tables 14 and 15. The standard deviations listed in those tables were calculated using propagation of errors theory by the equation

$$\sigma = (\sigma_s^2 + \sigma_u^2)^{1/2} \qquad (11)$$

where σ_s is the standard deviation in the area of the standard sample as determined by the ICPEAX computer program and σ_u is calculated by Equation 10.

In the analysis of the first "unknown" two of the rare earths are bordering on the five percent error region, Er (-5.0 percent) and Lu (+ 5.2 percent), when analyzed by the internal standard method. These two rare earths, however, can be analyzed to + 3.6 percent and - 2.7 percent respectively by an external standard technique. This behavior is the reverse of what one might expect in that an internal standard method is usually considered the more accurate of the two since it eliminates any errors due to inconsistent

Table 14. Analysis of "unknown" 1

Isotope	Actual composition (mg)	Internal standard method (mg)	External standard method (mg)
^{153}Sm	0.1286	0.1302 ± 0.0021	0.1280 ± 0.0022
^{152m}Eu	0.0056	0.0054 ± 0.0001	0.0055 ± 0.0001
^{159}Gd	0.2046	0.1977 ± 0.0063	0.2124 ± 0.0079
^{160}Tb	0.1062	0.1018 ± 0.0028	0.1055 ± 0.0028
^{165}Dy	0.4630	0.4641 ± 0.0110	0.4587 ± 0.0055
^{166}Ho	0.3192	-	0.3191 ± 0.0032
^{171}Er	0.3802	0.3611 ± 0.0112	0.3938 ± 0.0122
^{170}Tm	0.1050	0.1080 ± 0.0050	0.1065 ± 0.0057
^{175}Yb	0.3728	0.3735 ± 0.0176	0.3621 ± 0.0087
^{177}Lu	0.0888	0.0934 ± 0.0031	0.0864 ± 0.0033

Table 15. Analysis of "unknown" 2

Isotope	Actual composition (mg)	Internal standard method (mg)	External standard method (mg)
^{153}Sm	0.2095	0.2036 ± 0.0068	0.1919 ± 0.0101
^{152m}Eu	0.0150	0.0148 ± 0.0002	0.0139 ± 0.0006
^{159}Gd	0.6285	0.6416 ± 0.0113	0.6043 ± 0.0403
^{160}Tb	0.3995	0.3910 ± 0.0262	0.3673 ± 0.0428
^{165}Dy	0.8088	0.8143 ± 0.0137	0.6119 ± 0.0100
^{166}Ho	0.3202	-	0.3008 ± 0.0104
^{171}Er	0.7932	0.8102 ± 0.0150	0.7617 ± 0.0212
^{170}Tm	0.2465	0.2391 ± 0.0068	0.2257 ± 0.0098
^{175}Yb	1.1922	1.2176 ± 0.0720	1.1381 ± 0.0540
^{177}Lu	0.0735	0.0744 ± 0.0273	0.0696 ± 0.0045

flux. The analysis was, in general, satisfactory for all of the rare earths present.

An excellent case in favor of the internal over the external standard method can be made from the data in Table 15. Due to an apparent pipetting error one of the "unknown" samples contained far less activity for each of the rare earths. Normally the data for that sample would be discarded since the external standard method yields results up to 15 percent low. However, by an internal standard method the largest error is 4.1 percent high since the ^{166}Ho activity in the sample whose composition was significantly lower than the others is also lower. Therefore, where the ratios of rare earth to holmium are taken the pipetting error is compensated.

ERROR ANALYSIS

One of the most difficult problems associated with any analysis method lies in the approximation of errors which are inherent to the method. This is especially true of activation analysis since the common systematic errors such as incorrect weighing or pipetting are also complicated by radiochemical errors such as interfering gamma rays, interfering reactions and those based purely on counting statistics.

Many of the chemical uncertainties have been previously discussed (64) and it has been pointed out that when extreme care is taken in weighing and pipetting of samples the error introduced in an activation analysis procedure is relatively small. One important potential source of error is the very high sensitivity of the method for trace impurities introduced by the lack of cleanliness of items used in handling samples. To check on any impurities which might be added through contamination of pipettes, polyethylene capsules or impure acid three spectra (Figures 15, 16 and 17) were taken. The first is a spectrum of the Ge(Li) normal background, the second a polyethylene capsule which had been cleaned in nitric acid and rinsed with distilled water and the third a polyethylene capsule which had been cleaned and had nitric acid evaporated in it. The two peaks in Figure 16 are those of Na probably added through handling even though plastic

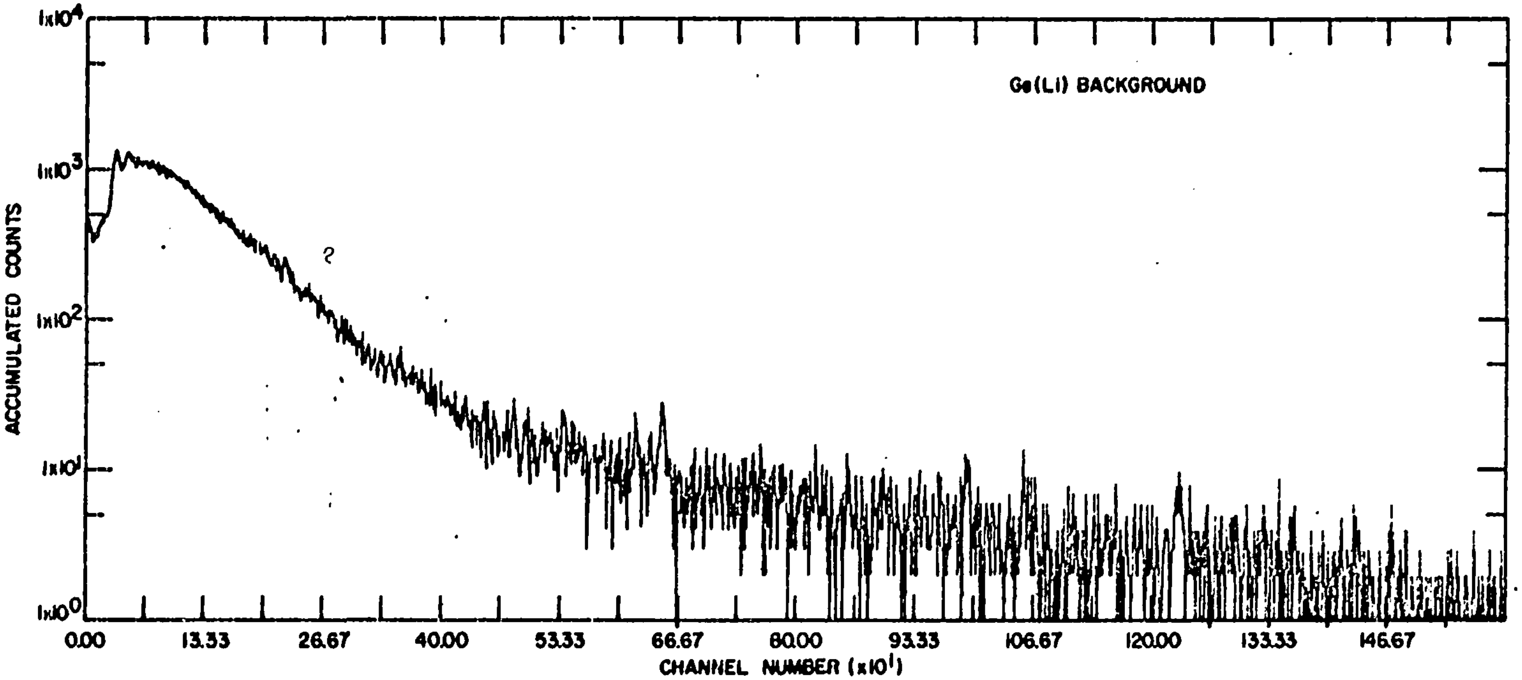

Figure 15. Gamma ray spectrum of Ge(Li) background

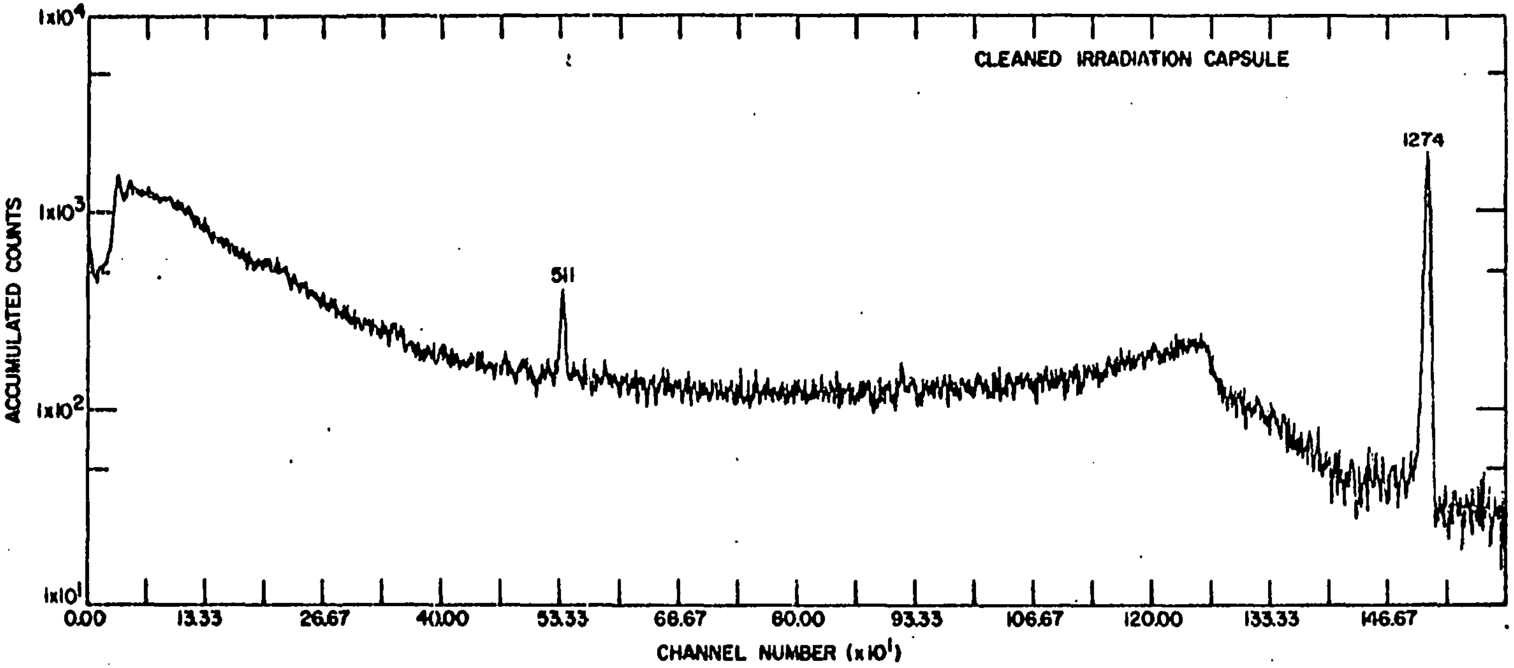

Figure 16. Gamma ray spectrum of cleaned irradiation capsule

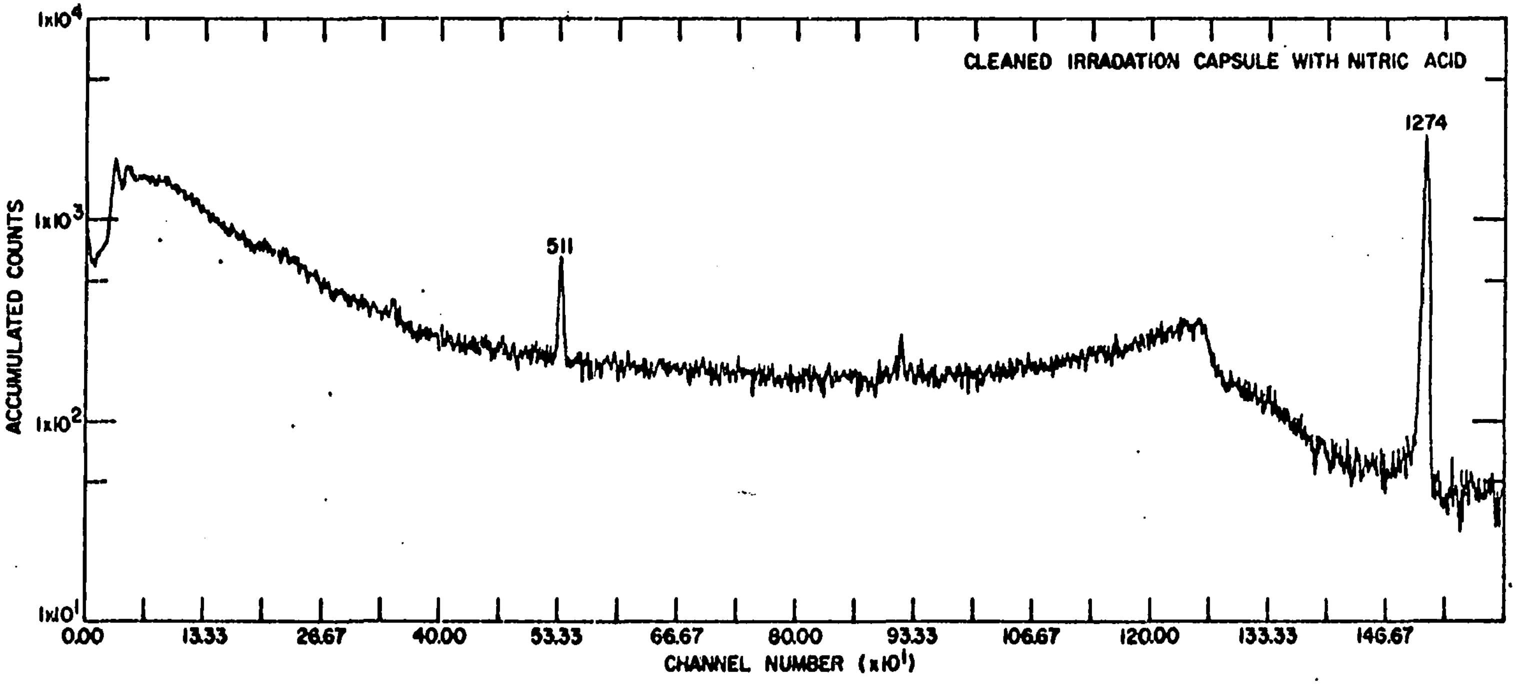

Figure 17. Gamma ray spectrum of cleaned irradiation capsule with nitric acid

gloves were worn at all times. The absence of any peaks in Figure 17 which do not appear in Figure 16 indicates that no contamination was introduced from nitric acid. There is no reason to suspect that loss of sample could have occurred during the drying process since the rare earths are of a nonvolatile nature and evaporation took place in a relatively cool (80° C) oven at a slow rate.

It is also believed that the errors associated with uncertainties in decay times, counting times and half-life accuracy are relatively unimportant in the current study. The decay time is calculated by taking the difference between the time at which the samples were removed from the reactor and the time at the midpoint of the counting interval. As long as the half-life is long in comparison to the uncertainty in the decay time the errors introduced into the analysis by virtue of the uncertainties in the time will be small. The shortest half-life studied was 2.3 hours (^{165}Dy) and a value of ± 2 minutes over a minimum of 8 hours and a maximum of 40 hours is believed to be reasonable for the uncertainty in the decay time. The counting interval is measured using a stopwatch which reads in one-hundredths of minutes and thus the uncertainty in the county interval should be ± 0.005 minutes for the worst case. Counting times were either 40, 75 or 90 minutes long so that the relative error is small. The uncertainty in the half-life is considered to be one half of the least significant digit and thus the isotope with the greatest relative error is ^{165}Dy at 139.1 ± 0.05 minutes.

The possible interfering reactions due to processes other than (n, γ) are listed in Table 16. Of those listed, nine produce the same isotopes which are being used in the analysis for rare earths. Three of these produce ^{153}Sm with only one reaction, ^{154}Sm(n, 2n)^{153}Sm, having a high enough cross section to be significant. The error introduced by this reaction can be estimated through the ratio of the product of abundance and cross section for the ^{154}Sm(n, 2n) ^{153}Sm reaction to that for ^{152}Sm(n, γ)^{153}Sm (Table 1). This ratio is approximately 0.1/100 or 0.1 percent. By a similar analysis the error in ^{159}Gd due to the ^{159}Tb(n, p)^{159}Gd reaction can be estimated at 0.3 percent and for ^{162}Dy(n, α) ^{159}Gd, 0.4 percent. The error in the ^{165}Dy calculations will be uncertain by 0.2 percent due to the ^{165}Ho(n, p)^{165}Dy reaction whereas for ^{168}Er(n, α)^{165}Dy the extremely low cross section (0.5 mb) reduces the error introduced by this reaction to an insignificant level. The potential for the largest uncertainty is introduced by the ^{176}Yb(n, 2n)^{175}Yb and ^{175}Lu(n, p)^{175}Yb reactions the former being 2 and the latter 0.1 percent.

Two types of interfering gamma rays must be considered. The first comprises those gamma rays which are associated with nuclides produced by interfering reactions and have the

Table 16. Possible interfering reactions[a]

Target nuclide	Abundance of target (%)	Nuclear reaction	Cross section (mb)	Product nuclide	Half-life of product	Gamma-rays of product (kev)
^{144}Sm	3.16	(n, 2n)	610	^{143}Sm	9 m	511
^{147}Sm	15.1	(n, α)	0.16	^{144}Nd	2 x 10^{15} y	none
^{149}Sm	13.8	(n, α)	43.5	^{146}Nd	stable	-
^{152}Sm	26.6	(n, α)	8.9	^{149}Nd	1.8 h	114, 210, 270
		(n, p)	3.7	^{152}Pm	6.5 m	122, 245
^{154}Sm	22.5	(n, 2n)	225	^{153}Sm[b]	4.68 h	103
		(n, p)	3.5	^{154}Pm	2.5 m	none
		(n, α)	9	^{151}Nd	12 m	118, 174, 256
^{151}Eu	47.8	(n, 2n)	480	^{150}Eu	5 y	334, 439, 584
^{153}Eu	52.2	(n, 2n)	164	^{152}Eu	12.7 y	112, 344, 779
		(n, p)	7.4	^{153}Sm[b]	4.68 h	103
		(n, α)	9	^{150}Pm	2.7 h	334, 880, 1165

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[a] Nuclear data, reference (13).

[b] Indicates isotopes used in the analysis.

Table 16. (Continued)

Target nuclide	Abundance of target (%)	Nuclear reaction	Cross section (mb)	Product nuclide	Half-life of product	Gamma-rays of product (kev)
^{156}Gd	20.50	(n, α)	3.22	^{153}Sm^{b}	4.68 h	103
^{160}Gd	21.9	(n, 2n)	1470	^{159}Gd	stable	-
		(n, α)	2	^{157}Sm	0.5 m	570
^{159}Tb	100	(n, 2n)	160	^{158}Tb	1200 y	80, 182, 950
		(n, p)	2.2	^{159}Gd^{b}	1.8 h	363
		(n, 2p)	0.08	^{158}Eu	46 m	80, 520
		(n, α)	2.2	^{156}Eu	15.4 d	812, 1150, 1240
^{162}Dy	25.5	(n, α)	3.56	^{159}Gd^{b}	1.8 h	363
^{163}Dy	24.9	(n, p)	3.0	^{162}Tb	7.5 m	180, 258, 810
^{164}Dy	28.2	(n, α)	4.0	^{161}Gd	3.6 m	102, 315, 361
^{165}Ho	100	(n, 2n)	2760	^{164}Ho	36.7 m	73, 91
		(n, p)	40	^{165}Dy^{b}	139.1 m	280, 362, 621
^{166}Er	33.4	(n, 2n)	1000	^{165}Er	10.3 h	none
^{167}Er	22.9	(n, p)	3.0	^{167}Ho	3.1 h	238, 321, 387

Table 16. (Continued)

Target nuclide	Abundance of target (%)	Nuclear reaction	Cross section (mb)	Product nuclide	Half-life of product	Gamma-rays of product (kev)
^{168}Er	27.1	(n, 2n)	190	^{167}Er	stable	-
		(n, p)	2.5	^{168}Ho	3.3 m	850
		(n, α)	0.5	^{165}Dy[b]	139.1 m	280, 362, 621
^{170}Er	14.9	(n, 2n)	1895	^{169}Er	9.6 d	8
		(n, p)	1.8	^{170}Ho	45 s	430
		(n, α)	1.0	^{167}Dy	4.4 m	none
^{176}Yb	12.7	(n, 2n)	786	^{175}Yb[b]	4.2 d	283, 396
^{175}Lu	97.4	(n, 2n)	1600	^{174}Lu	3.6 y	1240
		(n, p)	3.42	^{175}Yb[b]	4.2 d	283, 396

same energy as rare earths used for analysis. Of the nuclides listed in Table 16 only three have sufficiently large cross sections (greater than 500 mb) and half-life (greater than one hour) to warrant consideration of the gamma rays associated with these reactions as being possible interferences. The ^{166}Er(n, 2n)^{165}Er reaction produces no gamma rays whereas the ^{170}Er(n, 2n)^{169}Er and ^{175}Lu(n, 2n)^{174}Lu reactions have associated with them an 8 and a 1240 kev gamma ray respectively, neither of which are close enough to introduce uncertainties in the areas of gamma rays used in the analysis.

The second, and most important, source of interfering gamma rays lies in those which are of the same energy from two or more rare earths. With the decay times used in this analysis there is sufficient ^{171}Er remaining when the spectra are accumulated that its 308 kev gamma ray interferes with the 310 kev peak of ^{160}Tb as do the 296 and 299 peaks of the same two nuclides. The 105 kev peak of ^{155}Sm is approximately 2 percent as intense as the 103 kev of ^{153}Sm but when added to the area of the 103 peak introduces no error because it will be present in the same percentage in standard and unknowns and thus will cancel when ratios are calculated. The 103 kev gamma ray of ^{153}Gd could introduce as much as 0.4 percent uncertainty into the ^{153}Sm peak but the gamma rays at 102 kev in ^{161}Gd and at 105 kev in ^{177m}Lu introduce negligible error due to the low cross section and abundance of their target nuclei. An error of up to two percent is possible in the 963 kev peak of ^{152m}Eu due to the 966 kev gamma ray of ^{160}Tb but no interfering gamma rays exist (from rare earths) for the 841 kev peak.

Four possible interfering gamma rays exist for the 363 kev peak of ^{153}Gd: ^{161}Gd(361 kev, 2 percent), ^{165}Dy(362 kev, > 1000 percent), ^{166m}Ho(366, 0.14 percent), ^{177m}Lu(367, < 0.1 percent). The ^{161}Gd gamma ray will not affect the results for the same reasons mentioned above for ^{153}Sm and ^{155}Sm and since Gd is analyzed 30 to 40 hours after the end of the irradiation, any interference from ^{165}Dy should be gone due to the decay of that nuclide whose half-life is slightly over two hours. As noted above the ^{160}Tb 298 and 310 kev gamma rays cannot be used due to the ^{171}Er interference but the 879 and 1178 kev gamma rays are free from any such problems. During the analysis for Dy the ^{159}Gd 363 kev gamma ray will introduce a one percent error under the 362 kev peak of ^{165}Dy.

The ^{166}Ho 1378 kev gamma ray has no interferences from the rare earths. In addition to the ^{171}Er-^{160}Tb interferences mentioned earlier, the ^{177}Lu 113 kev gamma ray eliminates the 112 kev peak of ^{171} Er as a possibility for analysis. The 46 kev x-ray of ^{170}Tm has been found to yield the best results and although it is expected that other of the rare earths also emit x-rays in that energy range the

^{170}Tm peak is much more intense than any of the others. In a mixture of rare earths with Tm added the 46 kev peak is roughly 50 times more intense than when Tm is absent and thus an estimated uncertainty of two percent is attributed to other rare earth x-rays.

A total maximum uncertainty of 1.9 percent can be expected from interfering gamma rays near the 283 kev peak of ^{175}Yb due to ^{161}Gd (284, 1.2 percent) and ^{171}Er (277, 0.7 percent). A gamma ray at 280 kev due to ^{165}Dy is not expected to interfere with the Yb analysis since Dy will have decayed by that time. It is impossible to use the 113 kev gamma ray of ^{177}Lu due to the large interference of the 112 peak from ^{171}Er; the Lu analysis must be performed using the 208 kev peak whose only interference is also from ^{171}Er but amounts to less than 0.03 percent.

A common source of error in any activation analysis method is due to the counting statistics. Since the standard deviation is proportional to the square root of the total number of counts accumulated over the counting period (see Equation 10) an attempt is made to accumulate as many counts as possible. Generally a total of 10,000 counts at the peak center will furnish a large enough area to reduce the relative standard deviation to the one percent level. A problem related to the counting statistics is the shape of the peaks in the gamma ray spectra. Computer programs work best when the peaks are gaussian and when their height is at least twice their width. During this investigation there were few times when these criteria were not met. Even when poor areas were obtained from the ICPEAX program hand calculations of the areas yielded more accurate data.

A more prevalent problem than shape, height or width of an individual gamma ray peak was the effect which a higher energy peak had (via its Compton background) on peaks immediately below it in energy. This was especially true of the "unknown" analysis where a large ^{175}Yb 396 kev peak caused the other peaks in the 275 to 390 kev region to be differently shaped in the "unknown" and standard samples. The computer program was consistent in calculating the areas of the "unknown" samples but treated the standards differently necessitating a hand calculation of the areas in that energy region of the standard spectrum.

SUMMARY

The method which has been devised for the instrumental activation analysis of rare earth mixtures has been shown to be effective for several different mixtures. The ^{166}Ho 1380 kev gamma ray peak is used as an internal standard to analyze for the remaining heavy (Sm - Lu) rare earths. By a comparison of the internal standard ratio for a certain gamma ray in a standard spectrum to the ratio for the same gamma ray in an unknown spectrum, the composition of the unknown can be determined. The method has been used for the analysis of samples in which the weights of rare earths were equal except for Eu which was present at one-tenth that weight, samples in which a simulation of the rare earth ore gadolinite was analyzed, and samples of "unknown" composition.

As previously mentioned, there are two major trends in the development of rare earth analyses. One category is the analysis of a relatively few (two or three) rare earths while analyzing for other elements such as Fe, Cd, Sc, etc. and the second is the analysis of most or even all of the rare earths employing partial group separation or complete elemental separation via ion exchange or reversed phased partition chromatographic techniques. These separation methods, although analytically satisfactory, are time consuming and subject to numerous systematic handling errors. The separation is sometimes left to the natural radioactive decay process by counting samples repeatedly over a period of time which could range up to ten days. The instrumental activation analysis which was developed is fast (requiring only 60 hours for a complete analysis), accurate, requires no "wet chemistry" and enjoys the oft times important advantage of being nondestructive.

It is believed that the method could be applied as currently developed to mixtures of rare earths whose composition relative to Ho is one or even two orders of magnitude smaller than those previously analyzed. In addition there is no evident reason as to why the method could not be applied to other matrix rare earths by using that element as the internal standard. Additional possibilities for further investigation might include the use of a nonrare earth element as the internal standard thus eliminating the need for any external standard calculations among the rare earths.

The possibility of applying the method to trace rare earth analysis in other rare earth matrices without separation of a major portion of the matrix material is doubtful due to the large matrix activity which is invariably produced. It might be possible, however, to change irradiation, decay and counting times enough to obtain reasonable results at a trace quantity level.

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APPENDIX A. RARE EARTH OXIDES

Table 17. Spectrographic analysis of lighter rare earth oxides used

Impurity	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7	Dy_2O_3	Y_2O_3
Sm	-	< 150	< 200	-	-	< 500
Gd	~ 500	< 250	-	-	< 200	< 100
Eu	< 100	-	< 100	-	-	-
Tb	-	-	< 500	-	< 500	< 500
Dy	-	-	< 100	< 100	-	< 50
Ho	-	-	-	-	< 150	< 500
Er	-	-	-	-	< 50	< 50
Nd	< 200	-	< 500	-	-	-
Y	100	-	< 200	< 50	< 50	-
Ca	< 100	-	-	-	-	-
Si	< 60	< 50	-	-	-	-
Fe	< 60	< 30	-	-	-	-

Table 18. Spectrographic analysis of heavier rare earth oxides used

Impurity	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3
Dy	< 400	< 100	-	-	-
Ho	-	< 50	< 400	-	-
Er	< 70	-	< 50	< 50	< 10
Tm	< 100	< 100	-	< 20	< 10
Yb	∼ 200	∼ 200	< 30	-	5
Lu	-	-	< 30	< 30	-
Y	∼ 250	∼ 250	< 100	-	< 10
Ca	-	-	-	∼ 500	< 500
Fe	-	-	-	∼ 8	5

APPENDIX B. Ge(Li) SPECTRA OF RARE EARTH NUCLIDES

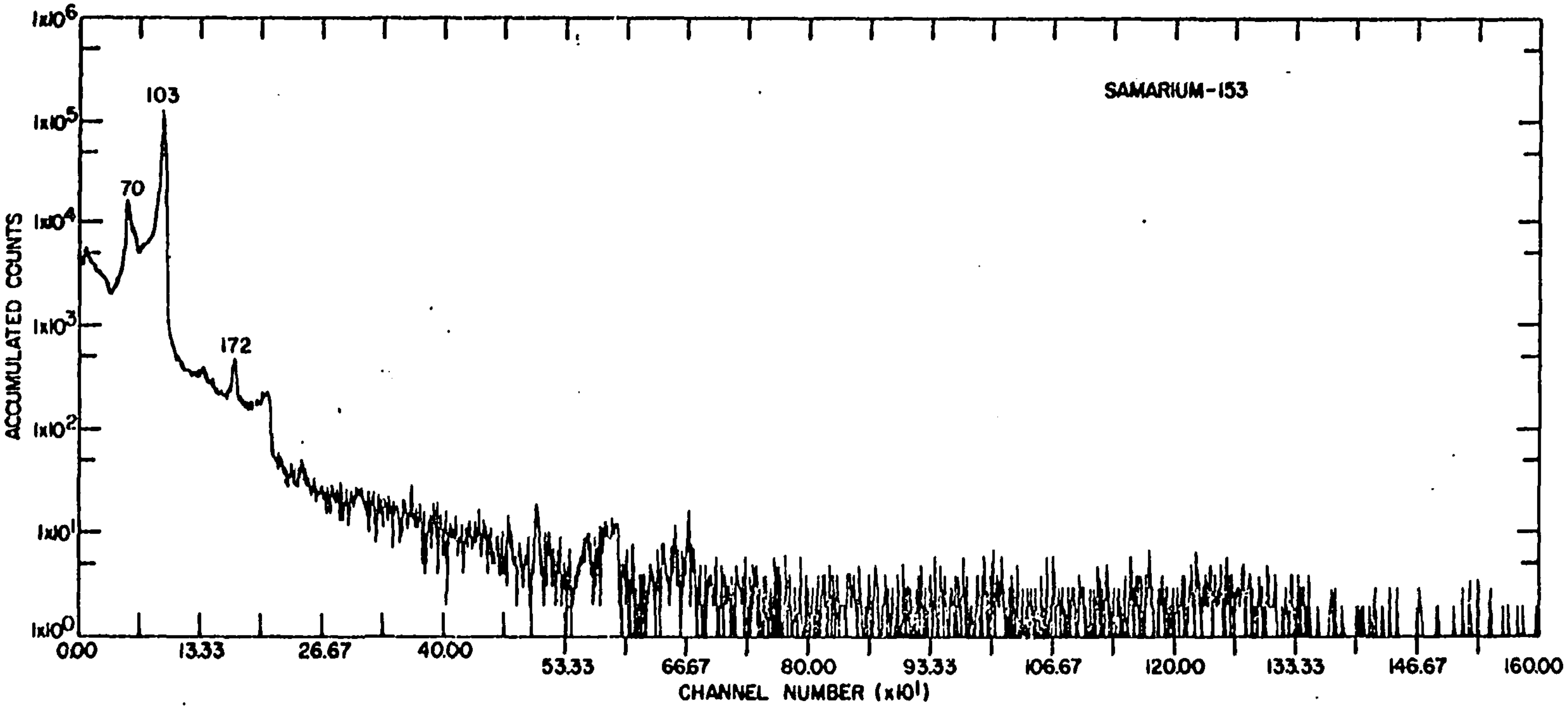

Figure 18. Gamma ray spectrum of ^{153}Sm

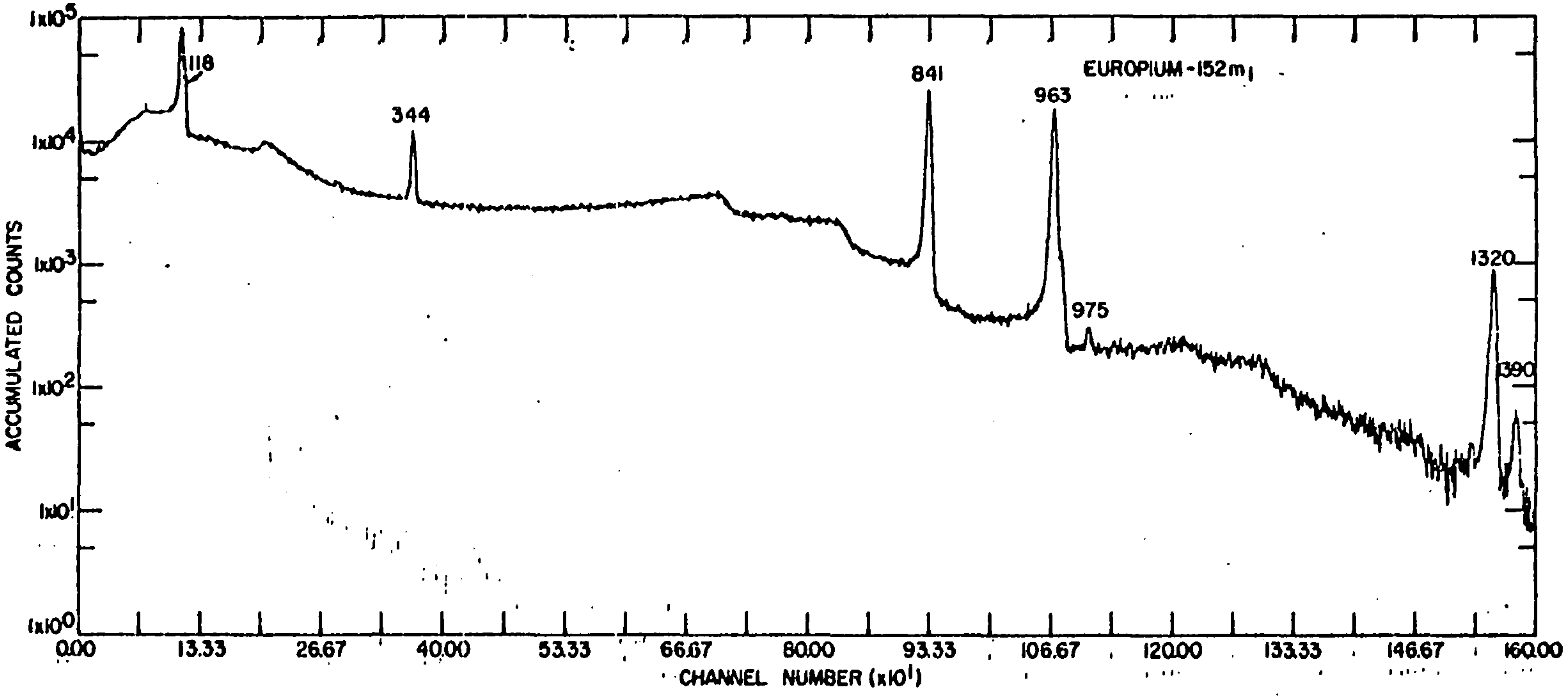

Figure 19. Gamma ray spectrum of $^{152m_1}Eu$

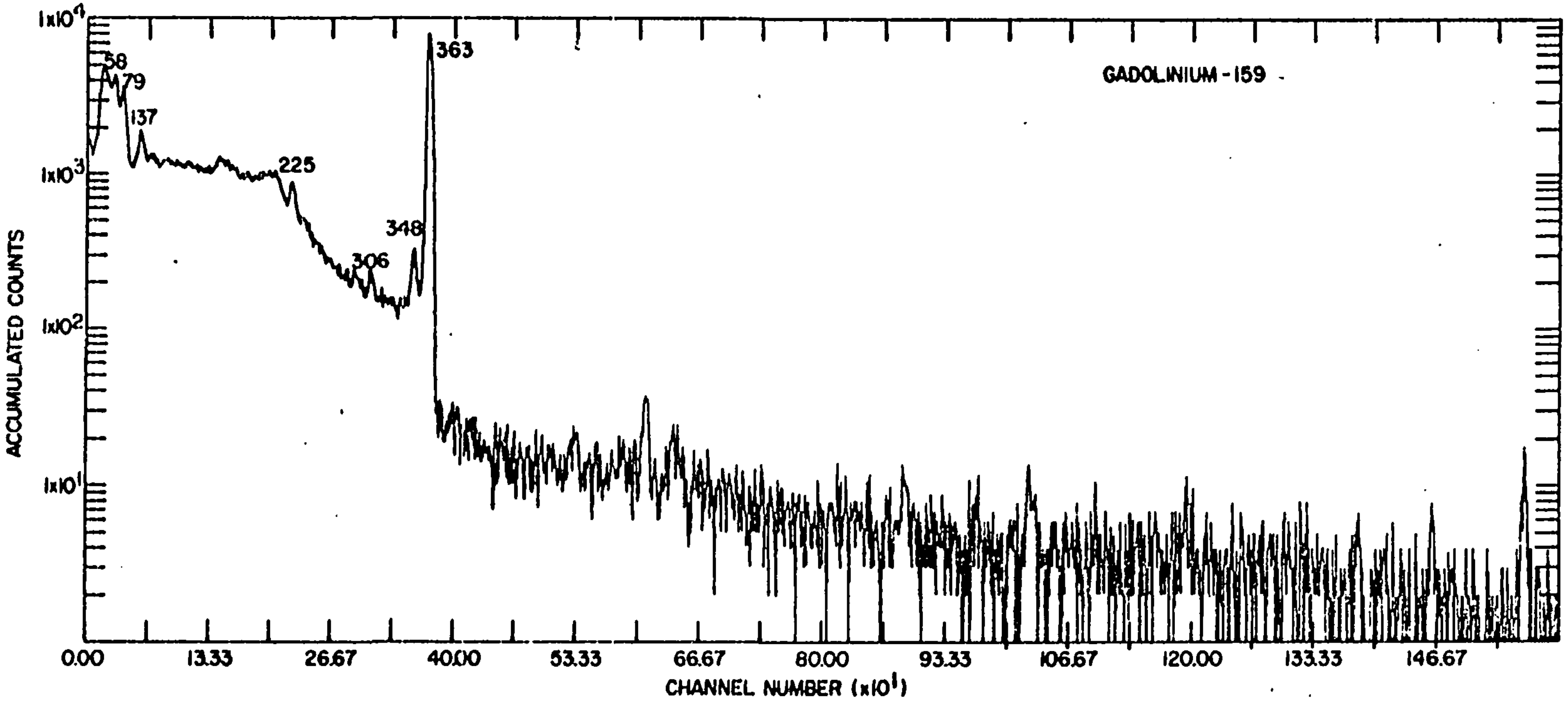

Figure 20. Gamma ray spectrum of ^{159}Gd

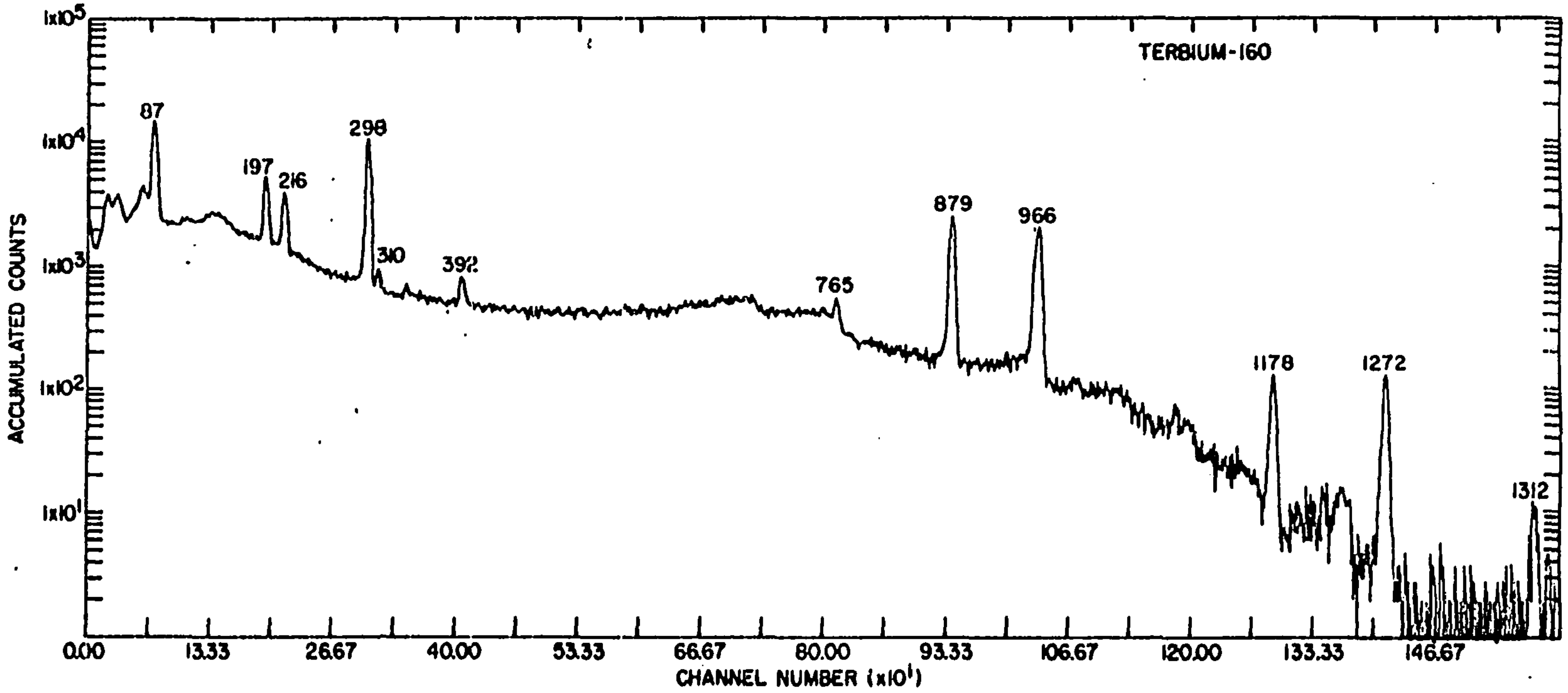

Figure 21. Gamma ray spectrum of ^{160}Tb

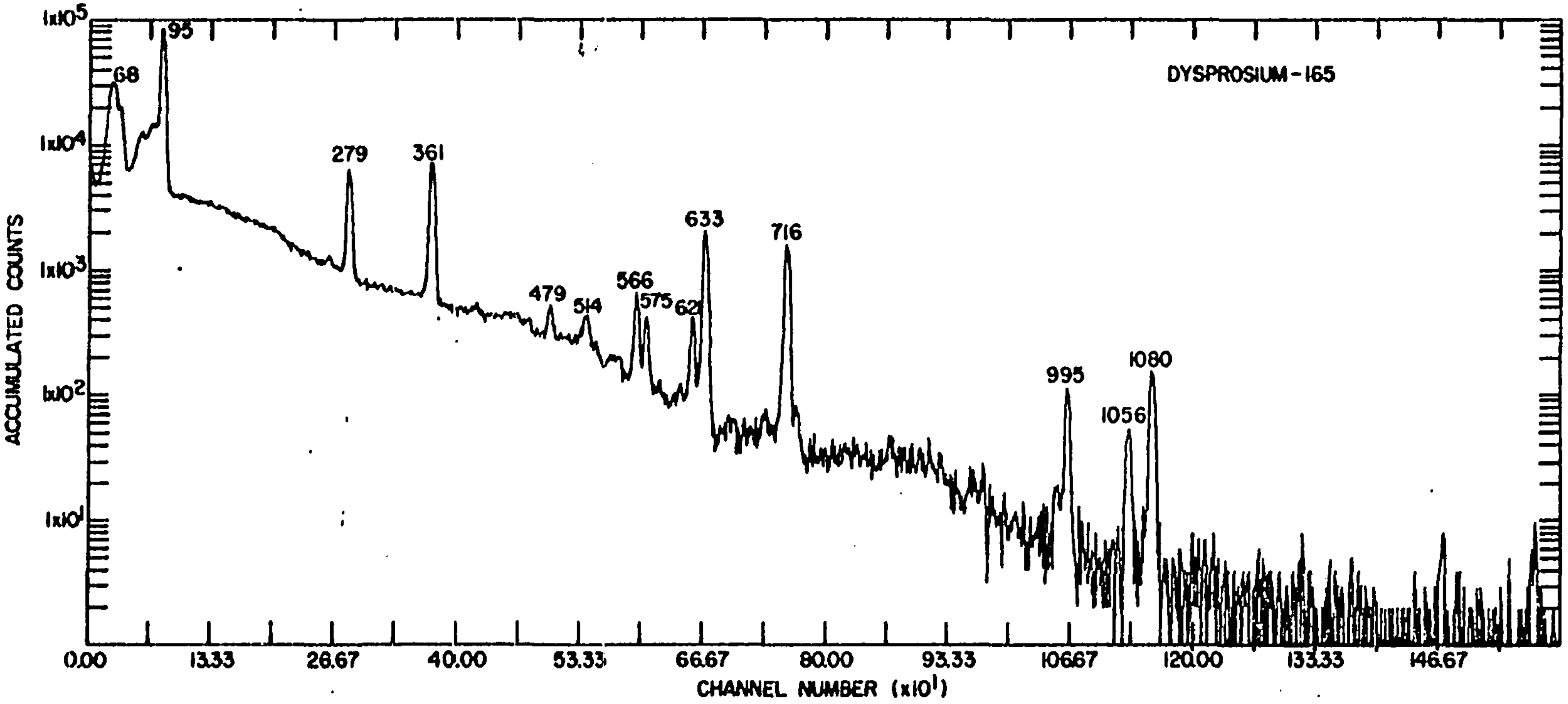

Figure 22. Gamma ray spectrum of ^{165}Dy

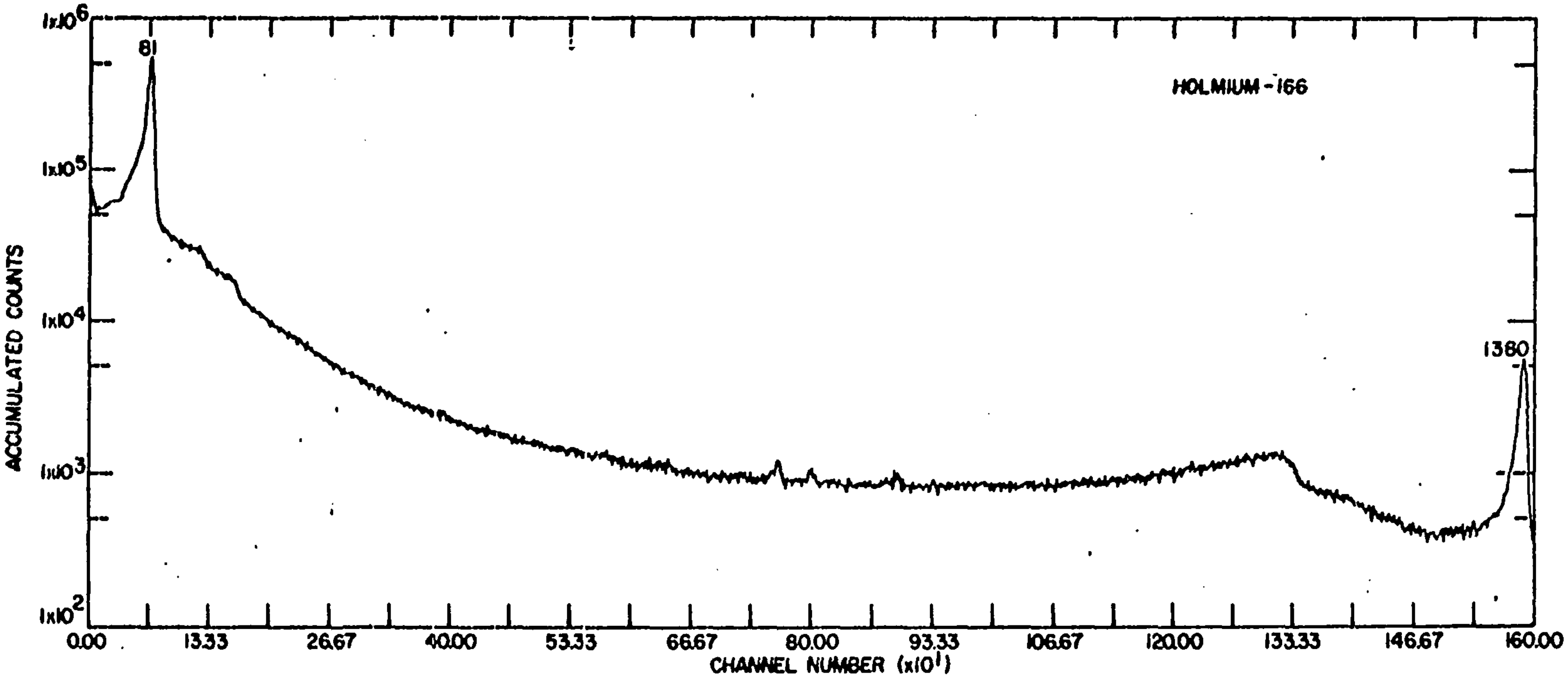

Figure 23. Gamma ray spectrum of ^{166}Ho

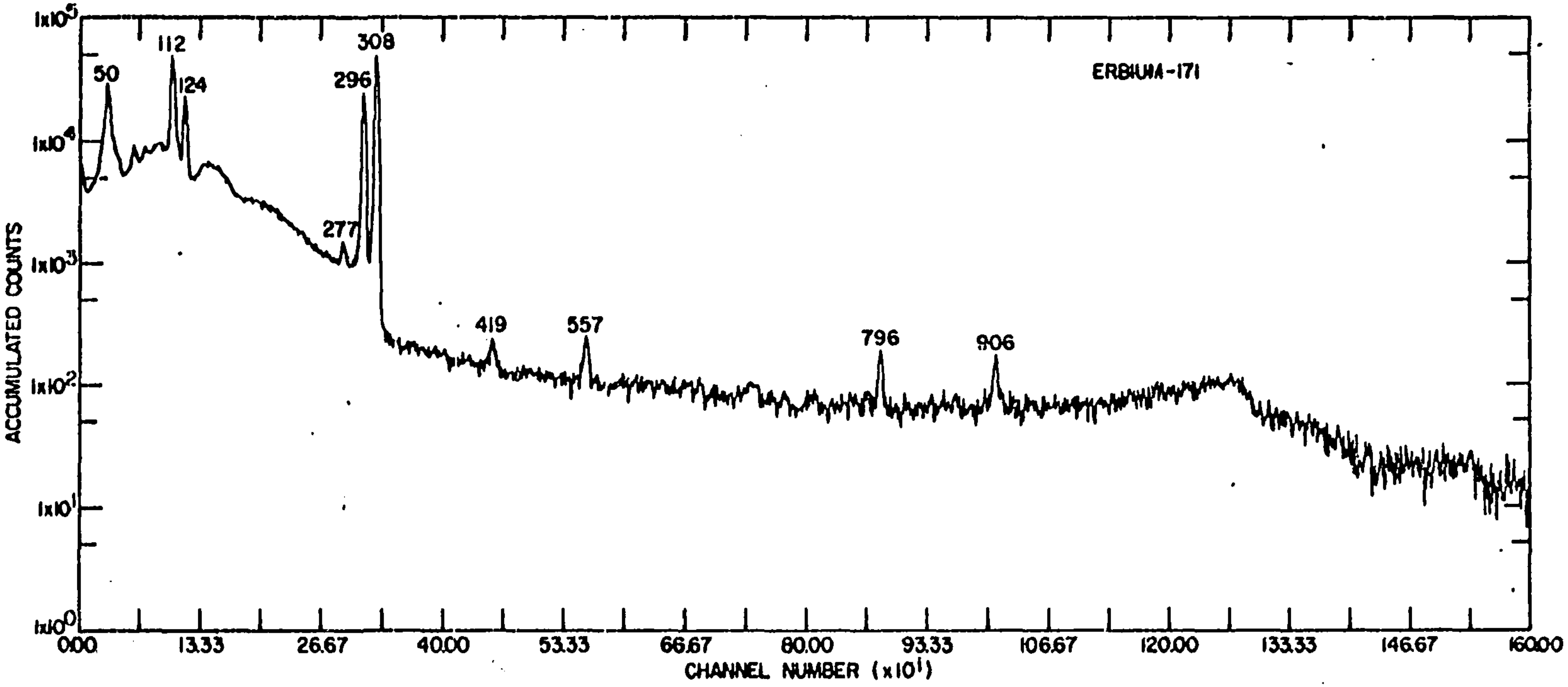

Figure 24. Gamma ray spectrum of ^{171}Er

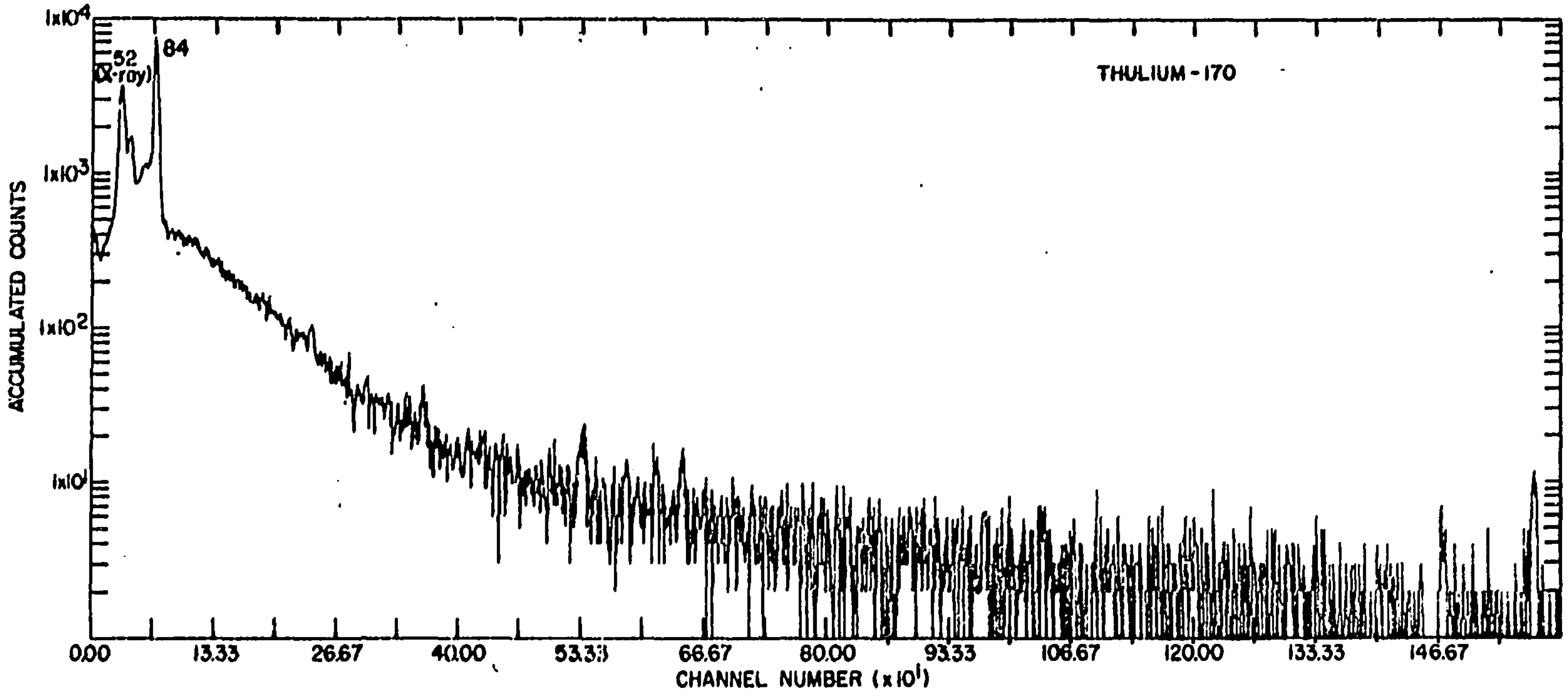

Figure 25. Gamma ray spectrum of ^{170}Tm

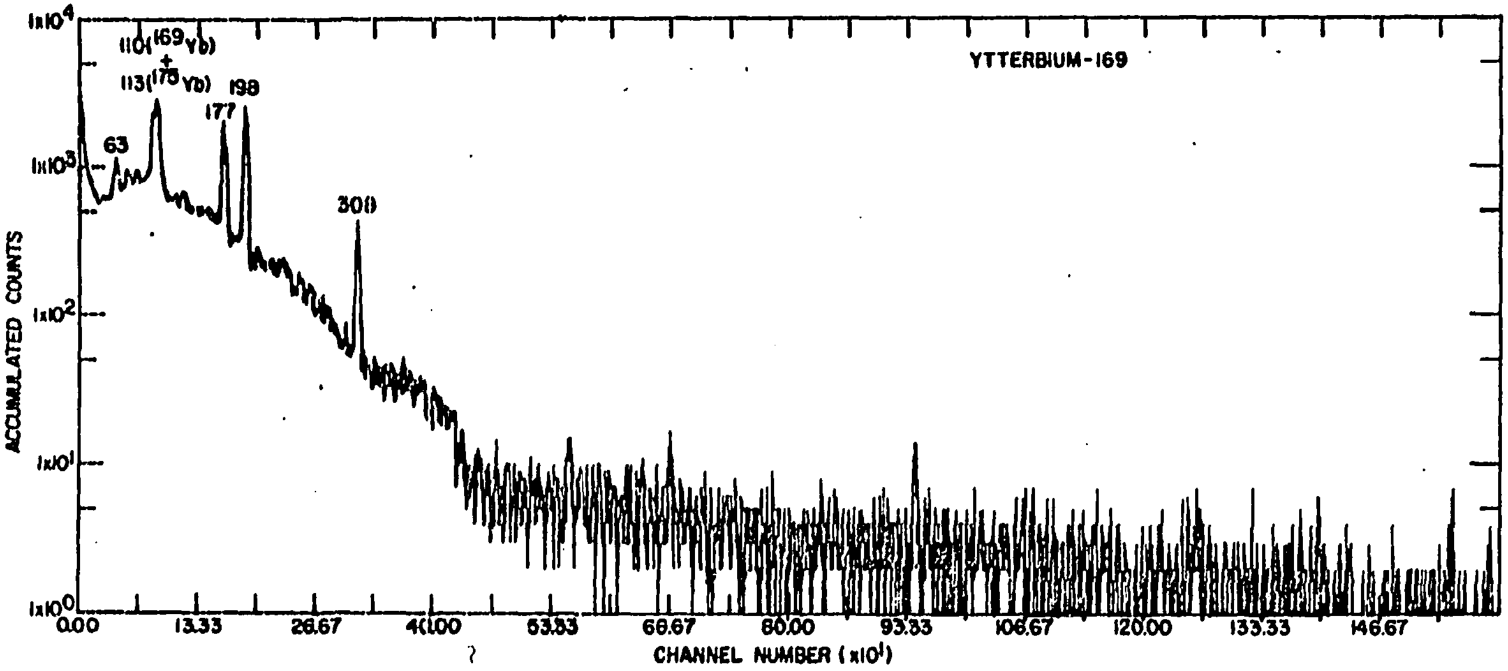

Figure 26. Gamma ray spectrum of ^{169}Yb

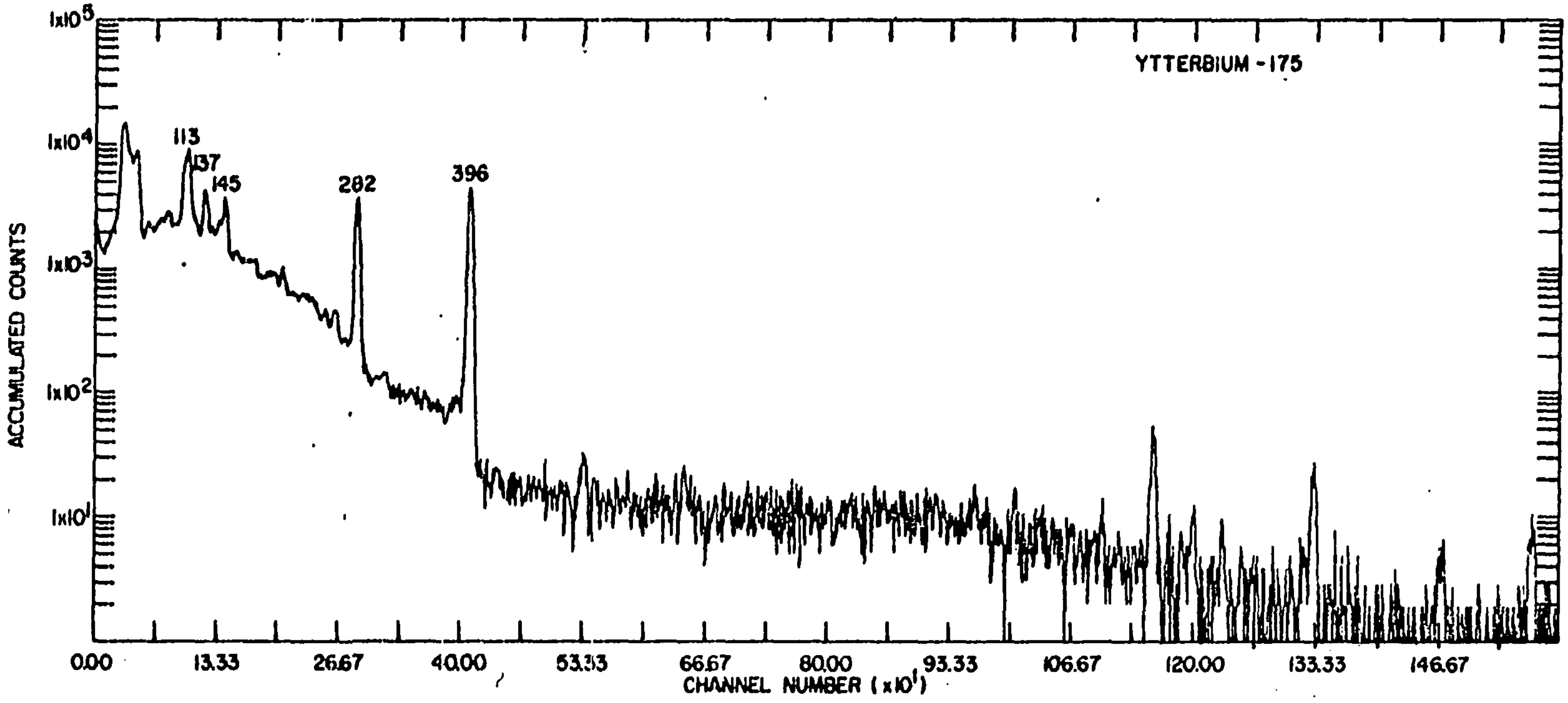

Figure 27. Gamma ray spectrum of ^{175}Yb

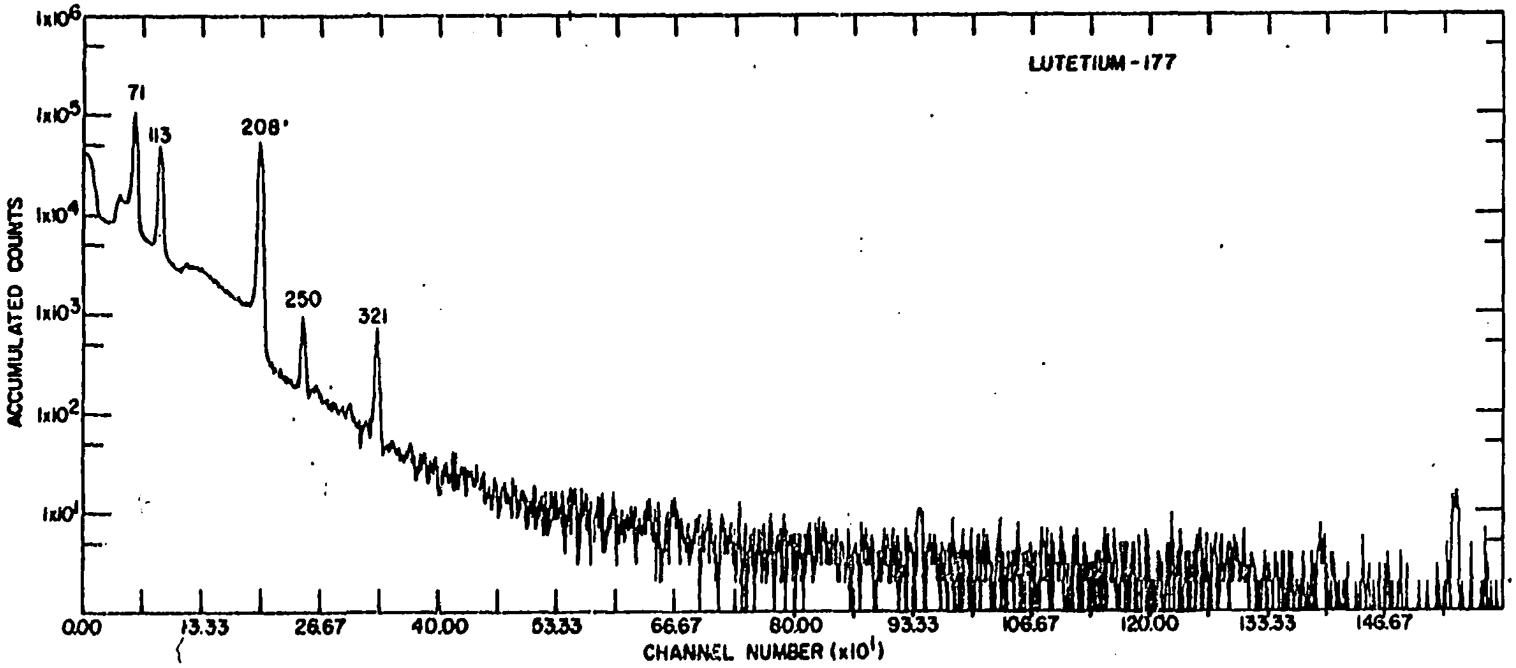

Figure 28. Gamma ray spectrum of ^{177}Lu

APPENDIX C. PRESTO

"PRESTO"[1] is a FORTRAN IV program written for the IBM 360/65 computer which converts data in the form of IBM 7-track magnetic tape to punched card format and/or listed data on the computer output. Data in the form of punched paper tape from the multichannel analyzer system are first transferred to magnetic tape. This tape is then submitted to the computer along with the program to obtain listings and decks of the data on IBM cards. The program will accept any number of 256, 512, 1024 or 1600 channel spectra. For each data set either listings, card decks, or both can be obtained from a single computer run. Any errors encountered during the transfer of the data from tape to cards or listings are indicated by the program on the output.

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[1] Haustein, Peter, Ames Lab, Ames, Iowa. PRESTO. Private communication, 1970.

APPENDIX D. ICPEAX

"ICPEAX-7"[1] is a FORTRAN IV program written for the IBM 360/65 computer. It automatically detects full-energy peaks in Ge(Li) spectra, determines the peak parameters, and can produce a plot of the spectra. Although the program was originally written to be used with a Ge(Li) detector, it also works with NaI(Tl) detector systems.

The input for "ICPEAX" is 1600 or less channels of raw data punched on IBM cards. The program detects full-energy peaks by analyzing a smooth second derivative of the spectrum. All negative minima are considered full-energy peaks if two conditions are met: the width of the peak must be between 3 to 15 channels, while the magnitude must be at least 0.35 times the standard deviation. After this preliminary search, the results of which are printed on the output, a gaussian fit is attempted on all peaks. The full-energy background is approximated by a straight line subtracted before the analysis. At this point the peaks are checked for a gaussian fit using a slightly modified version of the program written by Heath. The peaks are considered real only if they satisfy the gaussian fit routine.

The program uses the coefficients of the linear and guadratic calibration lines of the detector to assign energies to each of the peaks it considers real. The

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[1] Haustein, Peter, Ames, Lab, Ames, Iowa. ICPEAX-7. Private communication, 1970.

following information about each real peak is printed: location (kev), standard deviation, width, height, area, standard deviation of the area, line slope, line intercept, fit, and the energy (using both linear and quadratic calibrations). In addition, the program will yield either a log or linear plot of the spectrum on which each of the peaks is labeled with its approximate energy (quadratic calibration).

APPENDIX E. HRATIO

"HRATIO" is a FORTRAN IV program written for the IBM 360/65 computer. It calculates both internal and external standard ratios for any number of rare earth elements and any number of gamma-rays. The internal standard ratios are calculated using the ^{166}Ho 1380 kev gamma-ray as the internal standard. After reading and echo-check of the data all gamma-ray areas are converted to the end of the irradiation period. For the external standard calculation the corrected areas under the gamma-ray peaks of the same energy are compared in different spectra. For internal standard ratios the corrected areas of each component are first divided by the ^{166}Ho area in the same spectrum and this ratio is compared to the ratio of identical peaks in the remaining spectra. In both cases the standard deviation is calculated by a subroutine subprogram.

The output data are: uncorrected ^{166}Ho areas, time after the end of the irradiation (hours), live time count (minutes), uncorrected and corrected component areas, corrected ^{166}Ho areas, internal and external standard ratios with their associated standard deviations. The program has been applied to 15 gamma-rays, other than the ^{166}Ho 1380 kev, and for this uses less than 0.5 sec of CPU time at a cost of $2.10.

APPENDIX F. SELF-SHIELDING DATA

Table 19. Eu, Sm, Gd self-shielding data

1. ^{152m1}Eu, 841 kev gamma-ray, in V-3 (epithermal facility).

Sample	Actual composition (mg)	Corrected activity (cpm)	Determined composition (mg)
0	1.80×10^{-3}	167.34	-
1	2.83×10^{-3}	272.33	2.93×10^{-3}
2	3.85×10^{-3}	361.92	3.89×10^{-3}
3	5.90×10^{-3}	528.17	5.68×10^{-3}
4	$10.00 \times 10-3$	927.97	9.98×10^{-3}
5	22.30×10^{-3}	2037.90	21.92×10^{-3}

2. ^{152m1}Eu, 841 kev gamma-ray, in R-5 (thermal facility).

Sample	Actual composition (mg)	Corrected activity (cpm)	Determined composition (mg)
0	1.80×10^{-3}	3841	-
1	2.83×10^{-3}	6096	2.86×10^{-3}
2	3.85×10^{-3}	8638	4.05×10^{-3}
3	5.90×10^{-3}	12640	5.92×10^{-3}
4	10.00×10^{-3}	20150	9.44×10^{-3}
5	22.30×10^{-3}	45680	21.40×10^{-3}

Table 19. (Continued)

3. ^{153}Sm, 103 kev gamma-ray, in V-3.

Sample	Actual composition (mg)	Corrected activity (cpm)	Determined composition (mg)
0	0.2500	9837.7	-
1	0.5000	20059.1	0.5098
2	0.7500	29325.5	0.7453
3	1.2500	48409.8	1.2032
4	2.2500	79793.6	2.0278
5	5.2500	153831.0	3.9092

4. ^{153}Sm, 103 kev gamma-ray, in R-5.

Sample	Actual composition (mg)	Corrected activity (cpm)	Determined composition (mg)
0	0.2500	1202.4	-
1	0.5000	2475.7	0.5147
2	0.7500	3975.5	0.8268
3	1.2500	6275.0	1.3046
4	2.2500	11350.0	2.3600
5	5.2500	18692.6	3.8861

Table 19. (Continued)

5. ^{159}Gd, 363 kev gamma-ray, in V-3.

Sample	Actual composition (mg)	Corrected activity (cpm)	Determined composition (mg)
0	0.5042	2829.2	-
1	1.009	5714.6	1.018
2	1.514	8167.6	1.456
3	2.524	14643	2.610
4	5.554	32710	5.829
5	10.604	61331	10.930

6. ^{159}Gd, 363 kev gamma-ray, in R-5.

Sample	Actual composition (mg)	Corrected activity (cpm)	Determined composition (mg)
0	1.009	3252.0	-
1	1.514	3717.6	1.184
2	2.524	4509.0	1.476
3	5.554	6085.9	2.047
4	10.604	8096.6	2.796