NEUTRON ACTIVATION METHODS

FOR THE DETERMINATION OF

THE RARE EARTHS IN MINERALS

A Thesis submitted for

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by

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ABSTRACT

The geochemical significance of the lanthanum-yttrium distribution in minerals and rocks is discussed. A method is described which has been developed for the determination of these elements by comparative neutron activation analysis. Simple precipitation reactions only are employed for effecting radiochemical separations. All operations can be performed in a grade 'C' type radiochemical laboratory, and the method is thus capable of being used by most geochemical laboratories. The limiting sensitivity of the method is 0.5 p.p.m. La_2O_3 and 60 p.p.m. Y_2O_3 for a 100 mg-sample, with a coefficient of variation of ± 5 per cent. The overall accuracy of the method is estimated to be within ± 10 per cent.

The (n, γ) reactions which are utilised are:

$^{139}_{57}La$ (n, γ) $^{140}_{57}La$ ($t_{\frac{1}{2}}$ 40.2 hr. E_γ 1.62 Mev)

$^{89}_{39}Y$ (n, γ) $^{90}_{39}Y$ ($t_{\frac{1}{2}}$ 64.2 hr. E_β 2.26 Mev)

After irradiation inactive lanthanum and yttrium carriers are added to the samples, in solution. The rare earth activities are first isolated by a fluoride separation followed by an oxalate precipitation. The rare earth

oxalates are then dissolved in EDTA solution, and fractionally precipitated at pH5 with the aid of copper ions, added as demasking agents. Lanthanum, which has the least stability constant of all the rare earth-EDTA complexes, is preferentially released from its association with EDTA and is precipitated as oxalate. The 40 hour ^{140}La activity is measured by means of a gamma-ray scintillation spectrometer over its 1.62 Mev photo-peak. A standard lanthanum activity which has been similarly precipitated is counted for comparison.

From the solution remaining after the precipitation of lanthanum, rare earths that interfere in beta-counting of ^{90}Y are removed. This is achieved by using neodymium which is added as "scavenging carrier". Yttrium is then precipitated from solution by the addition of more copper. The only interfering isotopes which are partially co-precipitated with ^{90}Y are ^{152m}Eu and ^{166}Ho. Their possible interference is avoided by beta-counting the ^{90}Y activity after 80 hours' decay through aluminium absorbers of thickness 750 mg/cm^2. A standard ^{90}Y activity is counted for comparison.

The measured activities are corrected for losses during chemical processing. The chemical yields are determined by permanganate titration of the oxalate

precipitates.

The method has been applied to the determination of La/Y ratios in typical minerals.

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1. INTRODUCTION

1.1 GEOCHEMICAL IMPORTANCE OF THE RARE EARTHS

The term 'rare earth elements' usually includes yttrium (atomic no. 39) along with the lanthanides (the series of elements from atomic no. 57 (lanthanum) to atomic no. 71 (lutecium)).[1a] This is because of the close similarity in the chemical properties and mode of occurrence of yttrium with those of the lanthanides. Scandium (atomic no. 21), although it is often associated with this group, has less similarity with the true lanthanides and therefore is not usually considered as one of the rare earths.

The very similar chemical properties of the individual members of the lanthanide group are due to the fact that the additional electrons in successive elements are used for completing the inner '4f' atomic orbital so that the outermost electron configuration remains essentially unchanged throughout the series. The filling of this level deep within the atom, accompanied by the corresponding regular increase in nuclear charge (which results in an increasing attraction on the electrons) causes a regular decrease in the atomic volumes (and

ionic radii) of the lanthanides, which is known as the 'lanthanide contraction'. The decrease in ionic radius from lanthanum (1.22 Å) to dysprosium (1.07 Å) just balances the increase between the elements yttrium (1.06 Å) to lanthanum. The ionic radii of tripositive lanthanides nearest to yttrium are thus Dy^{3+} and Ho^{3+} (1.05 Å). It is this property together with their analogous electronic configuration which explains the very close similarity of yttrium to dysprosium and holmium and to the lanthanides in general. Scandium differs from the rare earth elements, especially from a geochemical point of view, because of its decidedly smaller ionic size (0.83 Å).

The differences in the ionic radii of the rare earth elements are very small, however, and therefore these ions tend to replace each other isomorphously in the crystal lattices of minerals. It is the similarity in space requirements in crystal structures, besides the similarity in chemical properties, that accounts for the geochemical coherency of the rare earth group.[2a]

The unusual degree of geochemical coherency of the group results in the rare earth elements behaving as a kind of entity in geochemical migrations. The

difficulty of chemical separation of the individual elements from one another in the laboratory is well known. This difficulty is reflected in the relative absence of fractionation during the natural mineral forming processes. The rare earths thus constitute the only large group of elements which is not liable to serious fractionation in the earth. It is believed that their relative abundance in some minerals may still approximate to their "primordial" abundance pattern on earth, and so provide critical data for theories of nucleogenesis.[3] The marked regularities which exist in the cosmic abundances of the elements have been explained on the basis of correlations of the nuclear properties with the relative abundances of the lanthanides.[4]

The general geochemical coherency of the rare earth group is however often broken in two important respects. These modes in which the primordial abundances of the rare earths are altered are caused respectively by (a) variable valency associated with stability of the empty, half-filled and filled 4f subshell, and (b) variation in the ionic radii from La^{3+} (1.22 Å) to Lu^{3+} (0.99 Å). Geochemical study of different minerals,[1b, 5] reveals that this results in (a) deficiency of cerium and (more so) europium in some

rare earth minerals, and (b) a variation in the proportion of the two sub-groups (the "Cerium earths": La, Ce, Pr, Nd, Sm and Eu; and the "Yttrium earths": Y, Gd and the rest of the lanthanides) within the rare earth series.

In a highly oxidising environment a selective migration of quadrivalent cerium may take place. Perhaps an extreme example of the formation of a cerium-deficient mineral after the migration of Ce^{4+} is Rhabdophane from Connecticut, U.S.A., which was found to be almost devoid of cerium.[6] In a reducing environment on the other hand, europium and (to a lesser extent) samarium and ytterbium are reduced to the dipositive state, in which condition they tend to concentrate in the minerals of calcium and strontium which they resemble in chemical properties. Europium has thus been found deficient in rare earth minerals formed under reducing conditions.

Differences in ionic packing ratios will tend to cause the preferential entry of the larger or smaller rare earth ions into mineral structures depending upon the co-ordination conditions necessary for formation of the crystal lattice. Thus, Allanite (a silicate of Fe, Ca and the rare earths) and Monazite (a phosphate of the rare earths and Th) have structures which favour the

larger ions of the cerium earths, whereas the yttrium earths predominate in niobate-tantalate minerals such as Fergusonite and Samarskite.[2b] The mechanism of fractional crystallisation during mineral-formation is also considered to be responsible for the variations in the ratio of the cerium earths to the yttrium earths that are found in some minerals.[7] On this basis, minerals in which the rare earths are essential constituents have been distinguished into three types in which (i) the cerium earth elements are predominantly concentrated, (ii) yttrium and the yttrium earth elements are concentrated, and (iii) the whole of the rare earth series is rather evenly represented. From a knowledge of the relative distribution of the rare earth elements connected with them, it has often been possible to recognise groups of genetically related rocks or mineral deposits.[8,9]

It is for these reasons that a study of the distribution of the rare earth elements constitutes an important aspect of Geochemistry.[1b]

1.2 SURVEY OF ANALYTICAL CHEMISTRY OF THE RARE EARTHS

1.21 Methods of Separation

The tripositive rare earth ions form oxalates which are insoluble in oxalic acid and in dilute mineral

acids, and fluorides which are insoluble in dilute hydrofluoric acid; they are also quantitatively precipitated by ammonium hydroxide. These three reactions, therefore, afford means of effecting group separation of the rare earths from all other elements except thorium and scandium, which invariably accompany them.[10a, 11a] Thorium can be removed from the group by precipitation with potassium iodate after ensuring that all cerium is in the trivalent state, and scandium by precipitation as scandium ammonium tartrate.

A partial separation of the rare earths into two sub-groups consisting of the cerium earths and the yttrium earths (also called the 'light' and 'heavy' rare earth groups) can be made by taking advantage of the different solubilities of their double sulphates with the alkali sulphates.[11b] Alternatively, the cerium sub-group can be separated from the yttrium sub-group with comparable efficiency by precipitating the former as oxalates from a mixture of the two in the presence of ethylene-diamine-tetracetic acid (EDTA) as chelating agent.[12]

The lanthanides which can exist in aqueous solution in oxidation states higher or lower than the tripositive one can be separated from the rest of the

group by chemical means. Cerium has been separated by precipitating with potassium iodate, after first oxidising to the quadrivalent state.[13] Europium and ytterbium have been separated from the other lanthanides by reducing them electrolytically at a mercury cathode or by means of zinc amalgam, the bivalent states formed affording a precipitate on addition of a soluble sulphate.[14,15] Europium, samarium and to a certain extent ytterbium have likewise been quantitatively separated from the rest of the group by means of the amalgams which they form when solutions of their acetates are shaken with sodium amalgam.[16, 17]

The most useful technique for the separation of all or most of the elements of the rare earth group is ion exchange chromatography.[18] Ion exchange methods were developed primarily for the determination of the rare earths formed as "fission products" during the fission of uranium. A series of papers on the subject were first published in 1947.[19-23] The rare earths are adsorbed on a column of ion exchange resin and are then eluted by means of a complexing agent. The differences in the distribution coefficients of the individual rare earths on the resins are improved because of the differences in the stability constants of their complexes. They

therefore move down the column at different rates so that, by taking judicious portions of the eluate, separations can be achieved. Special precautions are necessary, however, to obtain a particular rare earth that is being sought free from the adjoining elements in the series, e.g. elution at elevated temperatures improves separations by quicker attainment of equilibrium.

In a few other publications,[24-26] besides those mentioned above, the eluting agent used was a citrate solution adjusted to various pH values. Similar studies have since been made using other complexing agents as eluents, such as lactic acid,[27-29] glycolic acid,[30] α-hydroxy-isobutyric acid,[31, 32] EDTA, [27, 33-35] and other amino-polyacetic acids.[36-38] EDTA gives better separations than the other eluents studied because of greater differences in formation constants of the rare earth complexes; but the main difficulty in its use is the low solubility of the free acid. This problem was solved by Spedding[39] by the use of what he called "retaining ions", which formed soluble EDTA complexes. Instead of using the ion exchange resin in the normal hydrogen form he first converted it to the iron or copper form, Fe^{3+} or Cu^{2+} being the retaining ions. Later Fuger[40] also used Zn^{2+} and Co^{2+} as the retaining ions for

effecting a separation of the rare earths by EDTA.

1.22 Methods of Determination

The only rare earths which have been individually determined by the classical methods of analysis with any degree of accuracy are cerium and europium. Cerium is easily determined volumetrically in the presence of the other rare earths after oxidation to the quadrivalent state by means of alkali persulphate,[41, 42] or sodium bismuthate.[43, 44] Europium, which readily forms the bivalent salt, can be determined by reducing the trichloride in a Jones reductor, catching the effluent europous chloride under ferric sulphate, and determining the equivalent ferrous salt formed.[45] Europium and ytterbium are also the only two lanthanides that have been satisfactorily determined by means of the polarograph.[46-48]

Solutions of compounds of some of the lanthanides show absorption bands in the ultra-violet and visible spectrum, and advantage has been taken of this fact to determine them by means of the spectrophotometer. Thus, Rodden,[49] and Moeller and Brantley[50] have applied this method for the determination of Pr, Nd and Sm of the cerium group and Dy, Ho, Er, Tm and Yb of the

yttrium group after first effecting a group separation. The absorption bands of the different elements are subject to interference from one another, for which correction factors have to be applied.

The methods that have been most frequently employed for the determination of the individual rare earth elements are those of optical or fluorescent X-ray spectroscopy. Fluorescent X-ray spectrographic methods have been successfully used for the determination of the rare earths in minerals and rocks by Goldschmidt and Thomassen,[7] Minini[51] and Sahama and Vähätalao.[52] Recently Butler[53] has used a fluorescent X-ray method for the determination of yttrium in monazites and other minerals.

Optical spectrography has been used by a large number of workers for the individual determination of most or all of the rare earth elements in a variety of samples.[5, 54-60] The spectral lines from one or other of the rare earth elements (cerium, lanthanum and yttrium have been used) or iron, specifically added, are used as internal standards for comparison. In order to avoid errors due to differing matrices, prior separation of the rare earth group has to be made, which presents difficulties when they are present in trace quantities.

The technique of radio-activation analysis has in recent years been widely applied to the determination of trace elements, and is particularly suited for the determination of several of the rare earth elements. The method is, in general, more sensitive than spectrography and can even be applied to cases where the latter technique usually fails - namely the determination of traces of one rare earth element in another. Cornish[61] has compared the sensitivities he attained by neutron activation with those by spectrography, which is the next most sensitive method for the determination of the individual rare earth elements. These are shown in Table I. All published methods on the determination of rare earths by activation will be reviewed in the next section.

1.3 NEUTRON ACTIVATION ANALYSIS OF RARE EARTHS

1.31 Principles and Outline of Method of Activation Analysis

The general principles of the technique of activation analysis have been exhaustively discussed by Smales,[62-64a] Boyd,[65] Meinke,[66] Mapper[67] and others[68-77] and will be mentioned only briefly here.

Most elements when irradiated by nuclear particles give rise to artificially radioactive isotopes,

Table I

Sensitivities of Spectrographic and Neutron Activation Methods[61]

Element	Spectrographic		Neutron Activation
	D.C. Arc (Practical)	Copper Spark (Ideal)	
	gm.	gm	gm
Yttrium	4×10^{-7}	-	2×10^{-9}
Lanthanum	2×10^{-6}	5×10^{-9}	1×10^{-9}
Cerium	4×10^{-6}	5×10^{-8}	8×10^{-8}
Praseodymium	-	2×10^{-8}	2×10^{-9}
Neodymium	-	2×10^{-8}	4×10^{-8}
Samarium	3×10^{-6}	2×10^{-8}	2×10^{-10}
Europium	3×10^{-7}	2×10^{-9}	1×10^{-9}
Gadolinium	2×10^{-6}	1×10^{-8}	2×10^{-8}
Terbium	2×10^{-6}	-	1×10^{-9}
Dysprosium	1.4×10^{-6}	5×10^{-8}	7×10^{-8}
Holmium	1.4×10^{-6}	2×10^{-8}	2×10^{-10}
Thulium	-	5×10^{-9}	1×10^{-9}
Ytterbium	3×10^{-7}	1×10^{-8}	4×10^{-10}
Lutecium	1.4×10^{-6}	2×10^{-7}	1×10^{-10}

which can be determined by measurement of their characteristic radioactivity. A variety of bombarding particles can be used for the irradiation, such as cyclotron-accelerated protons, deuterons and alpha particles, as well as slow (thermal) and fast neutrons. In general, slow neutrons are preferred to the high energy particles for this purpose, because of the much lower possibility of inducing a multiplicity of nuclear reactions, and also because of the higher capture cross sections of most elements for thermal neutrons. Besides, in practice the largest homogeneous flux can be obtained for thermal neutrons in nuclear reactors.

Normally, species of the same atomic number as the target elements are formed by neutron capture with the emission of gamma rays, if slow neutrons are used as the bombarding particles. For a nuclide X of atomic number z and mass m, the reaction may be represented as:

$$ {}^{m}_{z}X\,(n,\gamma)\quad {}^{m+1}_{z}X $$

The radioisotopes so formed being 'neutron-rich' are unstable, and decay almost invariably with the emission of beta and gamma rays. They have their own characteristic rates and modes of decay, and energies of radiations. The combinations of these are never exactly alike for any

two radionuclides, and it is this that gives the potentially high specificity to this method of analysis.

Besides the high sensitivity and specificity of activation analysis, the other main advantages of the method are (a) freedom from 'blank' from reagents during chemical operations after irradiation, (b) separations of trace quantities of constituents to be determined are avoided by the use of carriers, (c) semi-quantitative separation methods can be used since a final chemical yield determination is made, and (d) it is largely independent of the nature of the matrix material (provided "self-shielding" is avoided).

1.311 Growth of activity on irradiation

When an isotope is irradiated in a homogeneous flux of nuclear particles having a constant average energy, the activity of the radionuclide formed is given by the relationship:

$$A = \frac{f\sigma\theta WN}{M}\left(1 - e^{-0.693\ t/t_{\frac{1}{2}}}\right) \quad \ldots\ldots \quad (1)$$

where A = radioactivity in disintegrations per second.

f = flux of particles per sq.cm. per second.

σ = isotopic activation cross section for the nuclear reaction in units of sq.cm. per target atom (= barns x 10^{-24}).

θ = fractional abundance of the particular isotope in naturally occurring element.

W = weight of the target element in grams.

N = Avogadro's number

t = time of irradiation

$t_{\frac{1}{2}}$ = half-life of the radionuclide formed in same units as t.

M = chemical atomic weight of the element.

From this relationship it is seen that high sensitivity (i.e. high activity per unit mass) can be obtained if the flux, the isotopic activation cross section, and the relative abundance of the isotope concerned are high. The factor $(1 - e^{-0.693\ t/t_{\frac{1}{2}}})$ which controls the rate of growth of the activity on irradiation is called the "growth factor", and a saturation activity which determines the "limit of detection" is reached after about five half-lives of the active isotope formed.

1.312 Decay of radioactivity

As soon as the isotope is removed from the flux of irradiating particles, the induced activity starts to decay according to the equation:

$$Ad = A\ e^{-0.693\ td/t_{\frac{1}{2}}} \quad \ldots\ldots \quad (2)$$

where Ad = activity of isotope after decay time td.

td = decay time in same units as $t_{\frac{1}{2}}$

A = activity of the radionuclide on cessation of irradiation as given in equation (1).

In this relationship the factor $e^{-0.693\ td/t_{\frac{1}{2}}}$ has been called the "decay factor". After about five half-lives of the radioisotope, the amount of activity falls to such a low level that practical measurements are not possible. Figure I shows a plot of the growth and decay factors against the ratios $t/t_{\frac{1}{2}}$ and $td/t_{\frac{1}{2}}$ respectively.

1.313 Determination of required constituent

If the magnitude of the flux, the time of irradiation, the activation cross section of the target isotope and the half-life of the radionuclide formed are known, it should be possible to determine the absolute mass of the constituent required by measurement of the absolute disintegration rate. However, accurate values of the flux and cross section are not usually available; and an accurate determination of the absolute rate of disintegration is difficult. This difficulty is

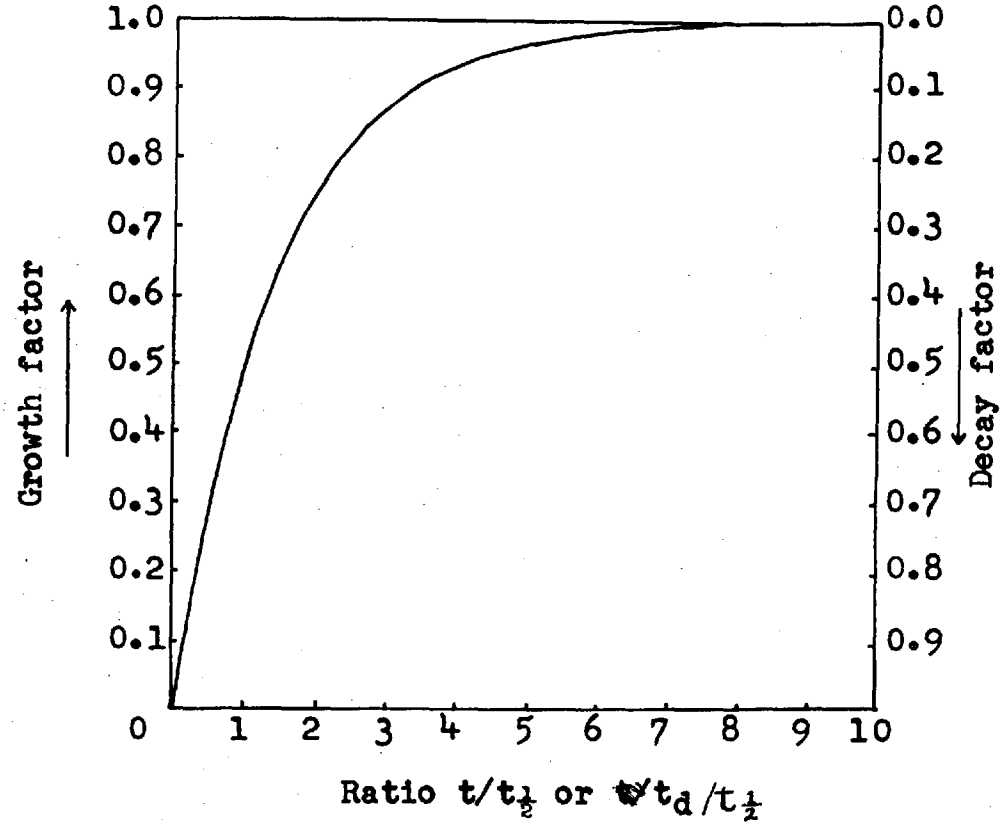
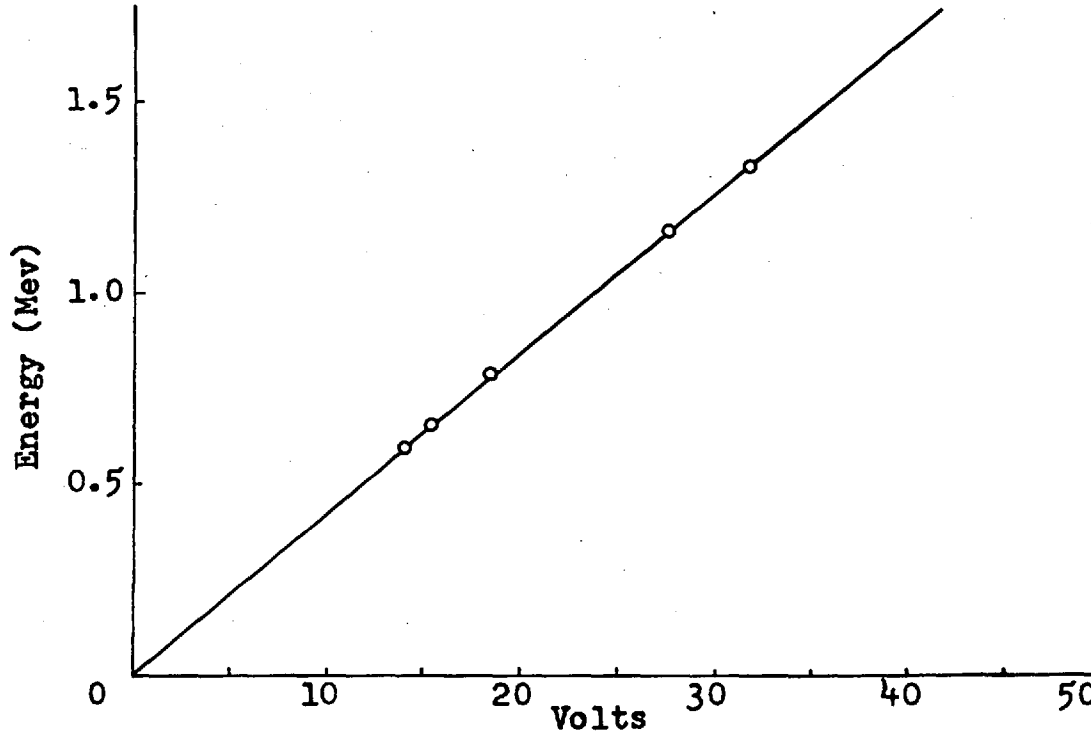


Fig. I Variation of Growth and Decay Factors with Time



Bias potentiometer setting corrected to zero channel

Fig. II Energy Calibration Curve

therefore avoided in practice by using a "comparative method", i.e. by irradiating standards of known composition along with the samples, and comparing their relative activities.

1.3131 Practical steps in analysis

Briefly stated, the practical steps for determining an element in a sample by the "comparative method" of neutron activation analysis are as follows:-

(a) Weighed quantities of the standard containing a known amount of the element to be determined, and of the sample are irradiated in a homogeneous flux of thermal neutrons for a suitable length of time. It may sometimes be necessary to dilute the standard or sample with a suitable material so as to minimise "self-shielding" effects.

(b) The irradiated sample and standard are brought into solution by appropriate chemical methods, and to each is added a known weight of the inactive element being determined, as carrier for the trace quantity of radio-isotope present. The carrier and element in the sample must be in the same chemical form at this stage, and a chemical ('redox') cycle may be necessary to ensure this.

(c) Using chemical separation methods, the element is isolated in a "radiochemically pure" form, i.e.

until it is free from other radionuclides which would interfere with the radioactive counting assay.

(d) The "chemical yield" of the added carrier is determined by any conventional method. This step enables the use of rapid semi-quantitative chemical separation methods in step (c), as the final measured activity can be corrected for losses.

(e) The radioactivities of the sample and standard are measured under identical counting conditions (i.e. "geometry", "self-absorption", etc., are held constant), with corrections for decay, if necessary.

(f) The radiochemical purity of the isolated activity must be established. This is usually done by measurement of its decay which should show a linear semi-log plot for at least five half-lives. Additional proof of radiochemical purity is obtained by measurement of the characteristic energies of the radiations emitted on decay, by aluminium absorption curves or gamma-ray scintillation spectra. This step combined with the chemical separation step is responsible for the very high specificity of radioactivation analysis.

(g) Then, the weight of the constituent to be determined is obtained from the relation:

$$\frac{W_1}{W_2} = \frac{A_1}{A_2} \times \frac{C_2}{C_1}$$

where,

W_1 and W_2 = weight of element in sample and standard respectively.

A_1 and A_2 = activity of element from sample and standard respectively.

C_1 and C_2 = chemical yield of element from sample and standard respectively.

In certain favourable cases steps (b) to (d) can be omitted. For example, if it is possible to resolve the gamma ray energies of the activities present by means of gamma ray spectrometry it is possible to completely omit (non-destructive analysis[64b]), or at least to curtail considerably the chemical separation procedures.

1.32 Errors in Neutron Activation Analysis

The main sources of errors in activation analysis are those arising from: (a) statistical and other variations in counting, (b) incomplete radiochemical separations, (c) inhomogeneity of flux, (d) self-shielding of samples and standards and (e) conflicting nuclear processes.

(a) Radioactive disintegration being a

random event, is subject to statistical variations, i.e. the number of disintegrations measured in successive fixed periods of time will not be constant. The error from this fact can be minimised by taking as large a number of counts as possible both for the activity as well as the background. Statistical considerations show that the standard deviation of any one counting measurement is reduced to one per cent. by taking a minimum of 10^4 counts. The other errors in counting such as those due to absorption and geometry of sample - mounting can be minimised by taking comparative counts for the sample and standard under strictly identical conditions. The errors due to changes in efficiency of the counting equipment can be corrected for, by making comparative efficiency measurements with the help of a long-lived radioisotope as standard.

(b) The radiochemical purity of the isolated constituent is checked by plotting its decay and aluminium-absorption curves and also the gamma-ray spectrum, whenever possible. The extent of radiochemical purification that is necessary can be ascertained in this way.

(c) As the induced activity is proportional to the flux, any variation in the flux at different positions will activate the sample and standard to a

different degree. This effect is minimised by irradiating the sample and standard simultaneously and as close to each other as possible.

(d) If the sample or standard has a high neutron absorption cross section, then the flux will get reduced during its passage through the substance being irradiated. This is known as "self-shielding". The errors arising from it can be minimised by preparing the standard in a matrix which has nearly the same absorption cross section as the sample, or by diluting the sample and standard with a material of very low cross section such as pure sucrose alumina or magnesia.

(e) In a flux of slow neutrons, the main reaction taking place is the (n, γ), giving rise to an isotope of the same atomic number and of mass one higher than the target nuclide; but the possibility of other transmutations occurring during and after irradiation must be considered. Thus, there are several routes by which a nuclide 'X' of atomic number 'z' and mass 'm' may be formed. They are:-

i) $^{m-1}_{z}X$ (n, γ) $^{m}_{z}X$

ii) $^{m}_{z+1}X$ (n, p) $^{m}_{z}X$

iii) $^{m+3}_{z+2}X$ (n, α) $^{m}_{z}X$

iv) $^{m+1}_{z}X\ (n, 2n)\ ^{m}_{z}X$

v) $^{m+1}_{z}X\ (\gamma, n)\ ^{m}_{z}X$

vi) $^{m+1}_{z+1}X\ (\gamma, p)\ ^{m}_{z}X$

vii) $^{m-1}_{z-1}X\ (n, \gamma)\ ^{m}_{z-1}X \xrightarrow{\beta} {}^{m}_{z}X$

viii) $^{m-2}_{z-1}X\ (n, \gamma)\ ^{m-1}_{z-1}X \xrightarrow{\beta} {}^{m-1}_{z}X\ (n, \gamma)\ ^{m}_{z}X$

ix) $^{m-2}_{z-1}X\ (n, \gamma)\ ^{m-1}_{z-1}X\ (n, \gamma)\ ^{m}_{z-1}X \xrightarrow{\beta} {}^{m}_{z}X$

x) Heavy Element (n, f) elements of intermediate mass number.

Of these, reactions (ii), (iii) and (iv) take place with fast neutrons only and have a very low cross section.[72] They may, therefore, be neglected when the flux used consists of an overwhelmingly large proportion of slow neutrons. Reactions (vi) to (ix) are a potential source of interference and must be taken into account particularly when one element is being determined in the presence of a considerable excess of another which is adjacent to it in the periodic table. Reaction (x) is important when analysing samples having a large uranium content.

1.321 Interfering nuclear reactions in lanthanides

Cornish[61] has investigated the difficulties that are likely to arise due to transmutation reactions

when analysing samples of rare earths by neutron activation. The transmutations considered are those due to (n, γ) reactions and beta decay shown in reactions (vii), (viii) and (ix). A consideration of the nuclear properties of the rare earths[75] leads to the conclusion that the following interfering transmutations are possible:

a) (n, γ) reaction followed by β decay:

$^{176}_{70}Yb\ (n, \gamma)\ ^{177}_{70}Yb \xrightarrow{\beta} {}^{177}_{71}Lu$

$^{170}_{68}Er\ (n, \gamma)\ ^{171}_{68}Er \xrightarrow{\beta} {}^{171}_{69}Tm$

$^{160}_{64}Gd\ (n, \gamma)\ ^{161}_{64}Gd \xrightarrow{\beta} {}^{161}_{65}Tb$

$^{154}_{62}Sm\ (n, \gamma)\ ^{155}_{62}Sm \xrightarrow{\beta} {}^{155}_{63}Eu$

$^{146}_{60}Nd\ (n, \gamma)\ ^{147}_{60}Nd \xrightarrow{\beta} {}^{147}_{61}Pm$

$^{148}_{60}Nd\ (n, \gamma)\ ^{149}_{60}Nd \xrightarrow{\beta} {}^{149}_{61}Pm$

$^{142}_{58}Ce\ (n, \gamma)\ ^{143}_{58}Ce \xrightarrow{\beta} {}^{143}_{59}Pr$

b) (n, γ) reaction followed by β decay, followed by (n, γ) reaction:

$^{168}_{68}Er\ (n, \gamma)\ ^{169}_{68}Er \xrightarrow{\beta} {}^{169}_{69}Tm\ (n, \gamma)\ ^{170}_{69}Tm$

$^{164}_{66}Dy\ (n, \gamma)\ ^{165}_{66}Dy \xrightarrow{\beta} {}^{165}_{67}Ho\ (n, \gamma)\ ^{166}_{67}Ho$

$^{158}_{64}Gd\ (n, \gamma)\ ^{159}_{64}Gd \xrightarrow{\beta} {}^{159}_{65}Tb\ (n, \gamma)\ ^{160}_{65}Tb$

$^{152}_{62}Sm\ (n,\gamma)\ ^{153}_{62}Sm \xrightarrow{\beta} {}^{153}_{63}Eu\ (n,\gamma)\ ^{154}_{63}Eu$

$^{140}_{58}Ce\ (n,\gamma)\ ^{141}_{58}Ce \xrightarrow{\beta} {}^{141}_{59}Pr\ (n,\gamma)\ ^{142}_{59}Pr$

$^{139}_{57}La\ (n,\gamma)\ ^{140}_{57}La \xrightarrow{\beta} {}^{140}_{58}Ce\ (n,\gamma)\ ^{141}_{58}Ce$

c) (n, γ) reaction followed by (n, γ) reaction followed by β decay:

$^{164}_{66}Dy\ (n,\gamma)\ ^{165}_{66}Dy\ (n,\gamma)\ ^{166}_{66}Dy \xrightarrow{\beta} {}^{166}_{67}Ho$

d) Fission of uranium -235

^{235}U (n,f) fission products

e) The following transmutation reaction must also be taken into account when analysing for traces of lanthanum in barium-rich minerals:

$^{138}_{56}Ba\ (n,\gamma)\ ^{139}_{56}Ba \xrightarrow{\beta} {}^{139}_{57}La\ (n,\gamma)\ ^{140}_{57}La$

1.33 Nuclear Properties of the Rare Earths

As a preliminary requirement in radioactivation analysis, a study must be made of the nuclear properties of the constituents to be determined. The relevant nuclear and other data necessary for considering the application of the technique to the determination of the rare earth elements is given in Table II. The

Table II

Nuclear Properties of Rare Earths

Element	Fractional Abundance in Natural Mixture F	Isotope for Activation Analysis: Isotope	Relative Abundance θ	Cross Section in Barns σ	Product F.θ.σ	Radio isotope Produced	Half Life	Gamma Ray Energy in Mev (Number of Photons per 100 Disintegrations in brackets)	Maximum Beta Energy Mev
Scandium	-	^{45}Sc	1.000	13	-	^{46}Sc	84d	0.89(100), 1.12(100)	0.36
Yttrium	0.310	^{89}Y	1.000	1.4	0.434	^{90}Y	62.2h	-	2.26
Lanthanum	0.190	^{139}La	0.999	8.8	1.670	^{140}La	40.2h	1.62(95), 0.49(40), 0.82(27), 0.33(19), 2.54(4)	2.20
Cerium	0.440	^{140}Ce	0.885	0.6	0.234	^{141}Ce	33d	0.145(30)	0.58
		^{142}Ce	0.111	1.8	0.088	^{143}Ce	33h	0.29, 0.57, 1.10, 0.06	1.37
Praseodymium	0.056	^{141}Pr	1.000	11.0	0.616	^{142}Pr	19.3h	1.57(4)	2.15
Neodymium	0.240	^{146}Nd	0.172	10.0	0.413	^{147}Nd	11.1d	0.09(30), 0.52(15)	0.80
		^{148}Nd	0.057	3.0	0.041	^{149}Nd	1.8h	0.03 to 0.65	1.50
Samarium	0.065	^{150}Sm	0.075	-	-	^{151}Sm	73y	0.02	0.08
		^{152}Sm	0.266	150	2.59	^{153}Sm	47h	0.10(37), 0.07(4)	0.80
		^{154}Sm	0.225	5.0	0.073	^{155}Sm	22m	0.10(76), 0.25(3)	1.65
Europium	0.010	^{151}Eu	0.478	1400	6.69	^{152m}Eu	9.3h	0.12(7), 0.34(3), 0.84(11), 0.98(9), 1.39(1)	1.88
				7200	34.41	^{152}Eu	13y	0.12(33), 0.34(26), 0.78(12), 0.96(15), 1.1(25), 1.41(25)	1.50
		^{153}Eu	0.522	400	2.088	^{154}Eu	16y	1.3, 1.0, 0.69, 0.12	1.85

Table II (continued)

Element	Fractional Abundance in Natural Mixture F	Isotope for Activation Analysis Isotope	Relative Abundance θ	Cross Section in Barns σ	Product F.θ.σ	Radio isotope Produced	Half Life	Gamma Ray Energy in Mev (Number of Photons per 100 Disintegrations in brackets)	Maximum Beta Energy Mev
Gadolinium	0.063	^{152}Gd	0.002	120	0.015	^{153}Gd	236d	0.10(46)	-
		^{158}Gd	0.249	4.0	0.063	^{159}Gd	18h	0.36(19)	0.94
		^{160}Gd	0.219	0.8	0.017	^{161}Gd	3.6m	0.37	1.50
Terbium	0.010	^{159}Tb	1.000	44	0.440	^{160}Tb	72d	1.27, 1.18, 0.97, 0.88, 0.09	0.86
Dysprosium	0.043	^{164}Dy	0.282	2700	32.8	^{165}Dy	1.3m/ 2.3h	0.10, 0.17, 0.36, 0.76	1.25
Holmium	0.012	^{165}Ho	1.000	64	0.768	^{166}Ho	27h	0.08(6), 1.36(1), 1.53(0.2), 1.61(0.1)	1.84
Erbium	0.024	^{168}Er	0.271	2.0	0.013	^{169}Er	9.4d	-	0.33
		^{170}Er	0.149	20	0.072	^{171}Er	7.5h	0.31(69), 0.11(22)	1.5
Thulium	0.003	^{169}Tm	1.000	120	0.360	^{170}Tm	127d	0.08	0.97
Ytterbium	0.026	^{174}Yb	0.318	50	0.413	^{175}Yb	4.2d	0.11(3), 0.40(9)	0.50
		^{176}Yb	0.127	7	0.023	^{177}Yb	2.0h	0.15(6), 1.1(2)	1.3
Lutecium	0.007	^{175}Lu	0.974	34	0.205	^{176}Lu	3.7h	0.09, 0.20	1.2
Thorium	-	^{232}Th	1.000	7.5	-	^{233}Th	23m	0.09, 0.029	1.24

data for column 2 of the table is after Goldschmidt[73] and shows the estimated abundances of the different rare earth elements as they occur in the earth's crust. The nuclear data has been taken from Seaborg's[74] Table of Isotopes and other sources.[75, 76] Column 6 shows the product of the activation cross section, the isotopic abundance and the fractional natural abundance of the element, and is a measure of the relative radioactivity which will be induced in the various isotopes of a "natural mixture".

1.34 Survey of Published Methods

Hevesy and Levi,[77] who were the first to utilise radioactivation as an analytical tool, applied the technique to the determination of some of the rare earth elements. They were able to determine small amounts of dysprosium impurity in samples of yttrium, and europium impurity in samples of gadolinum, using a 300 millicurie radium-beryllium source of neutrons. They utilised the 2.3 hour ^{165}Dy and 9.3 hour ^{152m}Eu activities for the purpose.

Ketelle and Boyd[19] determined 100 p.p.m. of thulium in a sample of highly purified erbium oxide by activation. A 5-mg sample was bombarded with neutrons

in an atomic pile and processed on an ion exchange column of Dowex-50. Five per cent. ammonium citrate buffered at pH 3.2 was used as eluent at a temperature of 100°C. As the eluate emerged from the column, its activity was measured and peaks due to the impurities of lutecium, ytterbium and thulium were obtained. After separation, the thulium activity was counted at known geometry, and its concentration determined from a knowledge of the activation cross-section, half-life, magnitude of the flux and duration of the irradiation.

Kohn and Tompkins[78] have also analysed purified rare earths for contamination by other rare earth elements. Without separating the components, and from a study of the decay and absorption curves only, they were able to determine the presence of 0.63 per cent samarium in a sample of cerium, 1.18 per cent. dysprosium in yttrium, 0.23 per cent neodymium and 0.01 per cent. cerium in praseodymium and 0.03 per cent cerium in lanthanum. They state that two conditions are essential before an analysis of this type can be made, viz. (i) there should be an appreciable difference in the half-lives of the constituents, and (ii) the samples should be of high purity, since low purity samples yield extremely complicated decay curves which are difficult to resolve.

Meinke and Anderson[79] have determined milligram quantities of some of the rare earth elements by neutron activation using a very low neutron flux, and compared the results with spectrophotometric procedures. For the activation they used a 25-mg radium-beryllium source enclosed in paraffin, which gave them a maximum thermal neutron flux of about 100 neutrons/sq.cm./sec. The advantage of using a low neutron source was that only those isotopes having very high cross sections and short half-lives were activated. Thus a large number of elements remained inert at this flux level and did not interfere in the analysis. They chose for their determinations samarium, europium, dysprosium and holmium, which have the most favourable combination of large activation cross sections and short half-lives among the rare earth elements. They have shown that their method is superior to the spectrophotometric method for the determination of europium and dysprosium; whereas the latter method is better for the determination of samarium and holmium. However, for a mixture of two pairs of neighbouring elements (e.g. determination of Eu in presence of Sm, and Dy in presence of Ho), the spectrophotometric method suffers from serious drawbacks because the absorption bands of one element tend to coincide with

those of the neighbouring element.

Nelson[80] has worked out a method for analysing a mixture of rare earths (such as that separated from uranium and thorium bearing materials) using a 2.5 g radium-beryllium source. After irradiation, gamma decay was recorded with the aid of a gamma-scintillation counter and a time-integrated strip chart recorder. The gross decay curve so obtained was then resolved into its components. The rare earth elements most easily detected were europium, dysprosium and samarium because of their high neutron cross sections and lanthanum which is usually a major constituent of a rare earth mixture. The method is sensitive to 0.05 mg Eu, 0.5 mg Dy, 0.7 mg Sm and 1.2 mg La. A single analysis requires several days and a sample size of at least 10 mg rare earth concentrate is necessary. The other prerequisites before the method can be applied are: (i) the sample should be relatively pure to avoid complicated decay curves and (ii) an approximate composition of the rare earth concentrate should be known in order to evaluate the results of the neutron activation.

Jakovlev[70] has estimated the total content of rare earth elements in "nuclear materials" such as graphite, beryllium, bismuth, lead and germanium, on the

basis of the activity of some of the rare earth elements in the samples. From a consideration of the relative abundances of the individual elements in a "natural mixture", and their atomic activation cross sections, he has shown that, following a 48 hour irradiation in a flux of about 2 x 10^{11} neutrons/cm^2/sec., the activity of the rare earths will in the main be due to the activity of ^{165}Dy, ^{152m}Eu, ^{153}Sm and ^{140}La. An analysis of the decay curve of an irradiated artificial mixture corresponding in composition to the content of rare earth elements in a natural mixture lent proof to this supposition.

Due to the length of time normally required (about 15 hours) for isolating the rare earth group from the sample, the short-lived activity of ^{165}Dy had practically disappeared by the time activity measurements could begin. The amount of rare earth elements was estimated from a determination of the ^{152m}Eu activity measured after about 15 hours, or on the basis of the ^{153}Sm activity measured after 3 days. A correction was applied for the ^{140}La activity. Graphite and germanium were analysed on the basis of europium activity and beryllium, bismuth and lead on the basis of samarium.

One of the most thorough investigations that

have been made on the determination of sub-microgram quantities of the individual rare earths by activation is by Cornish.[61] The rare earth mixtures were bombarded by the mainly thermal neutrons in the self-serve positions of BEPO, at Harwell, at a flux of 2×10^{12} neutrons/sq.cm./sec. After addition of carriers, the individual rare earths were separated by ion exchange chromatography by a procedure similar to that of Ketelle and Boyd.[19] The rare earths were adsorbed on a 100 cm. long column of fine Zeocarb 225 (cation exchange resin) and the separations achieved by eluting with a 5 per cent. citrate solution of pH varying between 3.2 and 3.98. The gradual increase in pH of the eluent as well as heating of the column to a higher temperature (80°C), effected a more rapid separation. The activities of individual rare earths passing out of the column were recorded as "peaks" by means of a Geiger-Müller counter to which was connected a rate-meter and a strip-chart recorder. The fractions corresponding to the various rare earths were collected by means of an automatic fraction collector, and counted separately. Corrections for chemical yield were made from a determination of the ratio of chemical yields of the individual rare earths isolated from the sample and standard. This ratio was

determined by a secondary activation procedure, i.e. the isolated elements with carriers were again subjected to bombardment in the pile and counted. Cornish also applied the results of these investigations to the determination of the rare earth elements in samples of graphite and "Specpure" samarium oxide.

Kirby et al.[81] determined radioactive rare earths in reactor effluent water. The rare earths as a group were first separated and then fractionated by means of ion exchange chromatography. For the fractionation they used a 40-cm. long column of fine Dowex-50 resin at a temperature of 60°C, and 1M lactic acid -ammonium lactate solution at a pH of 3.25 as eluent. The fractions were collected with an automatic fraction collector and location of the individual rare earths made by radiometric monitoring of the column effluent. The rare earth elements were then recovered from the various fractions by oxalate precipitation and identified and analysed from decay measurements made by means of beta-proportional and gamma-scintillation counters.

Kirby et al. have also shown that the half-lives, energies and abundances of the radio-isotopes ^{140}La, ^{141}Ce, ^{143}Ce, ^{152m}Eu and ^{153}Sm in reactor effluent water were such that they could be determined directly by

use of a gamma ray spectrometric technique without resort to fractionation. Essentially this technique consisted in taking the gamma ray spectrum of the rare earth group at various intervals of time, i.e. by allowing one or the other short-lived activity to decay. ^{140}La, which has the highest gamma-ray energy in the group, was counted from a direct measurement at its photo-peak. ^{152m}Eu, which has the next highest gamma-ray energy was determined after making a correction for the contribution of ^{140}La at the photo-peak due to ^{152m}Eu. Similarly by making successive corrections, they were able to determine the ^{143}Ce and ^{153}Sm activities. ^{141}Ce, which was the longest lived in the group, was determined after a three-week decay period, by which time all the other activities had decayed.

Bate et al.[82] determined europium and scandium (along with chromium) in stone meteorites by simultaneous neutron activation analysis. After complete removal of protactinium, zirconium and iron, the scandium was isolated and purified by extraction from hydrochloric acid solution by means of tributyl-phosphate, and precipitation as ammonium scandium tartrate. From the hydrochloric acid phase after extraction of scandium, the rare earth group was first isolated by precipitation as

fluorides. Europium was then reduced to the 2+ state by means of zinc dust and the other rare earths separated by precipitation as hydroxides.

The scandium and europium activities were allowed to age for nearly a year, and were gamma-counted by means of a 200-channel pulse-height analyser. The scandium concentration was determined from the 1.2 Mev photopeak produced by the decay of ^{46}Sc, and the europium calculations were based on the intense, sharp K X-rays at 48 Kev produced by the long-lived ^{152}Eu and ^{154}Eu.

Schmitt et al.[83] determined all the lanthanides in chondritic meteorites by neutron activation. The method of determining the lanthanides and scandium as applied to chondritic as well as achondritic and iron meteorites was later reported in detail by Mosen et al.[84] 5g samples were irradiated alongside all the lanthanides and scandium standards in a flux of about 2×10^{12} n./cm^2/sec. for about 2 hours. As the activity was high, the dissolution and chemical separations on the sample were carried out by means of remote handling equipment.

The rare earth group was separated from the other activities by repeated alternate precipitations as fluorides and hydroxides. The rare earths were then

separated from one another by passing through a column of specially prepared "Dowex-50W x 12" ion exchange resin maintained at 80°C, and eluting with 1M ammonium lactate solution at an initial pH of 3.2, which was continuously changed to higher pH values at the rate of approximately 0.1 pH unit per hour. The effluent from the column was collected by means of a fraction collector. The rare earths were identified from their elution positions and also by means of their gamma ray spectra, taken with the help of a 256-channel analyser, and compared with the standards. Quantitative measurements on the various fractions and their comparison with standards were then made by means of an automatically operated well-type scintillation spectrometer. Only two of the rare earths, 9.4-day ^{169}Er and 129-day ^{170}Tm were beta-counted. Very small quantities (0.5 mg) of each of the rare earth elements were added as carriers in order to facilitate the ion exchange column operation. Their chemical yields were therefore determined by re-irradiating the decayed carriers and comparing them with similarly irradiated known amounts of the individual rare earth standards. A correction had to be applied for the ^{24}Na activity formed from sodium which accompanied the lactate solutions of the rare earths.

An omission which may be noticed on perusal of the report by Mosen et al. is that no mention has been made of yttrium. This element, if present in the sample, should elute from the ion exchange column in the region of holmium and dysprosium; but being a pure beta-emitter has not, presumably, interfered with their gamma-counting by means of the 256-channel analyser.

The authors have also suggested how the ion-exchange fractionation step could be eliminated in cases where only the relative abundance ratio of the light and heavy rare earth groups is required. They have suggested that lanthanum and dysprosium may be taken as representatives of the two groups, because the characteristic, high energy gamma ray of 40-hour ^{140}La and the short half-life of 2.3 hour ^{165}Dy would make the determination of the abundances of these two elements in a mixture of all the rare earths particularly suitable.

Okada[85] has devised a method for the non-destructive simultaneous determination of scandium and dysprosium in mineral samples. He utilised the activities of the very short-lived ^{46m}Sc (19.5 sec.) and ^{165m}Dy (1.25 min.). The 0.142 Mev gamma-ray of ^{46m}Sc and 0.108 Mev gamma-ray of ^{165m}Dy were measured by means of a 256-channel pulse-height analyser. The sample was

irradiated for 30 seconds in a flux of 4 x 10^{10} n/sq.cm./sec., "cooled" for 10 secs., counted for 30 secs., again cooled for 30 secs., and counted for 30 secs. The first counting was utilised for the measurement of Sc and the second for the Dy activity. The relations between photo-peak height of the gamma-spectrum and the amounts of Sc or Dy were obtained by comparison with standards.

1.4 OBJECT OF PRESENT WORK

Although a knowledge of the abundances of all the rare earth elements is of considerable importance, it is evident from the survey that the activation methods which have to be employed for their accurate determination are so elaborate and expensive in equipment, that they would be beyond the means and scope of most geochemical laboratories. A knowledge of the relative proportions of the two sub-groups of the rare earth elements is also of great significance, and would be of much importance particularly if they could be determined with relative ease and speed in a variety of minerals.

The biggest difficulty in the determination of the rare earths by activation lies in their separation on the ion-exchange column, which involves several days work and a number of manipulations.[61] It would thus be a

considerable saving in time and effort if the column separation step could be dispensed with by the use of some relatively simple chemical procedure which would provide radiochemical separation of representative elements of the two sub-groups. This would enable one to determine the relative amounts of the two sub-groups, since the variations in the relative abundances of the individual elements within the sub-groups is small. The present work describes how sufficient radiochemical purity has been achieved by simple precipitation reactions in the case of lanthanum and yttrium, which fact coupled with the favourable nuclear properties of these elements make them particularly suitable for determination as representatives of the two sub-groups.

Cerium is normally held as the main representative of the lighter rare earths group because of its preponderance over other members of the group. However, lanthanum, besides being a close second in its natural abundance, has such favourable nuclear properties, such as the easily resolvable 1.6 Mev gamma-ray of ^{140}La, that it is far easier to determine this element in a mixture as suggested by Mosen et al.[84] Furthermore, there is no question of selective migration of lanthanum in minerals due to variable valency as is the case with cerium.

Mosen et al. have also suggested taking dysprosium as a suitable representative of the heavier rare earths group because the short lived 2.3 hour ^{165}Dy activity could be resolved from the other rare earth activities. However, as pointed out by Jakovlev,[70] practically all ^{165}Dy activity would disappear during the time normally needed to isolate the rare earth group from an irradiated sample, especially if the chemical laboratory is not situated close to a nuclear pile. Yttrium is the natural, dominant representative of the sub-group of heavy rare earth elements which is named after it. Its abundance is greater by far than that of any of the other elements in its group. The radioactive 64 hour ^{90}Y isotope formed after neutron bombardment is a pure beta-emitter with a high maximum energy (2.26 Mev). This suggested that if a simple radiochemical separation could isolate it from the other hard beta-emitters among the rare earths, it could be easily discriminated from the remaining soft beta-emitters by counting through aluminium absorbers. It was found that sufficient radiochemical purity could be achieved for this purpose by controlled fractional precipitation as oxalate in presence of EDTA.

2. EXPERIMENTAL

2.1 OUTLINE PLAN OF INVESTIGATION

The determination of lanthanum and yttrium in mineral samples by comparative neutron activation analysis can broadly be divided into the following steps:-

a) The irradiation of samples and standards.

b) The dissolution of the samples and standards and addition of inactive carriers to each.

c) Isolation of the total rare earth group from samples and standards.

d) The radiochemical separation of lanthanum and yttrium from other members of the rare earth group.

e) The counting of separated lanthanum and yttrium activities.

f) The determination of chemical yields.

Each of these steps was investigated with the object of developing a method of analysis involving the minimum number of manipulations consistent with a reasonable degree of overall accuracy (within $\pm$ 10 per cent.) that would be useful for geochemical investigations. The problems investigated in the various steps are summarised below:

a) The possibility of errors arising from self-shielding during irradiation was investigated since some of the rare earth elements have very high absorption cross sections for thermal neutrons.

b) The problem of quantitative transfer of samples after irradiation was first investigated. The actual dissolution of the samples presented little difficulty because sodium peroxide which was used as a fusion flux is known to be a powerful disintegrator for all types of minerals.[10b]

c) Separation of the non-rare earths, sodium, niobium and phosphorous were investigated because of their somewhat unfavourable nuclear properties and the possibility of their being present as major constituents in some mineral samples.

d) and e) Isolation of the required constituents, lanthanum and yttrium, from the rest of the rare earths in a state of radiochemical purity sufficient for the measurement of their activities without undue interference from other rare earth activities was the crux of the whole investigation. For measurement of the lanthanum activity (^{140}La, 1.62 Mev, γ), the use of a gamma scintillation spectrometer minimised the separation needed from other rare earth elements. Praseodymium and holmium

were the only two rare earth elements which needed detailed investigation for their interference in measurement of the lanthanum activity. The hard beta-activity of ^{90}Y (2.26 Mev) was measured by beta counting through aluminium absorbers. The interference from other rare earths emitting betas of maximum energy greater than 1.5 Mev was considered (see Table II). It was found necessary to eliminate lanthanum and praseodymium activities completely. Fractional precipitation of the oxalates in presence of EDTA was investigated primarily with this end in view, but it was hoped also to minimise the interference from the other rare earth elements.

f) A rapid chemical method was required for determining the chemical yield of the isolated constituents within the required degree of accuracy. The relative utility of gravimetric and volumetric methods for this purpose was investigated.

2.2 COUNTING EQUIPMENT

2.21 Solid Geiger-Müller Counter

An end-window G.M. counter (G.E.C. Type EHM 2S; diam. of window 2.5 cm., window thickness 2.3 mg/cm^2) housed in a lead castle assembly was used for beta counting. A 'perspex' frame to hold the source tray

in the castle ensured constant geometry. The source was placed 3.5 cm from the G.M. window and the aluminium absorbers were placed between the source and the G.M. tube, and as close to the latter as possible to reduce scattering.[86]

2.22 Gamma Ray Scintillation Spectrometer

2.221 Apparatus

A scintillation spectrometer manufactured by Isotope Development Ltd. was used for gamma counting. The apparatus was the same (except in respect of the phosphor and the recorder) as used by Hsia[87a] who has given a detailed description of it. The gamma-ray detector was a thallium activated sodium iodide crystal. A large crystal (size: 36 mm diam. x 25 mm depth) was used because of greater detection efficiency.[88] It was in optical contact with a photo-multiplier tube, the output from which, after further amplification, was fed into a single channel pulse-height analyser. The function of this was to accept only those pulses which fell within a narrow pre-set range of amplitudes, called the channel-width. This acceptance slit was made to scan the entire range of pulse amplitudes by rotating the bias potentiometer either manually, or automatically by

coupling it to a rotating strip chart recorder (Elliott Recorder Type 230). In the former case, the output pulses were registered by means of a scaler assembly, and this arrangement was used for making quantitative measurements at any required bias setting. When it was desired to obtain gamma-ray spectra, automatic scanning was employed. In this case the channel count was integrated by means of a rate-meter which in turn was coupled to the recorder pen. In this way the pulse distribution was automatically recorded.

2.222 The scintillation process

The interaction of a gamma photon with the matter of the sodium iodide crystal produces a recoil electron, which in turn gives rise to a shower of light photons that are detected by the photomultiplier tube. The recoil electrons are produced by any of four distinct processes, viz.: Compton recoil, photo-electric effect, pair production, or escape X-rays.[89] Of these, the photo-electric effect is the most important and useful from the point of view of gamma-ray spectrometry. It produces a peaked response in the pulse-amplitude scan, called the "photo-electric peak", which occurs at a pulse amplitude proportional to the energy of the incident gamma rays.

The photo-electric peak is the result of total absorption of the energy of the gamma photon by the phosphor and is consequently also referred to as the "full-energy" peak.

In the Compton recoil process the gamma photon loses only part of its energy to the crystal resulting in a continuous curve below the photo-peak which is called the "Compton continuum". The Comptom continuum serves no useful purpose in full-energy peak analysis, and for most applications it is desirable to keep it to a minimum. It has been reported[90] that this can be achieved by placing a lead collimator between the gamma-source and the spectrometer crystal. But attempts to improve the peak height to Compton ratio by these means during the present work proved unsuccessful.

The effect of "pair production" becomes apparent in the gamma scan at energies above about 1.5 Mcv. In addition to the full-energy peak, there are peaks in the scan at full-energy minus 0.51 Mev and full energy minus 1.02 Mev. Gamma photons of very low energy (below 100 kev.), on the other hand, give rise to what is called an "escape peak" which occurs at 28 kev below the full energy peak.

2.223 Calibration of spectrometer

The calibration of the bias potentiometer settings in terms of Mev of gamma-ray energy was most conveniently accomplished using long-lived isotopes with gamma rays of known energy. Beaufait et al.[91] have suggested a set of standards for the purpose. Gamma-ray spectra of ^{137}Cs, ^{60}Co and ^{134}Cs were recorded and the positions of the peaks with respect to the bias setting located accurately by manual plotting of the respective photo-peaks. This bias setting corrected to zero channel width (i.e. to true peak position) was plotted against the known gamma-ray energy of the standards to obtain the energy calibration curve shown in Figure II. The known energies of the gamma rays of the various nuclides (Table II) were compared by reference to this curve. The energies corresponding to unknown photopeaks in some samples were determined in the same way.

2.3 IRRADIATION OF MATERIALS

2.31 Ampouling of Samples

The samples and standards were accurately weighed (on a micro-balance), transferred into polythene ampoules and sealed. Ampoules for standards were prepared by the technique described by Hsia.[87b] For

mineral samples, small ampoules (15 mm x 3 mm diam.) were used since they could be ignited more easily in a crucible, thus leaving the entire sample in the crucible for the fusion operation. This avoided the difficulties of quantitatively transferring small amounts of powdered sample from the ampoule to the crucible. The sealed ampoules were numbered for identification, packed in an aluminium irradiation can and sent for irradiation in 'BEPO', Harwell, at a flux of about 10^{12} neutrons/sq.cm./second.

2.32 Choice of Irradiation Time

Figure I (p. 17) shows that the exponential 'growth factor' of a radio-isotope formed by radiative capture has a value of a half for an irradiation time equal to one half-life of the radio-isotope, and approaches unity after irradiation times of more than about 5 half-lives. Although irradiation to saturation activity would increase the sensitivity of detection, it was considered that the unduly long irradiation period necessary to achieve this in the case of a comparatively long-lived radioisotope such as ^{90}Y, was not justified by the gain in sensitivity compared with an irradiation time of about one half-life. Moreover, longer irradiations would needlessly increase the activity from other elements which give long-lived

isotopes. This might make the sample too 'hot' for the initial processing as well as increase the possibility of errors from interferences. The comparative increase in activities induced in europium (^{154}Eu, 16 years) and yttrium (^{90}Y, 64 hours), shown in Figure III, illustrate this. The activities shown are for a ratio of 10 to 1 parts by weight of europium to yttrium, in order to accommodate the two curves on the same scale. It can be seen that the interference from ^{154}Eu in yttrium measurements would progressively increase with increasing irradiation times. On the other hand, irradiations of less than one half-life would unduly reduce the sensitivity of yttrium detection. An irradiation time of about one half-life of ^{90}Y (about 60 hours) was therefore decided upon.

2.33 Self-shielding

The attenuation of neutron flux during its passage through the sample being irradiated is known as "self-shielding". It depends, in large measure on the neutron absorption cross section of the substance. It was necessary to consider self-shielding effects when analysing rare earth samples because some of the rare earth elements have very high absorption cross sections for thermal neutrons (e.g. Gd 46,000, Eu 4,300, Sm 5,600

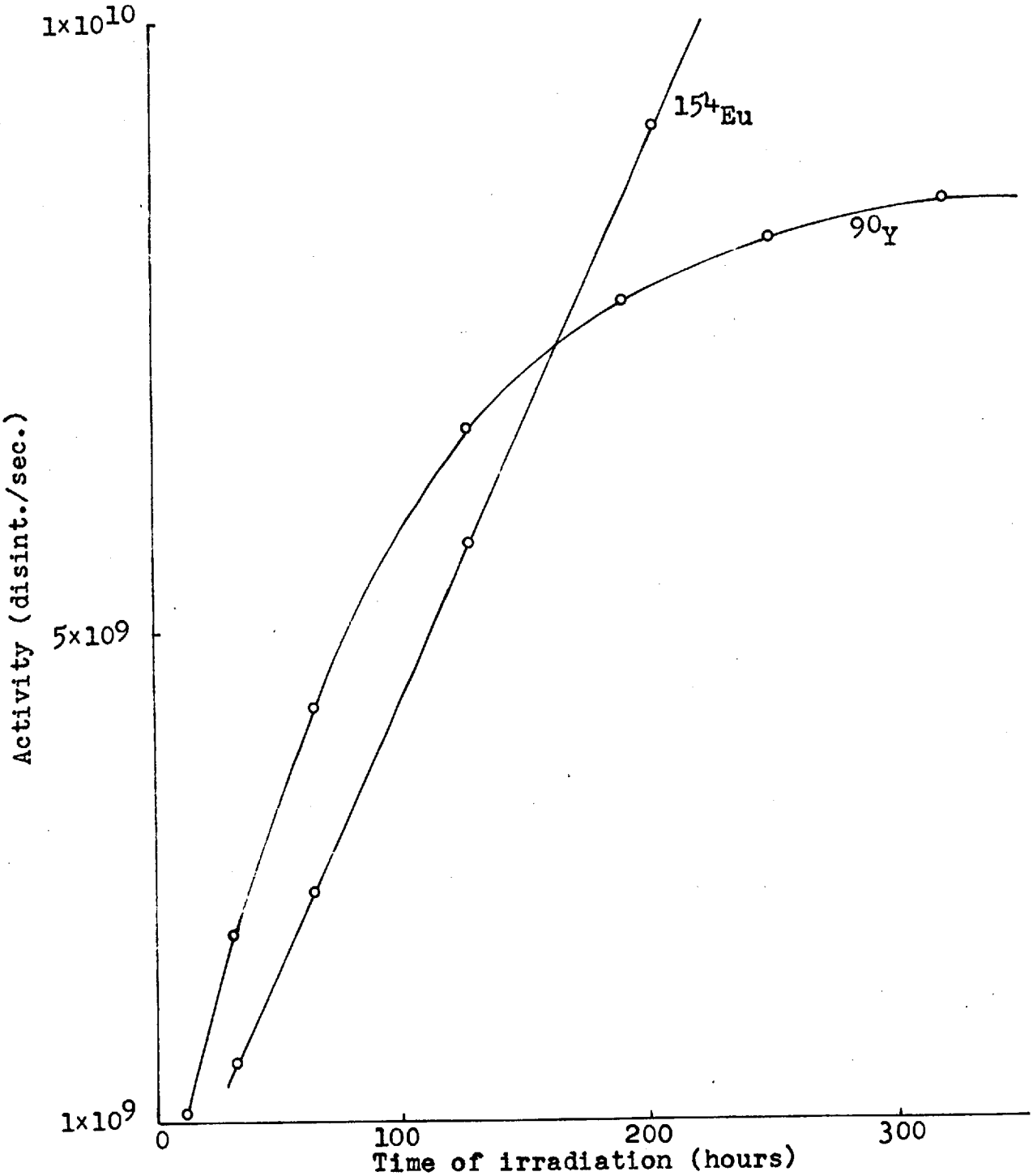


Fig. III Activities of ^{90}Y and ^{154}Eu as a Function of Irradiation Time

barns). It was quite likely, therefore, that a sample containing a relatively large proportion of these elements would show a sufficiently different self-shielding effect from that shown by the standard lanthanum or yttrium (which have comparatively low cross sections), and thus introduce negative errors into the analysis.

Approximate calculations can be made of the self-shielding factor by using mathematical relationships that have been proposed by Keyes[92] and Marshak.[93] But Plumb and Lewis[94] have shown that it is difficult to get a reliable value without a precise knowledge of the neutron energy distribution of the flux, the capture-resonance energies for neutrons of the various nuclides making up the sample, and the cross sections for the resonance energies. Self-shielding effects were therefore investigated experimentally by irradiating different dilutions of the substance and determining the specific activity.

2.331 Dilution of samples

Purified magnesium oxide was used for this purpose as it has a negligible cross section and was expected to be very similar to lanthanum oxide (which was first studied) from the point of view of dissolution in

Table III

Effect of Dilution on Specific Activity

Substance	Dilution Factor	Activity measured	Specific Activity (c.p.m.)
Lanthanum oxide	Nil	^{140}La	3040
	500		3090
Monazite oxides	Nil	^{140}La	585
	10		576
	100		598
	500		592
	2500		610
Lyndochite oxides	Nil	^{90}Y	274
	10		270
	100		280

dilute acid. The specific activity as a function of dilution was determined for lanthanum oxide and the oxides separated from monazite and lyndochite as representatives of lanthanum-rich and yttrium-rich minerals respectively. It can be seen from the results shown in Table III that there is no evidence of self-shielding

for lanthanum oxide and the samples even though the Gd_2O_3 content was as high as 1.5 per cent. for monazite oxides and 5.4 per cent. for lyndochite oxides (determined by spectrographic methods[95]).

The absence of self-shielding effect in the case of monazite oxides was also proved indirectly, since results on different sample weights showed close agreement as follows:-

mg of sample irradiated:	0.2	0.5	3.0
% La_2O_3 found :	20.0	20.4	19.7

Although there was no evidence of self-shielding for the samples studied, a ten-fold dilution with magnesia was adopted when analysing all samples. Dilution was also intended to minimise errors due to losses during ignition of the irradiated ampoule and the subsequent fusion.

2.332 Sodium from magnesia diluent.

It was necessary to have a knowledge of the major impurities in the magnesium oxide which might need separation. A sample was, therefore, irradiated and its gamma ray spectrum is shown in Figure IVA. The peaks which could be detected at 1.37 and 2.75 Mev, were identified as those of ^{24}Na from decay measurements and

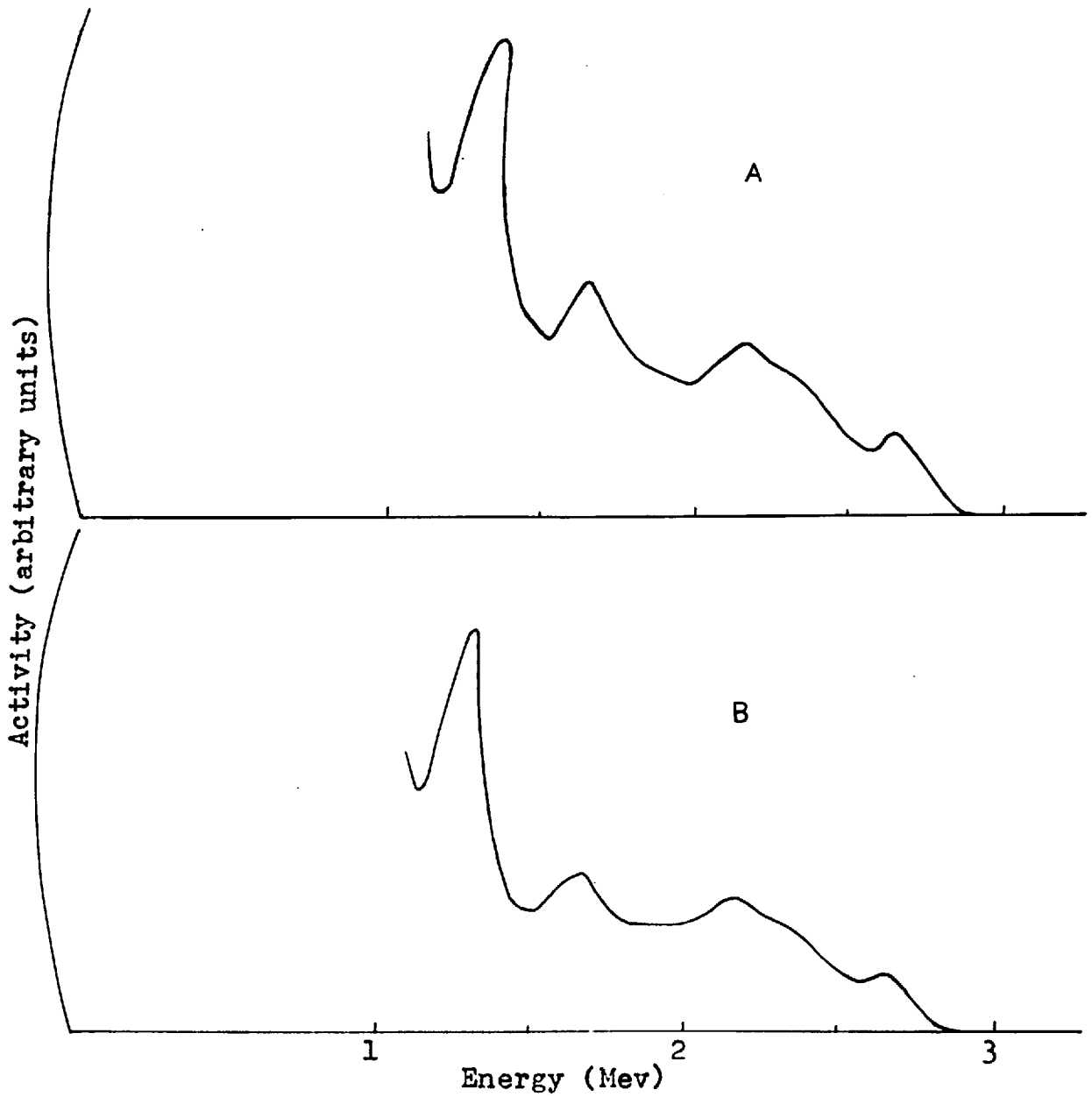


Fig. IV Gamma-ray Spectrum of Irradiated
A. Magnesia
B. Sodium Carbonate

comparison with a spectrum of irradiated pure sodium carbonate (shown in Fig. IVB). The intermediate peaks at 1.73 and 2.24 Mev were identified as the "pair-production" peaks due to the high energy (2.75 Mev) gammas. The sodium content of the magnesium oxide was determined by comparison with the standard sodium activity, and was found to be 86 p.p.m. It is likely that part of this was formed by transmutation from the magnesium by an (n, p) reaction as follows:-

$$^{24}_{12}Mg\ (n,\ p)\ ^{24}_{11}Na$$

The sodium, however, did not cause any interference in the analysis as it was easily separated from the rare earths during the hydroxide precipitations. The large quantity of sodium from the sodium peroxide used for fusion of mineral samples further aided separation by acting as a massive "hold-back" carrier.

Dilution was not resorted to in the case of the lanthanum oxide and yttrium oxide standards. The absence of self-shielding did not justify dilution, and the washing-out of the irradiated ampoules by means of warm dilute acid was found to be quantitative as shown by consistent specific activity values of replicate ampoules. Moreover, this avoided separations of the sodium activity.

2.4 RADIOCHEMICAL PURIFICATION OF LANTHANUM AND YTTRIUM

2.41 Removal of Non-Rare-Earths

Lanthanum and yttrium, along with the rest of the rare earth group, are easily separated from the non-rare-earth elements. But in the case of a few minerals, some elements which are likely to interfere may be present in very large amounts and hence special care was considered to be necessary to achieve radiochemical purity. The following elements were investigated from this point of view:-

2.411 Sodium

Sodium - 24 ($t_{\frac{1}{2}}$, 15 hr.) emits high energy (2.75 Mev) gamma rays, and, if present, would interfere in the measurement of ^{140}La activity. Sodium, besides being a common impurity was a contaminant of all samples because of its presence in the magnesia used as diluent. It was found, however, that two hydroxide precipitations in the presence of inactive sodium as hold-back carrier removed all sodium activity as can be seen from Table IV.

Table IV

Removal of Sodium Interference

Sample Counted	Activity (c.p.m.)
Pure lanthanum oxide	3130
Pure magnesia used for dilution	208
La_2O_3 diluted with MgO; no separations	3375
La_2O_3 diluted with MgO; after 1 hydroxide pptn.	3150
La_2O_3 diluted with MgO; after 2 hydroxide pptns.	3090

2.412 Niobium

Difficulty was encountered in the determination of lanthanum in niobate minerals, particularly when present in very small amounts ($< 0.1\%$ La_2O_3). Niobium - 93, which has a 100 per cent. isotopic abundance in natural niobium, gives rise, on neutron irradiation, to ^{94m}Nb which is transformed by isomeric transition to ^{94}Nb ($t_{\frac{1}{2}}$ 1.8×10^4 years). The latter emits a small percentage ($\sim 8\%$) of hard gammas of 1.57 Mev, which interfere in lanthanum counting.

Niobium, moreover, easily hydrolyses from solution, and is likely to be carried along with any

precipitate separated from its solution. As lanthanum was precipitated first during its separation from yttrium and the other rare earths, it was likely to be contaminated with niobium. This was proved from the spectrum of the lanthanum fraction separated from a niobate mineral (during the earlier part of this work), and its comparison with a standard ^{94}Nb spectrum (see Figures VA and B). The 1.62 Mev ^{140}La photopeak (cf. Fig. VIIA) is not apparent in Fig. VA because of the very low lanthanum activity and the reduced scale used for recording the larger niobium activity. The same spectrum persisted after several months as would be expected for the long-lived ^{94}Nb.

It was found that even two oxalate precipitations prior to the lanthanum fractionation, did not remove the niobium. As niobium forms strong fluoride complexes, a fluoride precipitation step was introduced, with the clear centrifuged solution of the sample being added drop by drop to the hydrofluoric acid precipitant.[84] In this way there was no occlusion of niobium in the rare earth precipitate and all niobium contamination was eliminated with a single precipitation. This was proved from decay measurements and gamma spectrum of the lanthanum fraction separated from the same niobate mineral (see Fig. VC). The ^{140}La

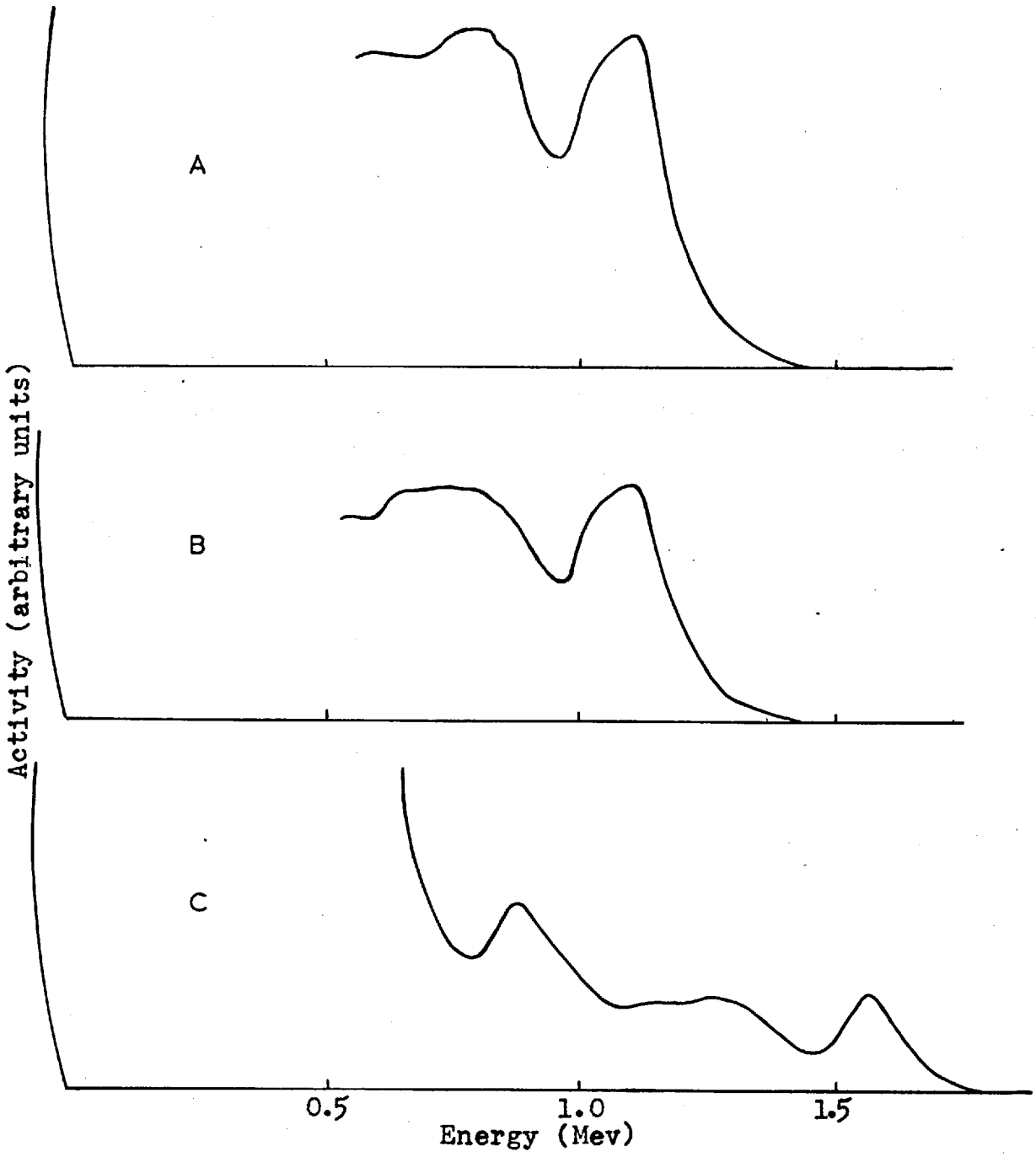


Fig. V Gamma-ray Spectra of:
A. La Fraction from Niobate Mineral Without Fluoride Separation
B. Irradiated Nb_2O_5
C. La Fraction from Niobate Mineral After Fluoride Separation

spectrum was now clear (cf. Fig. VIIA).

2.413 Phosphorous

Phosphorous - 32 emits betas of 1.71 Mev maximum energy. These are not completely stopped by the absorber thickness used for yttrium measurement. Interference from phosphorous in yttrium measurements was, therefore, possible during analysis of phosphate minerals such as monazite, which have a very low yttrium content. However, oxalate[11a] and fluoride[10c] precipitation are both known to give good separations of rare earths from phosphate and the combination of the two in sequence in the separation used was considered adequate to achieve radiochemical purity.

2.414 Isolation of the rare earth group

The following precipitation sequence was adopted for isolating the rare earth group from samples: To the solution were added the lanthanum and yttrium carriers as also iron, sodium (only when fusion was not resorted to) and phosphorous (in the case of phosphate minerals only) as hold-back carriers, and the hydroxides (and/or phosphates) precipitated with ammonia. The hydroxides were dissolved in dilute nitric acid and centrifuged after the addition of a little filter paper

pulp. The clear solution was added drop by drop to hydrofluoric acid to get the rare earth fluoride precipitate. This was dissolved in dilute nitric acid with the aid of boric acid. Hydroxides were again precipitated with ammonia and re-dissolved in dilute hydrochloric acid. From this solution the rare earth group oxalates were then separated.

2.42 Removal of Interfering Rare Earths

A consideration of the gamma energies of all the elements of the rare-earth group (see Table II) shows that it should be possible to resolve the high energy (1.62 Mev) gamma ray of ^{140}La by means of the gamma-ray spectrometer from all other neutron induced rare earth activities with the exception of ^{142}Pr (1.57 Mev) and ^{166}Ho (1.53 and 1.61 Mev). It was therefore necessary to ensure only that these two elements were present to a minimum in the lanthanum precipitate isolated for measurement.

For the beta-counting of yttrium (^{90}Y, E max 2.26 Mev) through absorbers, all the rare earths emitting betas of maximum energy greater than 1.5 Mev were considered, viz.: ^{140}La (2.2 Mev), ^{142}Pr (2.15 Mev), ^{155}Sm (1.65 Mev), ^{152m}Eu (1.88 Mev), ^{154}Eu (1.85 Mev) and

^{166}Ho (1.84 Mev). Of these ^{155}Sm has a very short half-life (23 min.) and soon decays to the soft β-, γ-emitter, 1.7 year ^{155}Eu. Attempts were made, therefore, to obtain a yttrium fraction that was free from lanthanum, praseodymium, europium and holmium. Of these, lanthanum and praseodymium had to be completely eliminated because their beta energies are about equal to that of yttrium.

2.421 Separation of lanthanum and yttrium

The problem of separating yttrium from lanthanum (and praseodymium) was essentially that of separating the "heavy" group of rare earth elements from the "light", and the method of Gordon and Shaver[12] was investigated as it showed considerable promise. They fractionated a mixture of cerium and yttrium in a 1:1 mole ratio by precipitation as oxalate in the presence of EDTA. The amount of ammonium oxalate precipitant added was so adjusted that between 15 and 50 mole per cent of the total oxides (about 0.5 g total) were precipitated after leaving overnight. Under these conditions the precipitate obtained, contained between 93 and 95 mole per cent. of cerium, the remainder being in solution with yttrium.

Not only was this method of precipitation

considered rather slow for the separation of short-lived isotopes, but for its successful application to the problem of separating all lanthanum (and praseodymium) from yttrium, conditions would have to be adjusted for a 50 mole per cent. precipitation from a solution which contained only a few milligrams of added rare earth carriers. This was extremely difficult merely by adjustment of the amount of oxalate added. The difficulty was overcome by making use of demasking agents like copper and zinc, which formed stable complexes with EDTA under the conditions and did not themselves form insoluble oxalates. The use of these was suggested by the corresponding use of "retaining ions" by Spedding[39] and Fuger[40] in the ion-exchange fractionation of the rare earths with EDTA. By the use of the demasking ions it was possible to release, from its association with EDTA, a desired quantity of a rare earth element which then reacted with the excess oxalate present to form an insoluble precipitate. Provided that the stabilities of the EDTA complexes of the rare earth elements differed sufficiently, it was argued that the element which formed the least stable complex would be precipitated first.

Table V shows the logarithms of stability constants of the EDTA complexes of the trivalent rare earths

Table V

Stabilities of EDTA Complexes

Rare Earth Ion (3+)	Metal Ion (2+)	Log. of Stab. Const.
La		15.1
Ce		15.6
Pr		16.0
	Zn	16.1
Nd		16.2
Sm		16.8
Eu		16.9
Gd		17.0
Tb		17.5
Y		17.7
Dy		18.0
	Ni	18.2
Ho		18.3
	Cu	18.4
Er		18.6
Tm		19.1
Yb		19.4
Lu		19.6

and the three metal ions which were used as demasking agents.[96] It is seen that yttrium is between terbium and dysprosium in its stability with EDTA.

Preliminary experiments using tracers with a mixture of lanthanum and yttrium were made. These showed that lanthanum which has the lower stability, was almost completely precipitated before the formation of any yttrium oxalate started, provided that precautions were taken to avoid co-precipitation. Results of separations achieved on a mixture of 10 mg each of La_2O_3 and Y_2O_3 in a volume of 10 ml are shown in Table VI. An amount of EDTA that was just sufficient to complex the total lanthanum and yttrium was added, the pH adjusted to about 5 by means of a universal pH indicator paper, an excess amount of ammonium oxalate added to the warm solution followed by zinc equivalent to the lanthanum present in the form of solution at a pH of about five. It is seen that co-precipitation of yttrium with the lanthanum precipitate was least with dilute solution.

Zinc was first selected as demasking precipitant for fractionating lanthanum and yttrium because its stability constant is intermediate between those of lanthanum and yttrium. However, it was also necessary to recover yttrium from solution and it was observed that

Table VI

Fractionation of Lanthanum and Yttrium

Strength of Zn^{2+} solution added for inducing precipitation of La	Tracer added	Activity in La ppt. %
0.06 M	La	99
0.015 M	La	98
0.06 M	Y	23
0.015 M	Y	5

the precipitation of this element and also neodymium, which have higher EDTA stabilities, was rather slow with zinc. It was also observed later that a higher proportion of the intermediate rare earths like europium remained in solution and were then carried with the yttrium fraction (see Table VIII). Copper was found to be better in these respects and was, therefore, selected as the demasking agent for inducing precipitations.

This method of fractionation did not give a complete group separation of the lighter and heavier rare earths. The elements distributed themselves between the two fractions, as was to be expected, depending on their EDTA complex stabilities.

2.422 Separation of praseodymium from yttrium

The EDTA complex of praseodymium has a stability constant which is closer to that of lanthanum than yttrium. Most of the praseodymium was therefore expected to accompany the lanthanum fraction in a lanthanum-yttrium separation. It was found that only about 70 per cent. of praseodymium (added as tracer) accompanied lanthanum, leaving the rest with yttrium. This was not good enough from the point of view of avoiding interference in yttrium counting. It was argued that the intermediate rare earth elements would be more efficient as carriers for precipitating out the praseodymium activity. This was confirmed by using inactive praseodymium or neodymium as carrier and effecting its separation from yttrium in the presence of tracer praseodymium. Table VII shows results of these separations which were made using exact equivalents of copper for effecting the precipitations. It can be seen that when either praseodymium or neodymium was used about 4 per cent. only of the praseodymium activity was left in solution with the yttrium. Neodymium was ultimately chosen as an intermediate "scavenging" carrier for removal of praseodymium (and other medium rare earths) activity from samples because of its ready availability. Two such precipitations

were found sufficient to leave the yttrium practically free of praseodymium.

Table VII

Separation of Praseodymium from Yttrium

Carrier element used for precipitating Pr activity	Pr in Yttrium fraction (% of total tracer	Chemical yield of yttrium %	Pr accompanying yttrium, after correction for yield %
Lanthanum	30.5	97.9	31.2
Praseodymium	3.5	86.6	4.0
Neodymium	3.5	86.0	4.1

2.423 Separation of europium from yttrium

The separation of europium (and holmium) from yttrium was of less importance as compared to the elimination of lanthanum and praseodymium, because of the lower beta-ray energies of ^{152m}Eu and ^{166}Ho. Moreover, their natural abundance in rare earth minerals is very much lower than that of yttrium. But their separation was attempted as that would permit counting of the yttrium through thinner absorbers, thus greatly increasing the sensitivity of yttrium determination.

The distribution of europium between the lanthanum and yttrium fractions when these were fractionated by precipitation as oxalate in the presence of EDTA was studied with slight variations in the conditions of precipitation. The fraction of europium accompanying the yttrium fraction under the various conditions is shown in Table VIII. The amount of copper or zinc added was in each case 5 per cent. higher than that equivalent with the amount of lanthanum present in the mixture and was added to hot solution ($\sim 90^{\circ}C$). From the results it can be seen that the proportion of europium accompanying the yttrium was lower when the lower pH (4) was used, and when inactive europium carrier was added. However, these conditions were not favoured because of very poor yield of yttrium in the former case and the possibility of an error in the chemical yield determination of yttrium in the latter.

2.4231 Separation after reduction to Eu^{2+}

Europium can exist as the dipositive ion in solution, in which state it resembles the alkaline earth metals. Attempts were made to reduce europium and then separate it from yttrium, either by precipitation of Eu^{2+} with added barium as carrier, or by precipitation of the

Table VIII

Distribution of Europium between Lanthanum and Yttrium

Number	Conditions of Precipitation of La Fraction	Eu in Y Fraction % of original tracer	Chem. Yield of Y %	Eu accompanying Y after correction for Chem. yield %
1	pH 5, Solution cooled immediately after addition of copper and then kept for 1 hr. before separating La.	73.6	96.3	76.5
2	pH5, After addition of copper, solution digested on water bath for 1 hr, cooled and left overnight.	73.0	92.8	78.7
3	pH4, Solution cooled immediately after addition of copper and then left overnight.	20.9	34.2	63.5
4	1 mg inactive europium oxide carrier added. Otherwise as in (1) above.	48.1	78.0	61.7
5	Zinc used in place of copper. Otherwise as in (1) above.	70.5	79.2	89.0

yttrium as hydroxide or oxalate. Various methods of reduction and separation of macro amounts of europium from the other rare earths have been reported in the literature.[14-16, 82, 97, 98] The attempts to separate europium tracer by some of these methods with or without the addition of small amounts of inactive carrier, together with the separations achieved, are recorded in Table IX. The separation was most satisfactory (about 70% removal) when the reduction was carried out with zinc amalgam in an acetic acid medium in the presence of sulphate and with added inactive europium oxide carrier (Exp. 13). But there was hardly any separation in the methods where no carrier europium was added. The separation of Eu^{2+} was not pursued further because the addition of europium carrier, which could not subsequently be completely removed, would entail an error in the chemical yield determination of yttrium. Moreover, in later work it was found that by using neodymium as an intermediate scavenging carrier, not only was praseodymium removed, but a considerable proportion of the europium also was carried on the neodymium oxalate.

Table IX

Separation of Europium after Reduction

No.	Method of Reduction	Carrier Eu_2O_3 added	Element precipitated (or attempted)	Precipitant added	Proportion of Eu accompanying yttrium %
1	Zinc dust in 2NHCl. Mg^{2+} as hold-back carrier for the precipitation	Nil	Yttrium	Ammonia	>95
2	Zinc dust in 2NHCl	Nil	Yttrium	Oxalate	>95
3	Zinc dust in 2NHCl	1 mg	Yttrium	Oxalate	>95
4	Zinc dust in 2NHCl in presence of Ba^{2+} carrier	Nil	Europium	Sodium Sulphate	>95
5	Sodium amalgam in 0.05N acetic acid	1 mg	Europium	(By Amalgam Formation)	>95
6	Sodium amalgam in 0.05N acetic acid, in presence of Na_2SO_4	1 mg	Europium	Ba^{2+} (as carrier)	>95
7	Sodium amalgam in 0.05N acetic acid, in presence of Ba^{2+} carrier	1 mg	Europium	Na_2SO_4	>95

Table IX (cont.)

No.	Method of Reduction	Carrier Eu_2O_3 added	Element precipitated (or attempted)	Precipitant added	Proportion of Eu accompanying yttrium %
8	Zinc amalgam in 0.05 NHCl, in presence of Na_2SO_4	1 mg	Europium	Ba^{2+} (as carrier)	~50
9	Ba^{2+} carrier added in 0.05 NHCl, and solution passed through Jones Reductor	1 mg	Europium	Na_2SO_4	~50
10	Ba^{2+} carrier added in 0.05 NHCl and solution passed through Jones Reductor	Nil	Europium	Na_2SO_4	>95
11	Zinc amalgam in 0.05 NHCl, in presence of Ba^{2+} carrier	1 mg	Europium	Na_2SO_4	~80
12	Ba^{2+} carrier added in 0.1 NHCl, and solution passed through Jones Reductor	1 mg	Europium	Na_2SO_4	~50
13	Zinc amalgam in 0.5 N acetic acid in presence of Na SO_4	1 mg	Europium	Ba^{2+} (as carrier)	~30
14	Zinc amalgam in 0.5N acetic acid in presence of Na_2SO_4	Nil	Europium	Ba^{2+} (as carrier)	>95

2.424 Separation of holmium from yttrium

The stability constant of the EDTA complex of holmium is higher than that of yttrium. Holmium would therefore be expected to remain almost entirely in solution with the yttrium after precipitation of the lanthanum fraction. Its stability constant is so close to that of yttrium, however, that a good separation between the two is expected to be difficult. In order to determine the extent of separation that could be achieved between yttrium and holmium, the former was precipitated under varied conditions. To a solution containing inactive yttrium carrier and holmium tracer, was added an amount of EDTA equivalent ø to the yttrium present, followed by an excess of ammonium oxalate. The copper (or nickel) precipitant was added under the conditions shown in Table X, the amount added being only 90 per cent. of that equivalent with the yttrium. By this means it was hoped to leave a greater part of the holmium in solution along with the partially unprecipitated yttrium. It can be seen from the results that a 30 per cent. separation could be achieved with the conditions of Expt. 2. Although the separations achieved using inactive dysprosium as holdback carrier (Expt. 4) or nickel as precipitating agent (Expt. 5), were slightly better, the improvement

Table X

Separation of Holmium from Yttrium

Number	Conditions of precipitation of Y	Ho in Y Fraction % of original tracer	Chem. yield of Y %	Ho accompanying Y after correction for Chem. yield %
1	pH5, Copper solution added to cold solution and left for 1 hour.	60.6	79.0	76.7
2	pH5, Copper solution added to solution at $\sim 90^{\circ}C$, cooled to $\sim 35^{\circ}C$ and ppt. centrifuged.	49.3	69.8	70.6
3	pH7, Copper solution added to cold solution and left for 1 hour.	56.4	70.6	79.8
4	pH5, 0.5 mg Dy_2O_3 added as hold-back carrier. Copper solution added to cold solution and left for 1 hour.	49.6	76.2	65.1
5	pH5, Nickel solution added as precipitant to cold solution and left for 1 hour.	26.6	44.4	60.0

did not warrant the adoption of these methods in view of the other difficulties which would be introduced, viz., incorrect yield and low yield values for addition of Dy and Ni respectively.

2.425 Procedure evolved for purifying La and Y

Based on the results of the foregoing tracer experiments, a procedure of EDTA-oxalate precipitation steps was decided upon for obtaining lanthanum and yttrium in a state of sufficient radiochemical purity. The distribution of the elements La, Pr, Eu, Y and Ho among the various fractions of the procedure was then studied by means of tracers. The average of duplicate results together with the variations are shown in Table XI. The different columns of the Table represent the various steps of the procedure which were as follows:

I. To a solution containing 5.0 mg each of La_2O_3 and Y_2O_3 in a centrifuge tube, the radioactive tracer being studied was added, followed by a solution of the disodium salt of EDTA in equimolar ratio with the total lanthanum and yttrium. Using glacial acetic acid as buffer, the pH was adjusted to about five by addition of ammonia. Bromo-cresol green was found to be a convenient indicator for this purpose. The

Table XI

Distribution of La, Pr, Eu, Y and Ho

in Oxalate Fractions

Tracer	I Lanthanum Fraction %	II 1st Neodymium Precipitate %	III 2nd Neodymium Precipitate %
Lanthanum	71.3 ± 1.3[a]	23.7 ± 1.3	0.1 ± 0.0
Praseodymium	33.4 ± 0.6	62.6 ± 0.6	2.2 ± 0.2
Europium	7.0 ± 0.2	63.1 ± 0.6	20.5 ± 0.5
Yttrium	0.6 ± 0.0	9.9 ± 0.4	8.7 ± 0.2
Holmium	0.6 ± 0.2	8.0 ± 0.2	10.5 ± 0.5

Tracer	IV Yttrium Fraction %	V Supernate from Yttrium ppt. %	VI Washings of Precipitates %
Lanthanum	0.0	0.0	4.9 ± 0.1
Praseodymium	0.1 ± 0.0	0.0	1.7 ± 0.2
Europium	7.6 ± 0.1	0.4 ± 0.0	1.4 ± 0.2
Yttrium	45.3 ± 0.3[b]	20.4 ± 0.6	15.1 ± 0.5
Holmium	29.5 ± 1.0	43.7 ± 0.7	7.7 ± 0.8

a. Chemical yield by permanganate titration 71.9 ± 1.0

b. " " " " " 47.8 ± 0.8

solution was diluted to a suitable volume (~ 10 ml), heated in a water bath at about 90°C and a solution of ammonium oxalate added. No precipitate was formed at this stage. To the solution (which was maintained at ~90°) was now added dropwise and with continuous stirring, copper equivalent to 80 per cent. of the lanthanum present, in the form of an approximately 0.015 molar solution which had previously been adjusted to a pH of about five. The solution was stirred for a further 5 mins., removed from the water bath and the precipitate centrifuged off before the temperature dropped to about 60°C. In this way a purer lanthanum fraction was obtained, with a yield of about 70 per cent.

II. To the supernate, which was transferred to a second centrifuge tube, was added a solution of EDTA equivalent to 5 mg Nd_2O_3, followed by this quantity of neodymium in the form of a solution previously adjusted to pH about five. The solution was heated in the water bath at 90°C and to it was again added dropwise and with continuous stirring, copper equivalent to all the neodymium plus the deficiency used for lanthanum precipitation in Step I. The solution was cooled to room temperature with occasional stirring, allowed to stand for an hour and centrifuged.

III. Step II was repeated, i.e. EDTA, neodymium and copper were added in that order to the supernate from Step II. The amount of copper used was, however 5 per cent. in excess of the neodymium equivalent.

IV. The supernate from Step III was warmed on the water bath at 90°C, and an amount of copper equivalent to 75 per cent. of the total yttrium added as before. The solution was cooled to room temperature with occasional stirring, allowed to stand for half an hour and centrifuged.

V. The supernate from Step IV was concentrated and mounted for counting along with the solutions of the precipitates of the previous four steps.

VI. The washings of precipitates from the different steps were combined, concentrated and counted to obtain a material balance of the total tracer used.

The following observations may be made on the results shown in Table XI:-

i) About a third of the praseodymium and less than 1 per cent. of the holmium present accompany the lanthanum precipitate. These do not cause an appreciable interference in the gamma-counting of lanthanum from mineral samples as will be shown later (see Section 2.514).

ii) All the lanthanum and practically all the praseodymium are removed from solution by the time the second neodymium scavenger is precipitated. Thus no lanthanum and a very small fraction only of the praseodymium (0.1%) accompany the yttrium fraction. The praseodymium would cause an error ($\sim$ + 3%) only when analysing for yttrium in Pr-rich minerals like monazite. For such minerals a slight modification in the procedure (see Section 2.742) reduces the interference to about + 1 per cent.

iii) About 8 per cent. of the europium and 30 per cent. of holmium present accompany the yttrium fraction. This causes only a small interference in beta-counting of yttrium through aluminium absorbers as will be shown later (see Table XIII).

iv) The percentage of lanthanum tracer accompanying the lanthanum fraction is approximately the same as the chemical yield determined by titration of the oxalate precipitate with standard permanganate, because hardly any yttrium is co-precipitated with the lanthanum. But the yttrium chemical yield is appreciably higher. This is due to the fact that the neodymium "scavenging" carrier is not completely precipitated in Step III and is therefore carried down with the yttrium precipitate.

Corrections which may be applied for this error are discussed in the chapter on chemical yield determination (see Section 2.65).

2.5 COUNTING TECHNIQUES

2.51 For Lanthanum

Measurement of lanthanum activities was made by means of the gamma-ray spectrometer.

2.511 Sample-mounting

A large phosphor (36 mm diam. x 25 mm deep) was used as it was found to be about five times as efficient as a small phosphor (15 mm. diam., 23 mm. deep) for counting the hard gamma rays of ^{140}La. The large phosphor had a flat aluminium cap of 6 inches diameter covering it. It was necessary to decide what type of mounting receptacle to use over it for mounting the liquid sample source in order to achieve reproducible geometry. It was also necessary to know what effect a slight variation in the volume of the mounted sample would have on the counting rate. For this purpose, 5 ml. of a ^{60}Co solution were placed in a polythene bottle, and the counting rate determined after successive

additions of 1 ml portions of distilled water. The count was corrected for variations in the efficiency of the counter by comparison with a standard ^{60}Co source which was counted alternately. The counting rate was plotted against variation in volume for different-sized bottles (1 oz., 2 oz., and 4 oz. cap.). The results are shown in Figure VI. The 4 oz. bottle which had a diameter of 45 mm was selected for sample mounting purposes because it showed the minimum variation in counting rate with change in volume around 10 ml, and the maximum counting efficiency.

All samples and standards for counting were made up to 10 ml, and when it was not practicable to pipette this volume, it was adjusted to 10 $\pm$ 0.5 ml with the help of a level mark on the bottle. This variation in volume caused an error of about $\pm$ 2 per cent. in the counting rate. Corrections were, therefore, applied by reference to the graph.

In order to determine the errors involved in positioning the bottle over the centre of the counter head, a standard ^{60}Co source was deliberately placed off-centre and the counting rate determined. This was corrected for "counter-efficiency" as before. The results for various positions are shown in Table XII.

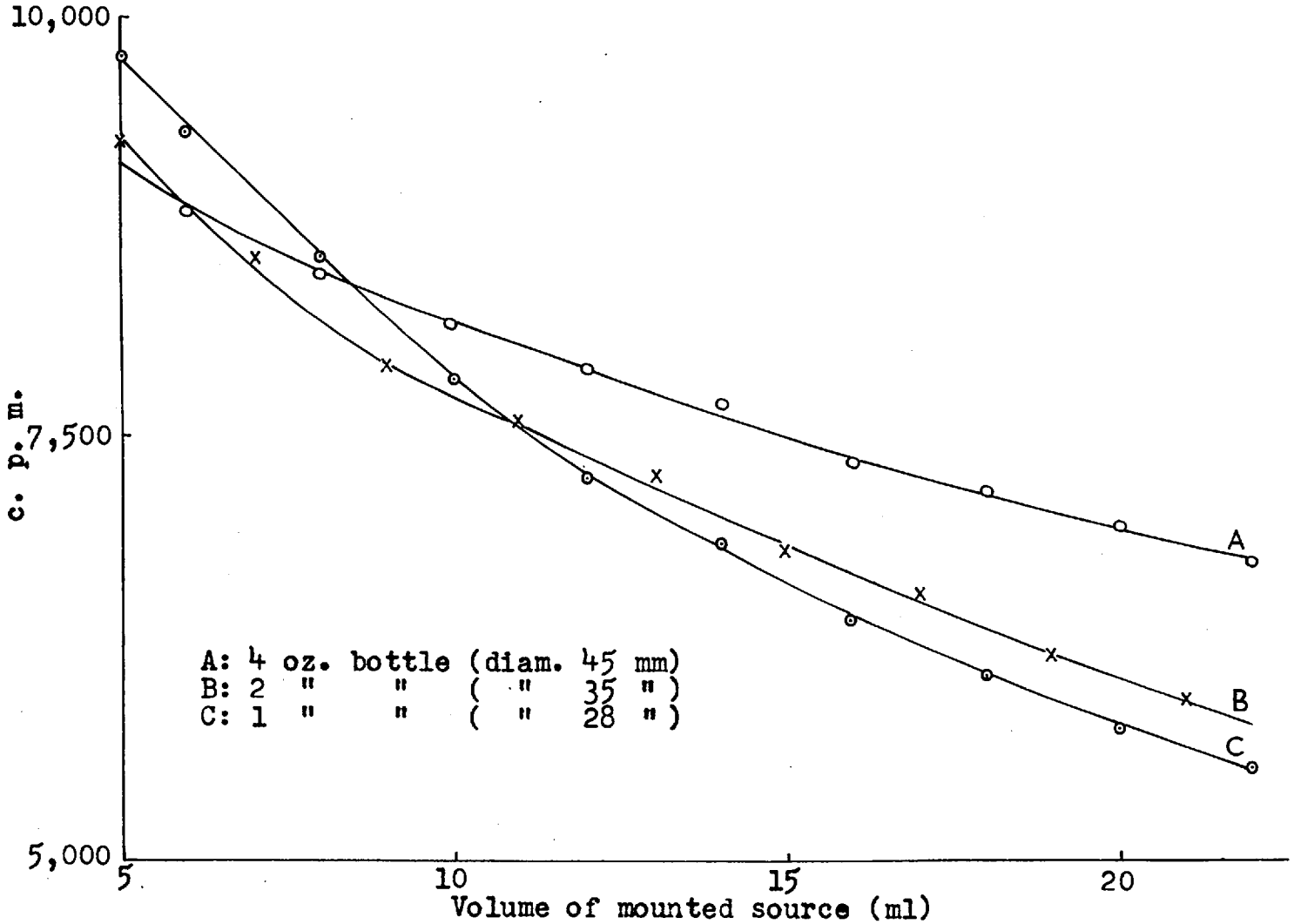


Fig. VI Variation of Counting Rate with Volume

It can be seen that the "slightly off-centre" position shows a small positive error only which is within statistical fluctuations.

Table XII

Effect of Position of Mounted Sample on Counting Rate

Position of bottle on counter head	Difference from count when bottle is exactly centred
Centre	0
Slightly off-centre	+ 0.3
Mid-way between centre and extreme edge of head	- 1.0
Extreme edge of head	- 6.0

2.512 Stability of counter

Gamma spectrometric systems, especially those based on single-channel analysers, are not known for high precision of counting.[89] It was, therefore, necessary to get a measure of the actual counting precision to expect during the analysis. ^{60}Co which is

long-lived and has a gamma-ray energy of 1.33 Mev was used for investigating the statistics of the measurements. It was found that when the measurements were made over a two-hour period on a single day the coefficient of variation of a count of 15,000 was about 1.5 per cent. This was higher than would be expected if only the statistical nature of the radioactivity was responsible for the variation, and can, therefore, be attributed to apparatus drift. The coefficients of variation of measurements made over longer periods were found to be considerably higher, viz., 7.0% and 8.2% for four- and seven-day periods respectively. Attempts to correlate the variation with changes in mains voltage, etc., were unsuccessful.

While making quantitative measurements, therefore, a count on a sample was always preceded and followed by a standard count with which it was compared. If the variation in the two standard counts was greater than about one per cent. of the average, the sample and standard was re-counted. In this way, the error due to counting was kept down to about one per cent. Similarly, when making decay measurements on samples, the sample count was corrected by comparison with a standard after taking into account the decay time of the latter.

The improved accuracy with which points, corrected in this way, fitted the decay curves (see for example Fig. XII) justifies the assumption that $\pm$ 1 per cent. reproducibility was obtained by counting under these conditions.

2.513 Gamma scintillation spectra

The gamma-ray spectra of ^{140}La and the rare earth radionuclides likely to interfere, viz.: ^{142}Pr, ^{166}Ho, ^{152m}Eu and the longer-lived ^{152}Eu + ^{154}Eu are shown in Figures VII and VIII. As ^{90}Y is a pure beta-emitter the response of the scintillation phosphor to its emissions does not produce any photo-electric peaks as is shown in Figure IXA. The spectra of neodymium-147 and cerium-141 and 143, which elements have a high natural abundance in rare earth minerals, are also shown (Figure IX).

2.514 Contribution of ^{142}Pr and ^{166}Ho to lanthanum count

All lanthanum measurements were made on the 1.62 Mev photo-peak with a channel-width of 0.2 Mev (corresponding to 5 volts on the single channel analyser). A wider channel width was not used in order to avoid any possible interference from the 1.39 Mev photo-peak of

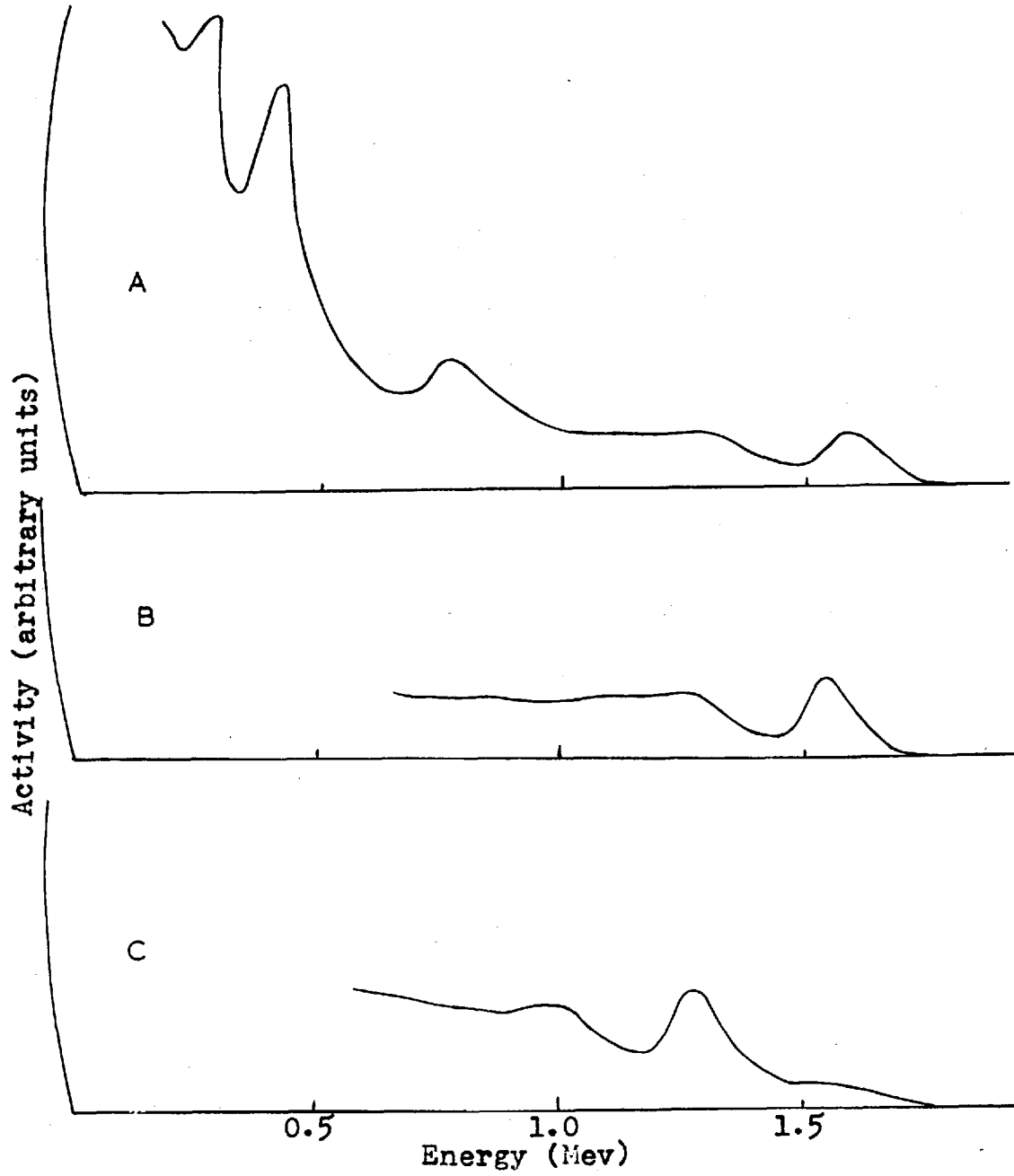


Fig. VII Gamma-ray Spectra: A: ^{140}La
B: ^{142}Pr
C: ^{166}Ho

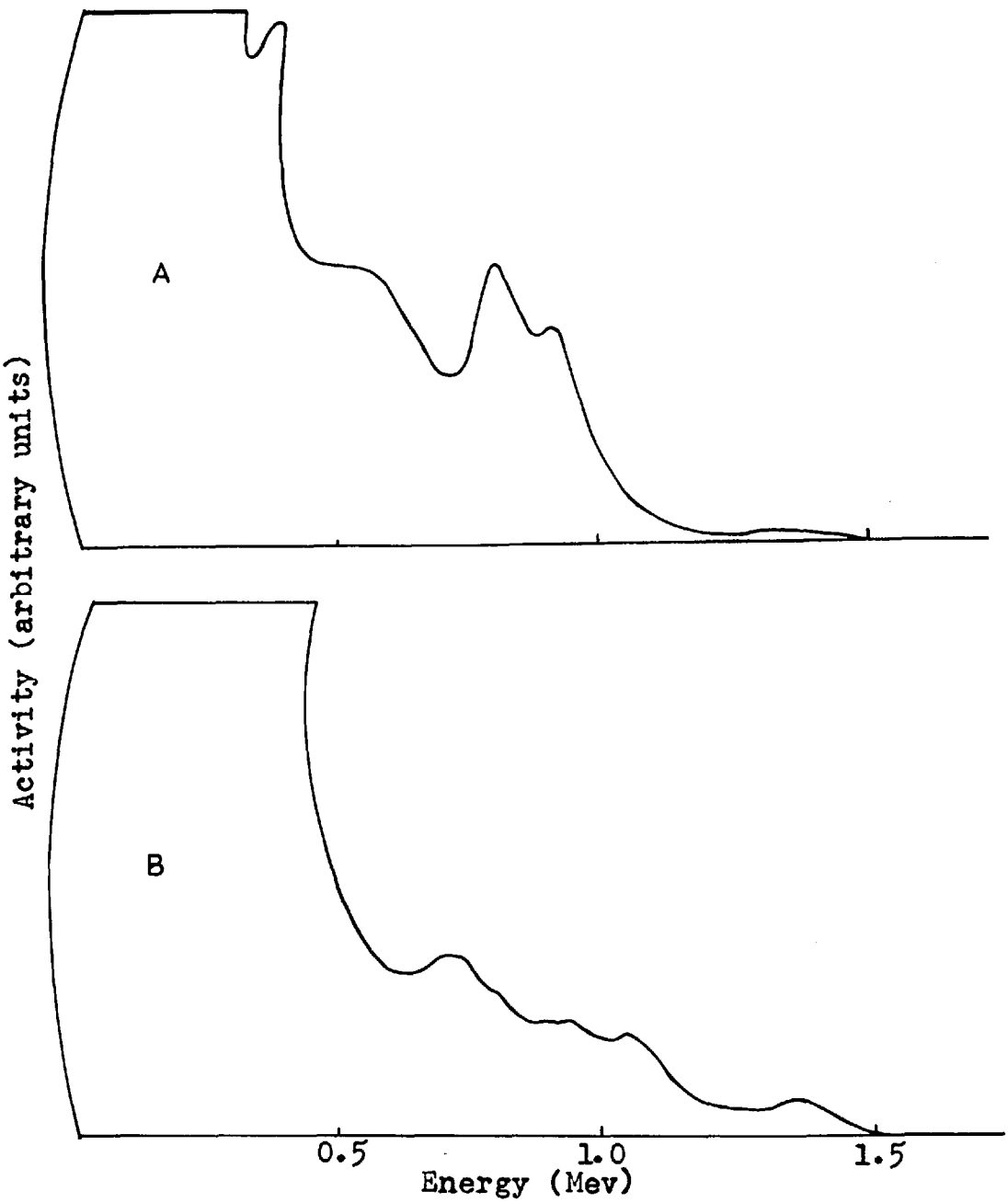


Fig. VIII Gamma-ray Spectra:
A: ^{152m}Eu (9.3 hr)
B: ^{152}Eu (13 y) + ^{154}Eu (16 y)

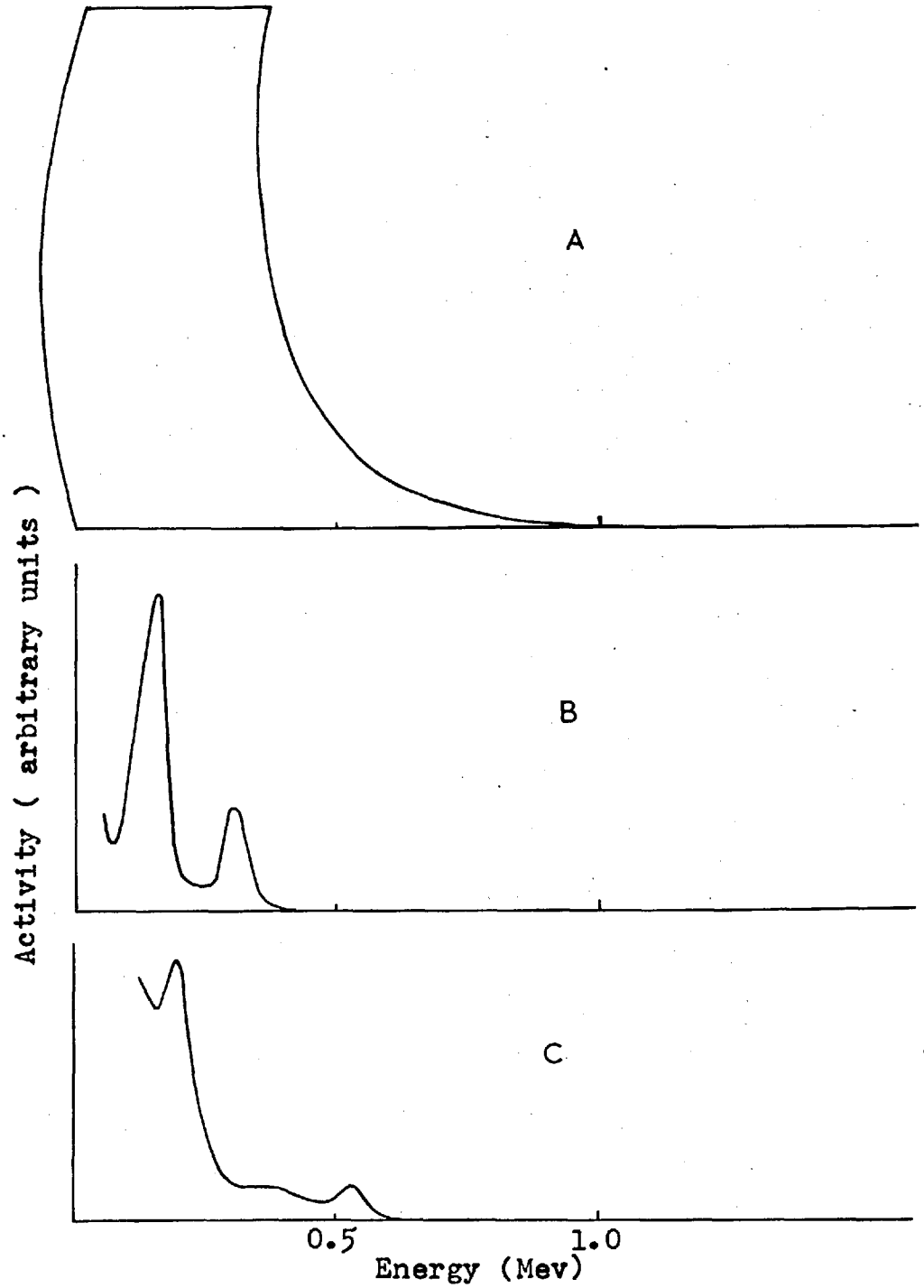


Fig. IX A: Scintillation Spectrum of ^{90}Y
B: Gamma-ray Spectrum of $^{141}Ce + ^{143}Ce$
C: Gamma-ray Spectrum of ^{147}Nd

^{152m}Eu although this was expected to be very low for most samples), and because the sensitivity (0.04 μg La_2O_3 gave 100 cpm after one $t_{\frac{1}{2}}$) with the 0.2 Mev channel was quite adequate.

The main criterion for resolving two gamma-emitters by means of a gamma spectrometer is that the energies of the two should differ by more than the width of the higher energy peak at half-maximum photo-peak height, when both are expressed in same units.[90] The 1.57 Mev photopeak of ^{142}Pr was too close to the 1.62 Mev photopeak of ^{140}La to enable any discrimination to be made between them by means of the gamma-spectrometer used. Similarly, it was not possible to resolve from the 1.62 Mev photopeak, the small proportion ($\sim$ 0.3%) of gamma radiations having energies of 1.53 and 1.61 Mev emitted by ^{166}Ho. It was, therefore, necessary to study the contribution that ^{142}Pr and ^{166}Ho would make to lanthanum counting.

Figure X shows the spectra around 1.6 Mev energy, for equal amounts (1 μg of each) of the three elements, corrected to zero time (i.e. time of removal from nuclear pile). It is seen that even for this ratio the contribution of both praseodymium and holmium would be quite low ($\sim$ 3% each). By the time

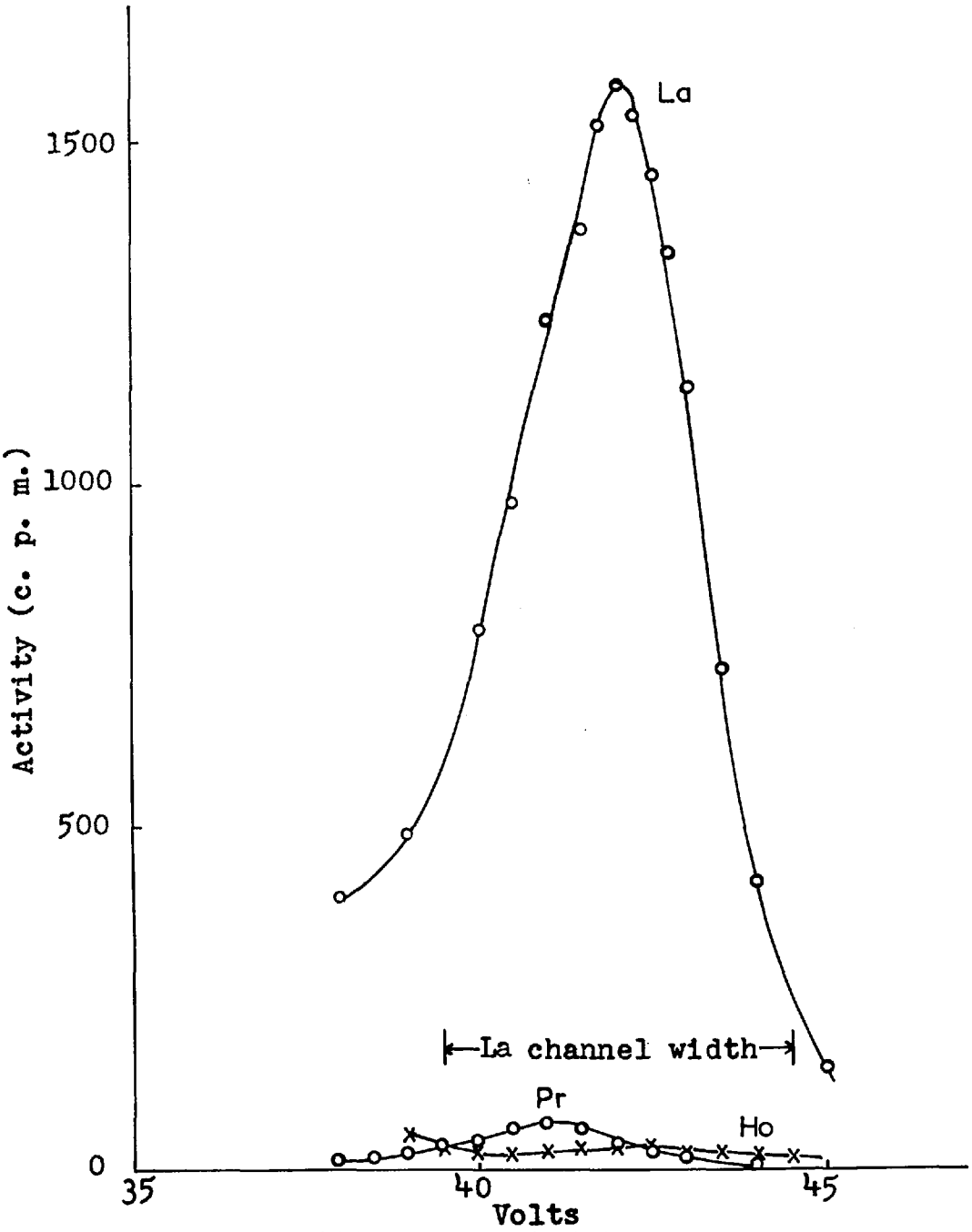


Fig. X Comparison of Gamma-activities from Equal Amounts of La, Pr & Ho

measurements were made on the lanthanum fraction in a normal analysis, about one lanthanum half-life had usually elapsed since removal of samples from the pile. In this time the praseodymium activity would have decayed to a fourth of that originally present, since its half-life is about half that of lanthanum. Moreover, when it is considered that the natural abundance of praseodymium is expected to be less than a third of that of lanthanum, and that only 33 per cent. of the praseodymium present accompanies the lanthanum fraction in a normal lanthanum-yttrium fractionation (see Table XI), it can be seen that the interference of praseodymium in lanthanum analysis will be negligible ($< 0.3\%$).

In yttrium-rich minerals the proportion of La:Ho is likely to be of the order of 2:1. For this ratio the contribution of holmium to the lanthanum count will be about 1.5 per cent. Holmium was liable, therefore, to give a slight interference in analysis for lanthanum in the yttrium-rich minerals if no separation was made. However, as holmium was almost completely eliminated during precipitation of the lanthanum fraction during the EDTA-oxalate fractionations (see Table XI), there could be hardly any interference from it under these conditions.

2.515 Spectra and decay curves of lanthanum separated from samples

Gamma spectra were taken of all lanthanum fractions separated during analysis as a proof of their purity. Figure XIA shows the gamma ray spectrum of the lanthanum fraction separated from Lyndochite, an yttrium-rich mineral. Measurements were also sometimes made over the lanthanum peak for a five half-lives period as a further proof of the radiochemical purity of the isotope. The decay curve for one of the samples analysed (Davidite) is shown in Figure XII. The sample count has been corrected for instrument variations by comparison with the standard lanthanum curve which is also shown. As a result of these corrections the deviations from the true decay curve due to variation in counter efficiency, are considerably reduced.

2.52 For Yttrium

The hard betas of yttrium (^{90}Y, E max 2.26 Mev) were counted with an end-window Geiger-Müller counter through aluminium absorbers.

2.521 Sample-mounting

The yttrium fraction was mounted for counting

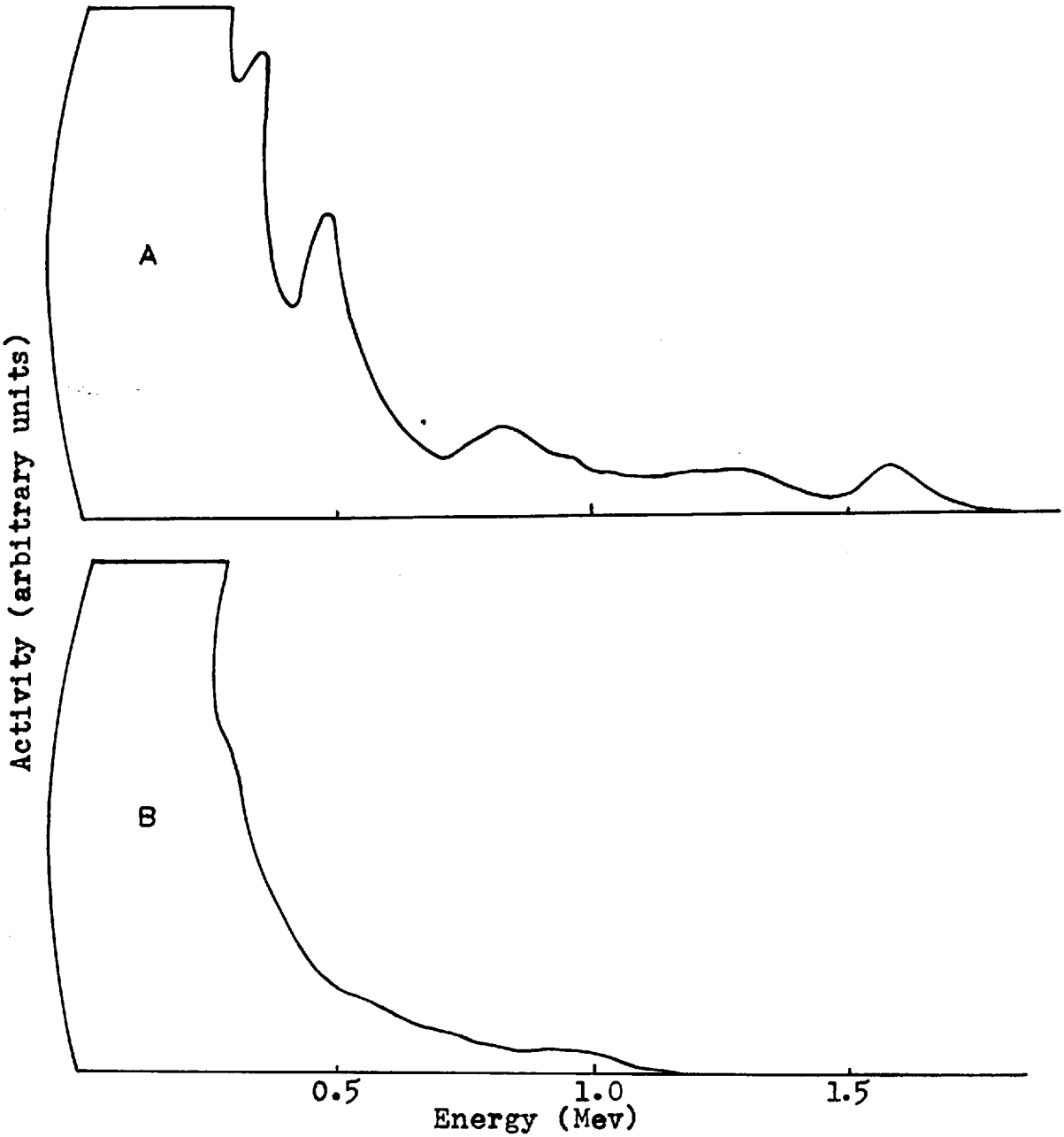


Fig. XI Typical Gamma-ray Spectra of (A) La Fraction & (B) Y Fraction Separated from Mineral Sample (Lyndochite)

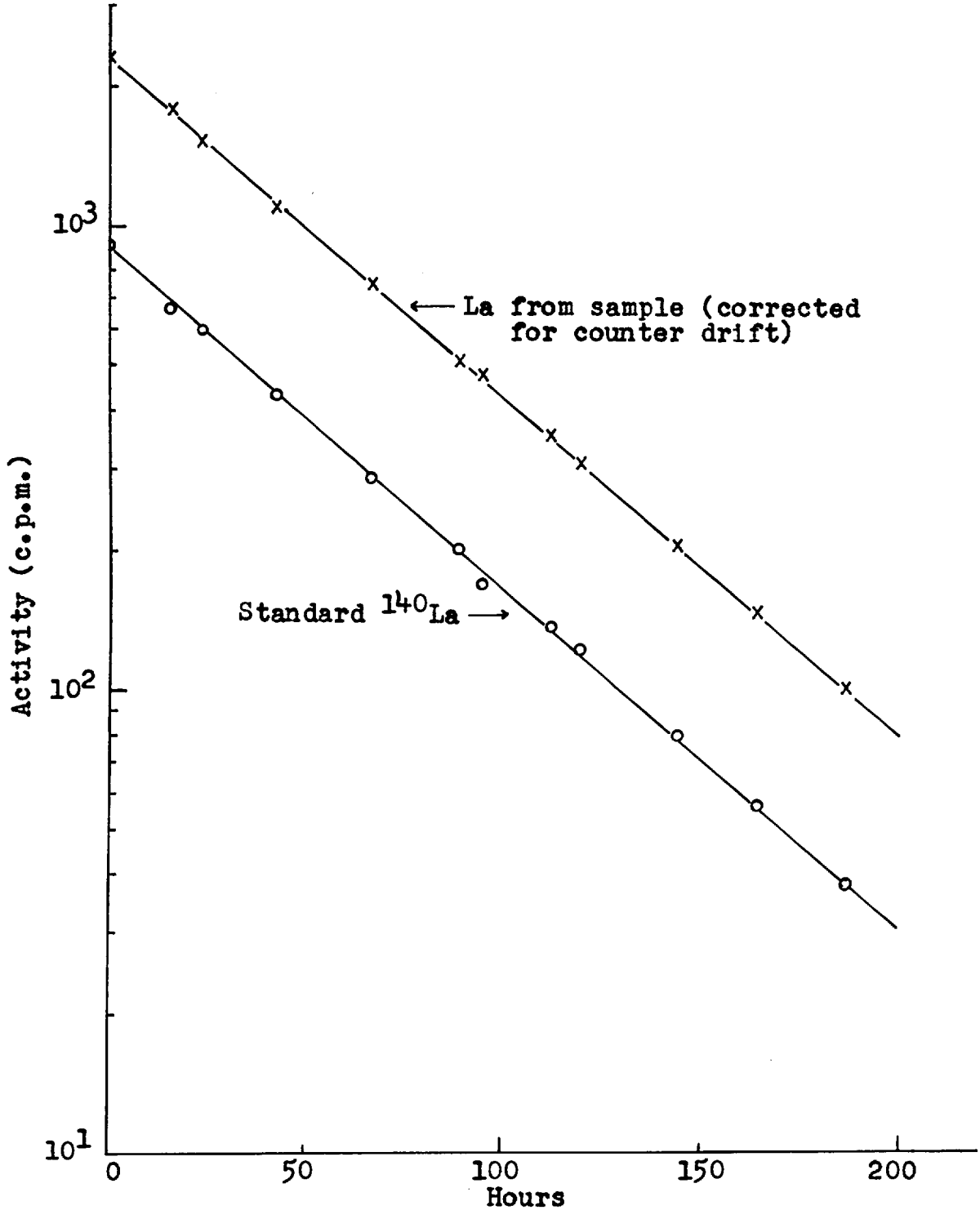


Fig. XII Typical Decay Curve of Lanthanum Separated from Mineral Sample (Davidite)

in aluminium trays (diam. 2 cm) by dispersing the precipitate with a drop of 1 per cent. "Teepol" solution and transferring the slurry by means of a dropper. It was not necessary to transfer quantitatively since the chemical yield was determined after counting. The tray was dried under an imfra-red lamp and mounted over a perspex square which fitted in the frame of the lead castle. The sample mounting technique was rather uncritical because the effect of self-absorption is negligible when counting hard beta rays.[107]

2.522 Absorber curves

The absorber curves of ^{90}Y and other rare earth radioisotopes emitting hard beta rays are shown in Figures XIII - XVII. The observed ranges in aluminium (except that of ^{140}La) agree with those calculated from the range-energy relationship proposed by Feather,[99] viz.: $R = 0.543\ E - 0.160$ (where R is the range in gms/cm^2, and E is the maximum energy in Mev of the beta particles). In the case of ^{140}La, which has a more complex beta spectrum and high gamma background, the different β max could not be resolved by the "Feather Plot" method.[99, 100]

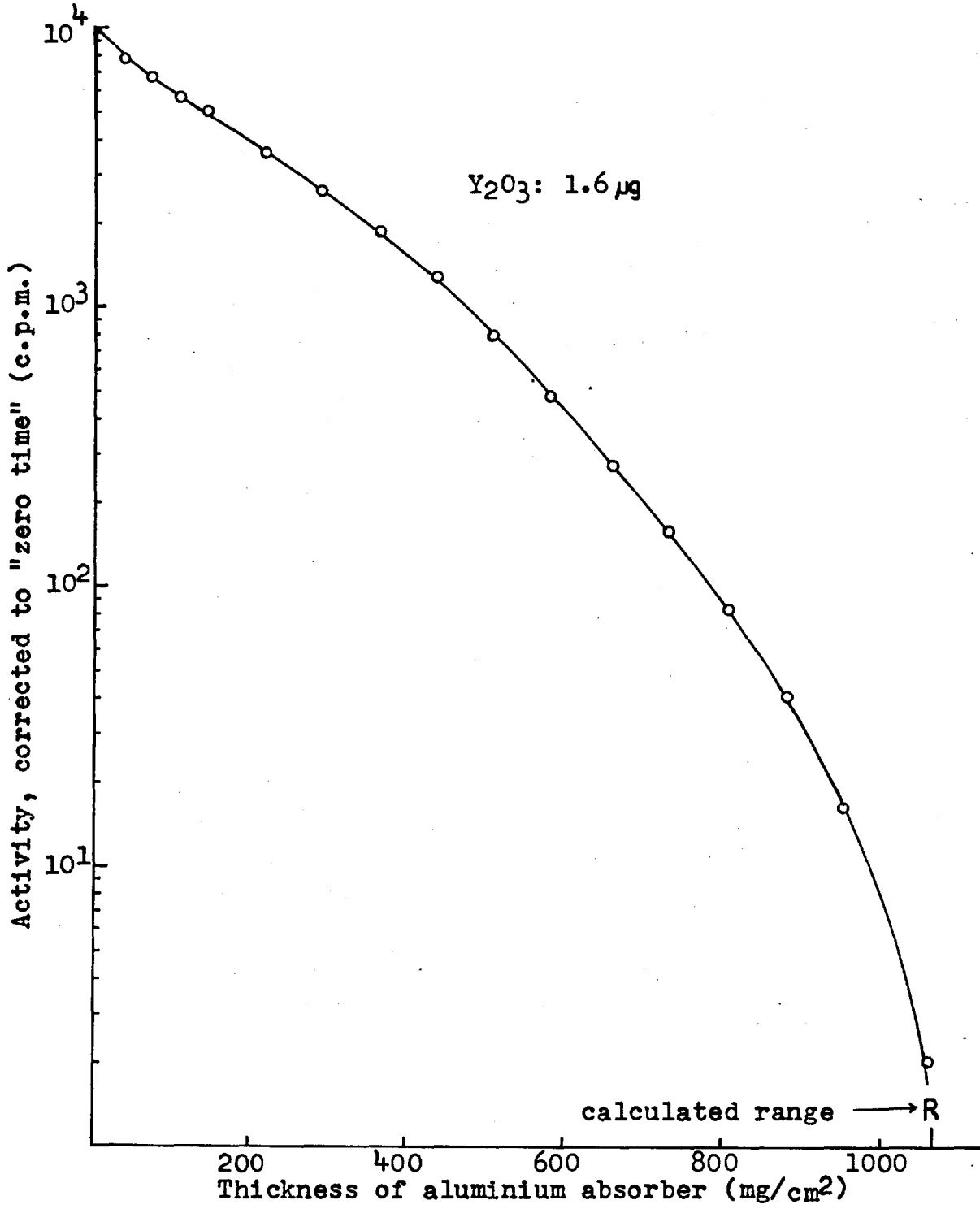


Fig. XIII Absorption Curve of ^{90}Y

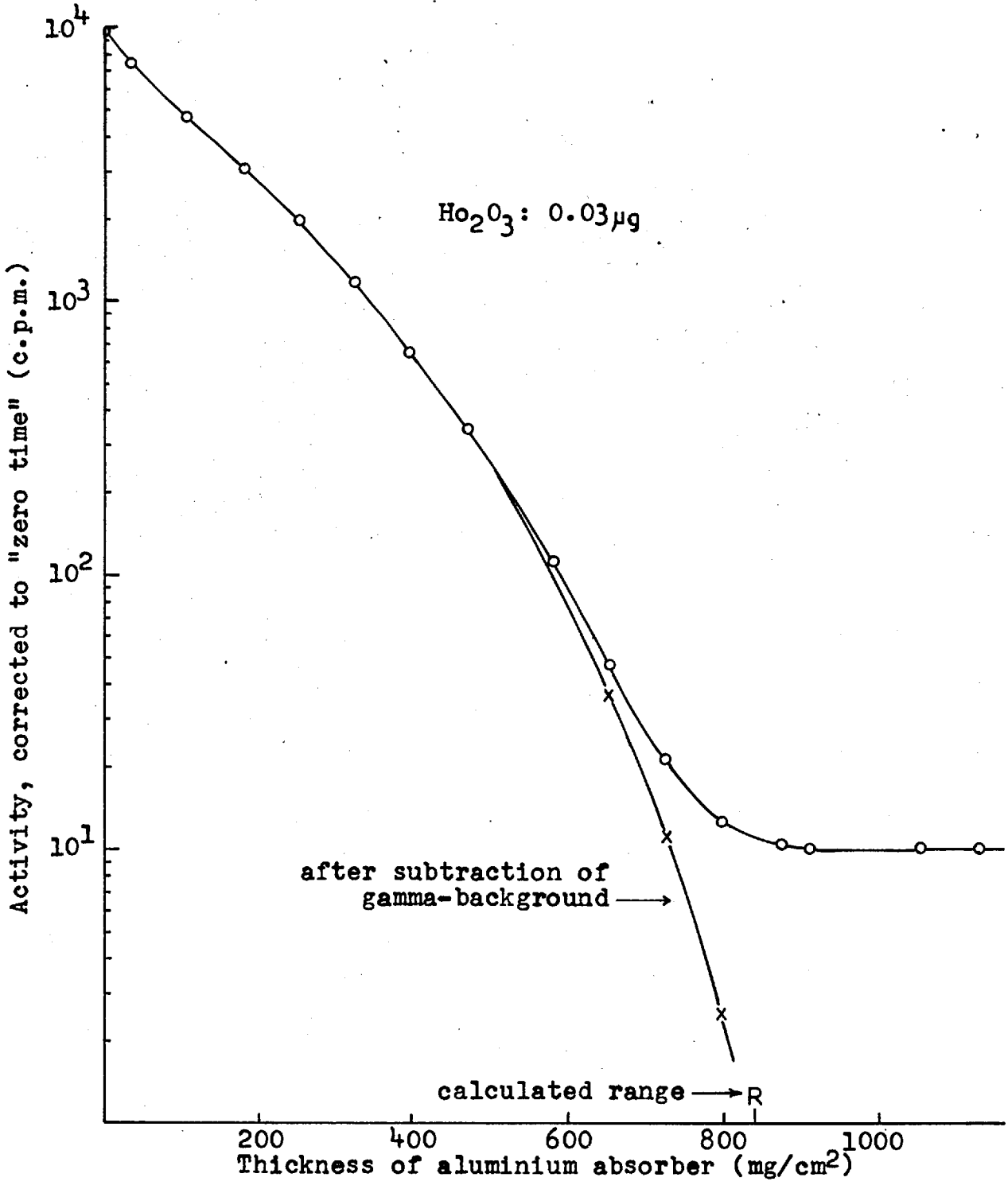


Fig. XIV Absorption Curve of ^{166}Ho

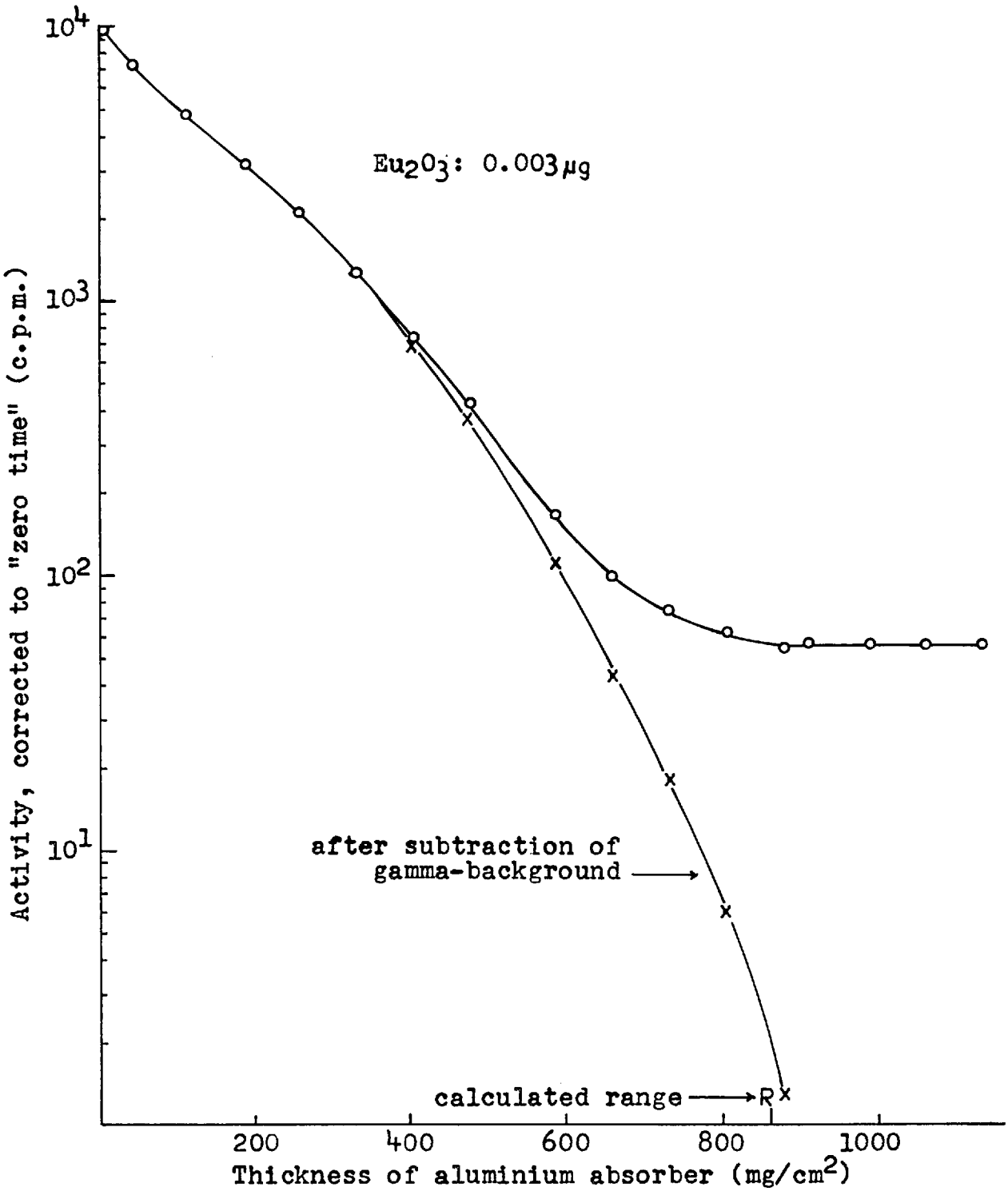


Fig. XV Absorption Curve of ^{152m}Eu

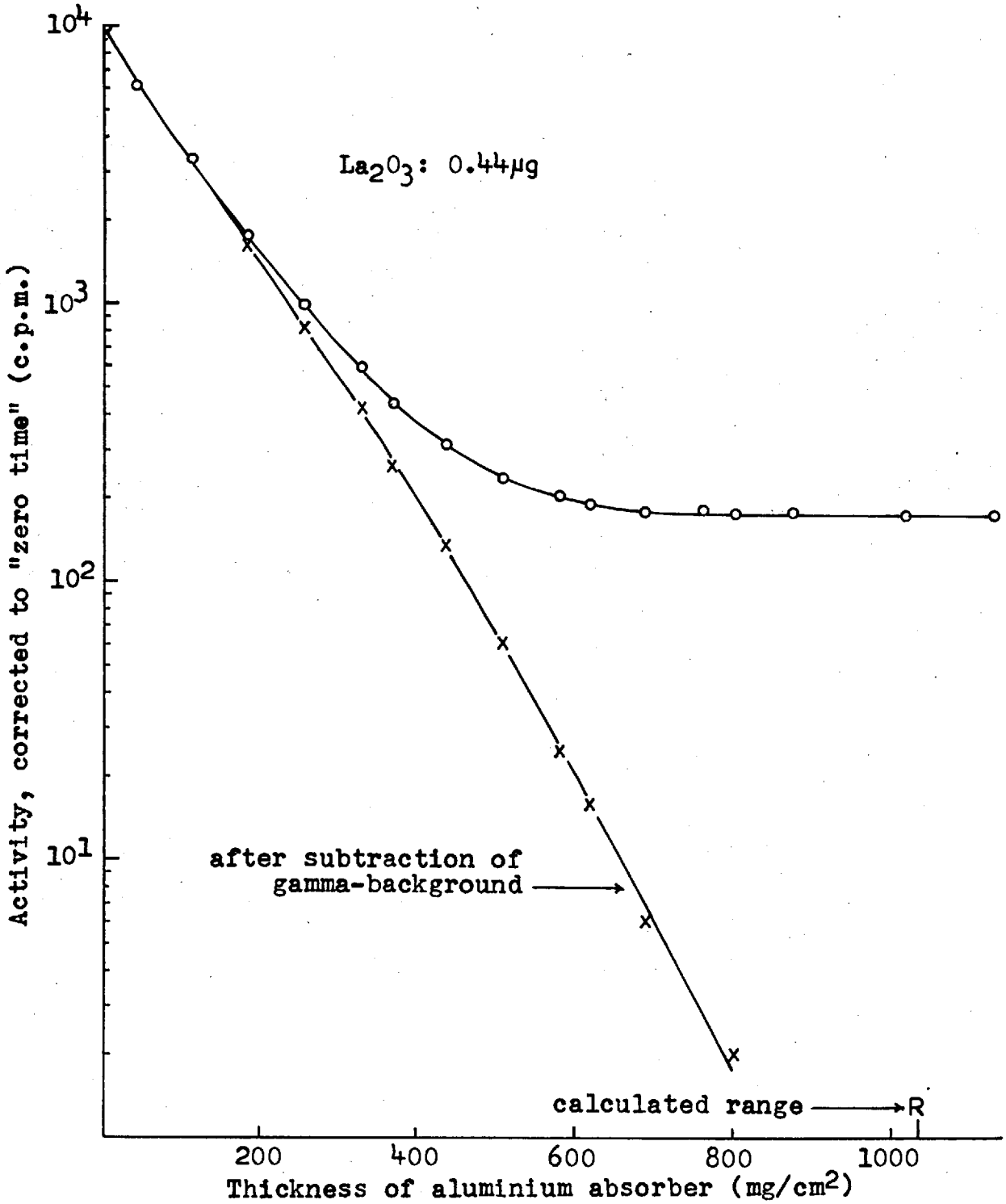


Fig. XVI Absorption Curve of ^{140}La

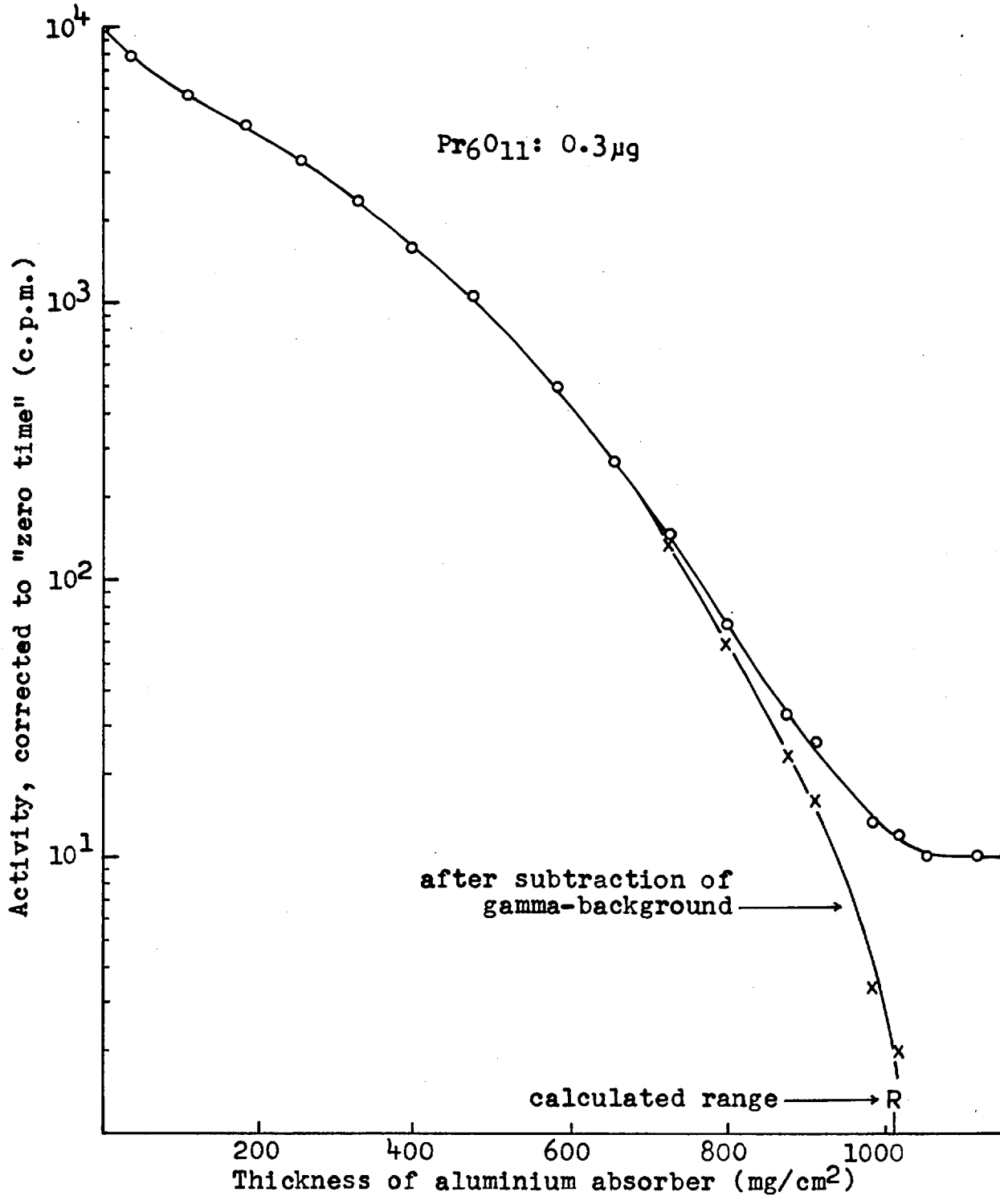


Fig. XVII Absorption Curve of ^{142}Pr

2.523 Contribution of ^{152m}Eu and ^{166}Ho to yttrium counting

It was shown by means of the tracer experiments (Section 2.425) that interference from lanthanum and praseodymium was eliminated by successive lanthanum and neodymium oxalate precipitations. The long-lived europium activity (16y ^{154}Eu + 13y ^{152}Eu) was found to be very low for the irradiation time used. Thus at an absorber thickness of 750 mg/cm^2 and counting after 80 hours, the contribution to yttrium activity was less than 0.1%. 27 hour ^{166}Ho and 9 hour ^{152m}Eu (E max 1.84 and 1.88 Mev respectively) were, therefore, the only radionuclides considered as a possible source of interference because they were partially precipitated with the yttrium fraction.

About 8 per cent. of europium and 30 per cent. of holmium present accompany the yttrium fraction during the oxalate fractionations. Attempts were made to correct for the contribution from ^{166}Ho to the beta-counting of yttrium by estimating the amount of holmium from a measurement of its 1.36 Mev gamma activity. However, the 1.36 Mev photopeak could not be detected in the gamma-ray spectra of yttrium fractions separated from any of the samples analysed.

The interference from ^{166}Ho and ^{152m}Eu was, therefore, reduced to the minimum, consistent with a satisfactory sensitivity for the yttrium, by using an optimum thickness of absorber and choosing an appropriate time for counting (so as to have maximum decay of the comparatively shorter-lived ^{166}Ho and ^{152m}Eu). The proportion of yttrium to holmium and europium in a natural mixture has been reported[73] as 0.31 : 0.012 : 0.010, and very few rare earth minerals have been reported in which this proportion is less favourable.[59,101,102] In a rare earth mixture ^{166}Ho would also be formed by transmutation reactions from dysprosium (see Section 1.321); but the amount so formed would be less than 0.2% of that formed from ^{165}Ho. A set of values for interference from holmium and europium in the beta-counting of yttrium at various absorber thicknesses was prepared by reference to their absorber curves (Figs. XIII - XV), and by assuming that these elements were present in the same proportion as in a natural mixture before the fractionations. Table XIII shows the calculated interference contributions at different times.

Table XIII

Contribution of Holmium and Europium to Yttrium Counting.

Absorber Thickness mg/cm^2	Time of Counting after removal from Pile Hours	Activity per microgram Y_2O_3 C.p.m.	Positive Errors from ^{166}Ho and ^{152m}Eu when present in sample in same proportion as "natural mixture" (Y:Ho:Eu = 0.31 : 0.012 : 0.010) From ^{166}Ho Per Cent.	From ^{152m}Eu Per Cent.
690	0	142	5.5	19.5
	60	71	2.3	0.5
	80	56	1.8	0.1
	90	50	1.6	<0.1
	120	35	1.0	<0.1
720	0	112	4.3	16.7
	60	56	1.9	0.4
	80	44	1.5	0.1
	90	40	1.3	<0.1
	120	28	0.8	<0.1
750	0	88	3.2	13.7
	60	44	1.4	0.4
	80	35	1.0	0.1
	90	31	0.9	<0.1
	120	22	0.6	<0.1
780	0	67	2.3	8.6
	60	34	1.0	0.2
	80	27	0.8	<0.1
	90	24	0.6	<0.1
	120	17	0.4	<0.1
800	0	58	1.8	6.7
	60	29	0.8	0.2
	80	23	0.6	<0.1
	90	20	0.5	<0.1
	120	15	0.3	<0.1
875	0	29	0.0	0.0

2.524 Choice of optimum absorber thickness - counting time

At an absorber thickness of 875 mg/cm^2 all beta rays from ^{166}Ho and ^{152m}Eu are completely cut off. However, using this thickness would greatly reduce the sensitivity of yttrium measurement (e.g. at 80 hours 1 μg Y_2O_3 would give only 12 c.p.m.). A thickness of 750 mg/cm^2 and a counting time of about 80 hours after removal from the pile, were chosen as the optimum conditions for yttrium measurements. An absorber thickness of 1100 mg/cm^2 was chosen for measuring the gamma-ray (and Bremsstrahlung) background count which was then subtracted from the count at thickness 750 mg/cm^2. Counting under these conditions, the limiting sensitivity (for a count of 100/min.) of yttrium determination was 3 μg Y_2O_3.

2.525 Absorber and decay curves of ^{90}Y separated from samples.

Figure XVIII shows the decay curve obtained, by measurements through these thicknesses, for the yttrium fraction separated from a sample of Tanteuxenite (which showed a high gamma-ray background), and its comparison with the yttrium standard. A gamma-ray

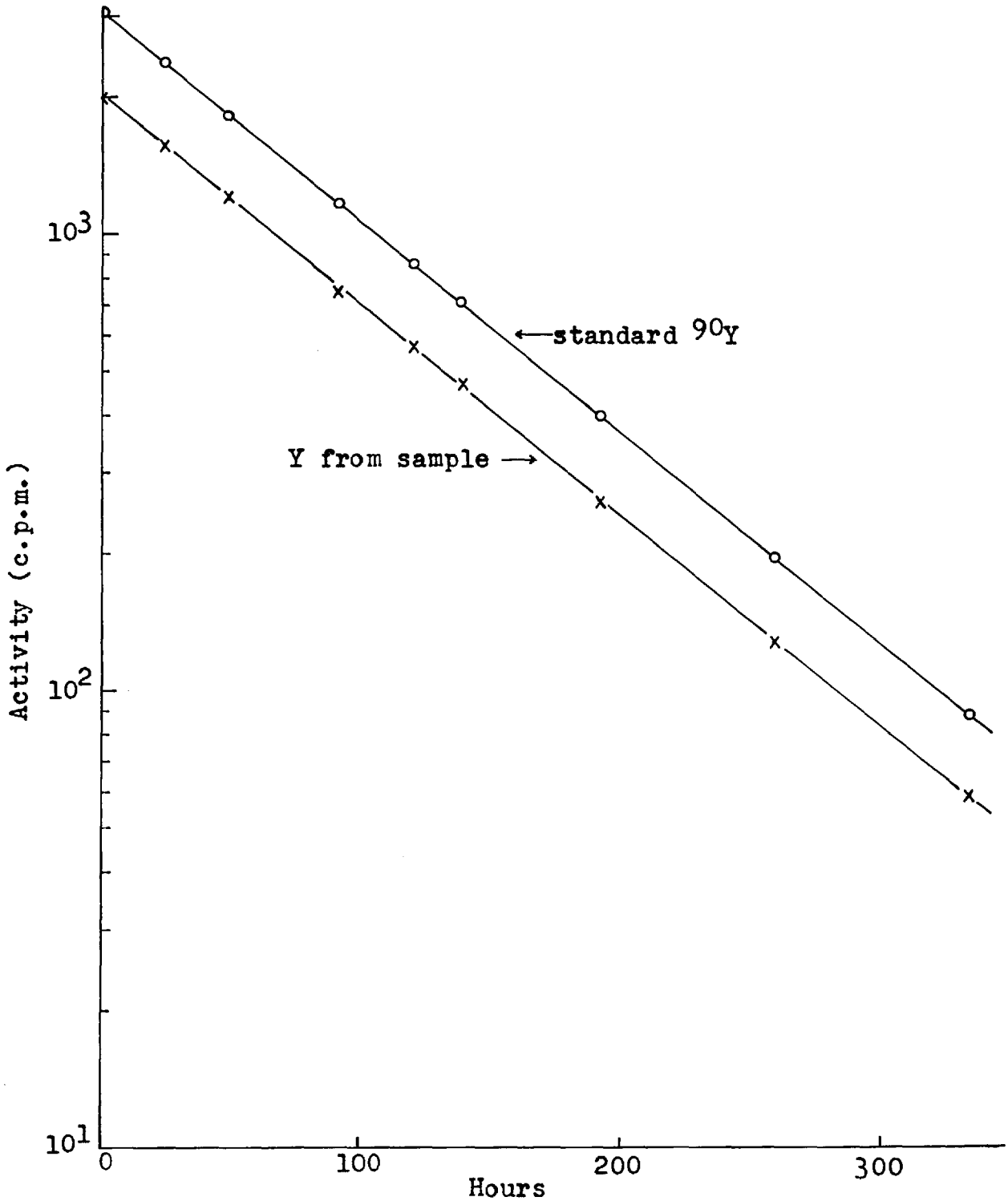


Fig. XVIII Decay of Yttrium Separated from Tanteuxenite

spectrum of the yttrium fraction was also taken as a check on radiochemical purity. A typical gamma-ray spectrum obtained is shown in Figure XIB.

Figure XIX shows the absorption curve for the yttrium fraction separated from Davidite. After subtraction of the gamma-ray background, the lower part of the curve is seen to be almost identical with that of pure yttrium (cf. Fig. XIII). By reference to these two curves, values for the Y_2O_3 content of Davidite at different absorber thicknesses were calculated and are shown in Table XIV.

Table XIV

Calculated Yttrium Content of Davidite as a function of Absorber Thickness

Absorber Thickness mg/cm^2	% Y_2O_3
800	2.50
750	2.56
700	2.54
650	2.57
600	2.58
550	2.60

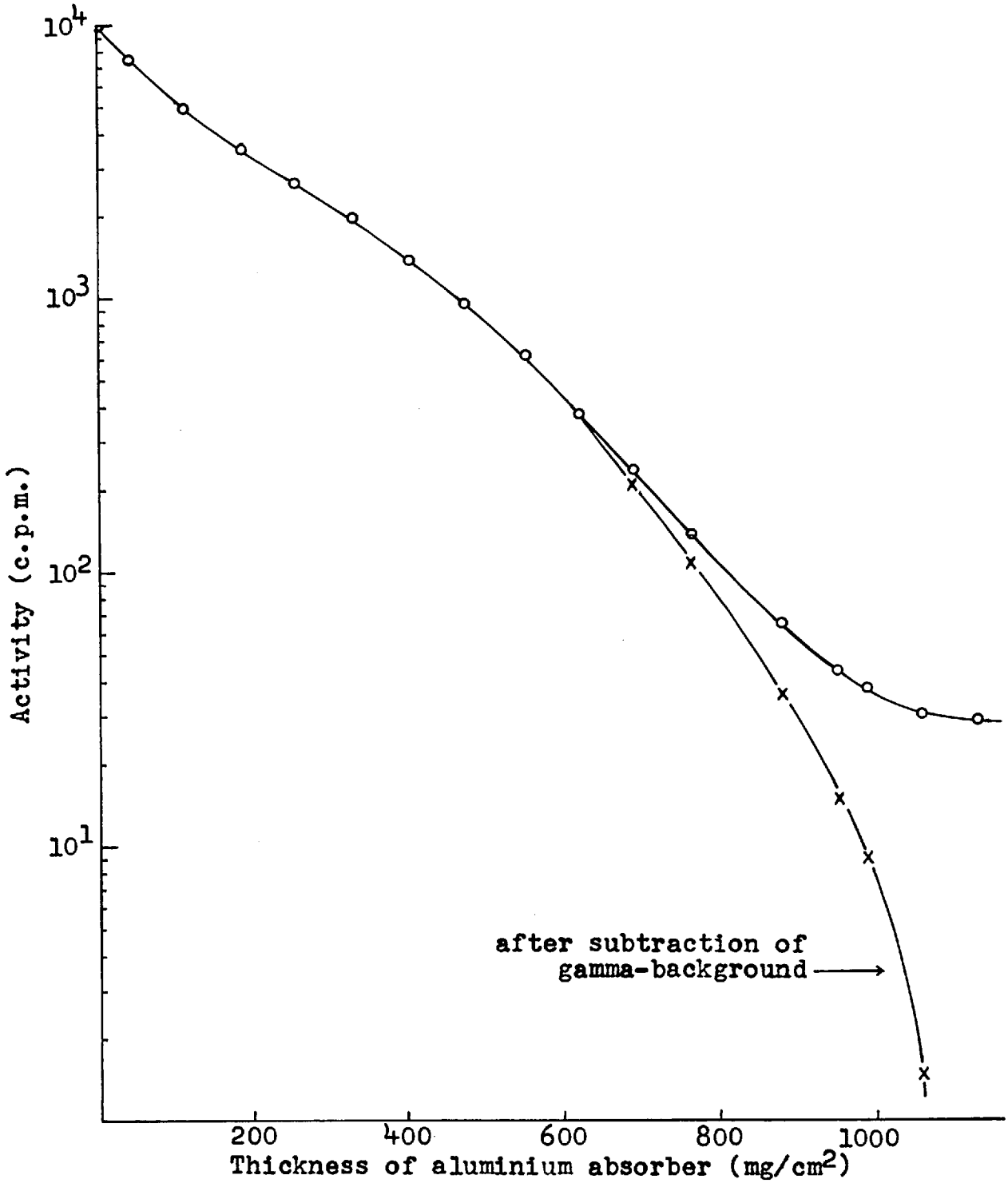


Fig. XIX Absorption Curve of Yttrium Fraction from Davidite

It can be seen that for this particular sample a much lower thickness than 750 mg/cm^2 can be tolerated. Thinner absorber would greatly improve the sensitivity of yttrium measurement, e.g. to about 0.7 μg Y_2O_3 at 550 mg/cm^2. However, this is not recommended unless it is known that the amount of holmium present in the sample being analysed is low.

2.6 DETERMINATION OF CHEMICAL YIELD.

Since the recovery of lanthanum and yttrium oxalate fractions was made deliberately non-quantitative in order to achieve greater radiochemical purity, it was essential to determine their chemical yields for quantitative measurements. Three different methods of doing this were investigated and were as follows:-

2.61 Dry Hydrated Oxalates - Gravimetric

This method was investigated only for yttrium oxalate. Lanthanum was liquid-counted and, therefore, it would have been inconvenient and an unnecessarily lengthy additional step to dry and weigh the lanthanum oxalate before getting it into solution for counting. Moreover, it has been shown by Wylie[103] that only when lanthanum oxalate is precipitated under

carefully controlled conditions is constancy in weight attained after drying. He also reported that yttrium oxalate, in all its hydrated forms, gives a residue having a constant molar ratio of water (2.1 - 2.2) when dried at 180°C. However, in the present work, when yttrium oxalate was weighed after drying to constancy in a platinum crucible at 180°C and again after ignition to yttrium oxide, the ratio of the two was constant, but the molar ratio of water was found to be 4.3. This was exactly twice that reported by Wylie. This mode of yield determination was used for some of the investigations into the radio-chemical separations of yttrium, but was later abandoned in favour of the simpler method of titration with permanganate.

2.62 Ignited Oxides - Gravimetric

Gravimetric weighing of the oxides was tried for lanthanum only. Hydroxides were precipitated from the sample solution after gamma-counting, ignited to the oxides, and weighed on the micro-balance. This was undoubtedly the most accurate method of determining the yield; but was rather time-consuming and, therefore, seldom employed.

This method was not attempted for yttrium as

it was solid-counted in aluminium trays which could not be ignited. If, however, platinum counting trays were available, it would have been very simple and accurate to ignite and weigh them either before or after counting.

2.63 Oxalate - Permanganate Titration

Titration with potassium permanganate was found to be most convenient and rapid for determining the chemical yields of both lanthanum and yttrium, and was, therefore, generally adopted. Lanthanum was titrated before, and yttrium after, radiometric counting. The ratio of oxalate to the rare earth oxide in the precipitate was investigated by means of tracers as well as by ignition and titration of different aliquots of a uniform, dry precipitate. It was found that although the stoichiometric ratio of two rare earth atoms to three oxalate radicals was valid for the normal oxalate precipitates, this was not true for the oxalate precipitates obtained in presence of EDTA under the conditions used for the radiochemical separations. The oxalate as determined by titration, was found to be between 17 and 18 per cent. higher than the theoretical value. This confirmed the observations of Gordon and Shaver[12] that rare earth oxalates precipitated in the presence of EDTA have a certain amount of EDTA co-precipitated in the rare

earth oxalate (which is also oxidised by the permanganate). However, the compounds formed under the conditions of precipitation were found to have a reasonably constant titre. It was, therefore, possible to use the titration method for the determination of the yield, provided that the permanganate was standardised against known amounts of lanthanum or yttrium which had been precipitated as oxalates in the presence of EDTA.

Table XV shows the chemical yields obtained by permanganate titration as compared to values obtained by tracer counting or ignition to oxides. The maximum variation found was within $\pm$ 3 per cent. and the standard deviation for the 5 determinations made was 1.7 per cent.

2.64 Choice of Method

In the absence of platinum counting trays, the gravimetric-oxides method could not be used for the determination of yttrium yields. The titration method could be conveniently used for the determination of the chemical yield of both the lanthanum and yttrium fractions isolated from samples. The error involved in the method was higher than that estimated for any other step of the procedure. However, it was well within the overall accuracy required ($\pm$ 10%). The titration method

Table XV

Accuracy of Titration Method

Y_2O_3 found by Titration mg	Y_2O_3 found by Tracer mg	Y_2O_3 found by Ignition to Oxide mg	Difference %
4.10	4.10	-	0
3.86	3.96	-	- 2.6
3.52	3.42	-	+ 2.8
3.39	-	3.37	+ 0.6
3.73	-	3.72	+ 0.3

was, therefore, generally adopted because of its simplicity and speed.

2.65 Effect of Co-precipitation of Nd with Yttrium

In the course of the fractionation investigations with yttrium tracer (see Section 2.425), it was observed that the chemical yield of the yttrium fraction was appreciably higher than the yttrium found by tracer. This was considered to be due to incomplete precipitation of neodymium used for scavenging, which was then precipitated along with the yttrium oxalate. Fractionation

studies using neodymium tracer confirmed this. The results are shown in Table XVI.

Table XVI

Co-precipitation of Neodymium with Yttrium

Conditions used for precipitation of Nd	Nd left in solution and precipitated with Y %
1) Cu added 5% in excess of that equivalent with Nd, and solution left for 1 hour.	6.0 ± 0.3
2) Cu added 15% in excess of that equivalent with Nd, and solution left for 1 hour.	3.7 ± 0.1
3) Cu added 5% in excess of that equivalent with Nd and solution left overnight.	4.1 ± 0.3

As the conditions of neodymium precipitation outlined in Expt. 3 of the Table were selected for the second neodymium scavenging operation, about 4 per cent. of the neodymium added accompanied the yttrium fraction isolated from samples. Calculations show that this

caused the permanganate titre for the yttrium oxalate precipitate to be higher by 5 ± 0.4 per cent. The chemical yield figures of yttrium were, therefore corrected accordingly.

2.7 RECOMMENDED PROCEDURE

2.71 Health Precautions and Handling

All radioactive materials were handled in a Grade 'C' type[104] radiochemical laboratory. The health precautions taken during the work and for the disposal of wastes were as outlined by Hsia.[87c] On receipt, all samples were first monitored by means of a beta-gamma radiation monitor. The maximum activity shown by any one sample analysed was about 100 m.rad/hr., which was equivalent to 40 tolerances. Only one sample showing such activity was handled per fortnight. The initial processing of a sample took only about an hour's time. This did not constitute any health hazard as shown by the absence of blackening of the film-badge worn during the work. All operations were carried out behind lead bricks in an almost closed, well-ventilated fume-cupboard. Special care was taken during the ampoule-ignition and fusion operations. The ignition was

carefully carried out in a slightly uncovered crucible and the fusion in a completely covered one to prevent spills. Once the sample was in solution and the rare earth group had been separated, the amount of activity was small and could be handled without lead-shielding.

2.72 Preparation and Standardisation of Reagents

A) Lanthanum and Yttrium Carrier Solutions: Dissolve separately 500 mg each of pure ignited lanthanum oxide and yttrium oxide in dilute hydrochloric acid and make up to 500 ml in separate volumetric flasks.

B) Neodymium Carrier Solution: Dissolve 260 mg pure ignited neodymium oxide in dilute hydrochloric acid. Dilute to about 75 ml and adjust pH to about 5 by addition of 2 N ammonium acetate solution and using universal pH indicator paper. Make up to 100 ml in a volumetric flask.

C) Iron Carrier Solution: Dissolve pure ferric chloride in acidulated water to give a solution containing approximately 10 mg Fe_2O_3 per ml.

D) Standard Copper Solution: Dissolve 784 mg electrolytic copper in dilute nitric acid. Dilute to about 750 ml and adjust pH to about 5 by addition of 2N ammonium acetate and using universal pH indicator

paper. Make up to one litre in a volumetric flask, 1 ml of this solution is equivalent to 2.0 mg La_2O_3 or 2.08 mg Nd_2O_3.

E) (i) EDTA Stock Solution: Prepare a 5 per cent. solution in water of the disodium salt of EDTA. Standardise by complexometric titration against the standard copper solution, using 1-(2-pyridyl-azo)-2-naphthol, ("PAN"), as indicator.[87d]

(ii) EDTA Solution A: Dilute a quantity of the standardised EDTA stock solution to a concentration of 5.75 mg/ml. 2 ml of this solution are equivalent to 5.0 mg La_2O_3 or 5.2 mg Nd_2O_3.

(iii) EDTA Solution B: Prepare a solution having a concentration of 14.0 mg/ml by similarly diluting the stock solution. 2 ml of this solution are equivalent to 5.0 mg La_2O_3 + 5.0 mg Y_2O_3.

F) (i) Potassium Permanganate Stock Solution: Prepare an approximately 0.1 N solution.

(ii) 0.01 N Permanganate: Dilute stock solution whenever required.

Standardise as follows:

For Lanthanum: Add lanthanum tracer solution to a solution containing 5.0 mg La_2O_3. Precipitate lanthanum oxalate in presence of EDTA as described in

Step (10) of Procedure (see p. 123). After washing precipitate free of ammonium oxalate, dissolve in dilute sulphuric acid and titrate with the 0.01 N permanganate solution. Compare the count with that from a separate aliquot of tracer solution. From the permanganate titre and the percentage yield obtained by the tracer counting calculate strength of permanganate in terms of equivalent La_2O_3 per ml.

For Yttrium: In the same manner standardise the permanganate for yttrium, using a liquid-Geiger-Müller counter for the tracer activity measurement.

G) Oxalic Acid: Saturated solution

H) Ammonium Oxalate: Saturated solution.

I) Boric Acid: Saturated solution

J) Bromo-cresol Green Indicator: 0.1 per cent. solution.

K) Ammonium Chloride Wash Solution: Slightly ammoniacal 2 per cent solution.

L) Oxalic Acid Wash Solution: Solution containing 1 per cent each of oxalic acid and conc. hydrochloric acid.

M) Hydrofluoric Acid: (i) 20 M, (ii) 5 M.

N) Hydrochloric Acid:

(i) 1 part conc. acid + 3 parts water

(ii) 1 part conc. acid + 4 parts water

(iii) 2 N acid.

(O) Nitric Acid: 2 N

(P) Sulphuric Acid, dilute: 1 part conc. acid + 14 parts water.

(Q) Ammonia: 1 part liquor ammonia (sp. gr. 0.88) + 1 part water.

(R) "Teepol" Solution: 1 per cent. solution in water.

2.73 Stepwise Procedure for Mineral Analysis

1) Dilute a quantity of the mineral sample to be analysed by dry-grinding in an agate mortar with nine times its weight of 'Analar' grade magnesium oxide. For silicates and similar samples which have a very low rare earth content, and a large proportion of the low neutron-absorbing silica, this step can be omitted.

2) Weigh out a quantity of the diluted sample to contain at least 0.1 μg La_2O_3 and 10 μg Y_2O_3. Seal in small polythene ampoules ($\sim$ 15 x 3 mm). Also weigh out in duplicate, small quantities of 'Specpure' La_2O_3 (1 mg) and Y_2O_3 (2.5 mg) as standards and seal in large polythene ampoules ($\sim$ 60 x 5 mm). Place the ampoules in an aluminium irradiation can and irradiate

in a uniform, thermal neutron flux of about 10^{12} neutrons /sq.cm/sec. for about 60 hours.

3) Cut open the ampoules containing the standards and wash out into beakers by means of hot dilute hydrochloric acid (1 + 3). Heat the solutions to dissolve the oxides completely, cool and make up in standard flasks.

4) Slit open the ampoule containing the mineral sample (to prevent expansion and sudden bursting during heating) and carefully ignite in a 15-ml nickel crucible over a micro-burner. Fuse residue with about 1 gm sodium peroxide, heat to dull redness and maintain for about 10 mins. After allowing the crucible to cool, dissolve contents in dilute hydrochloric acid (1 + 4) containing 5.0 mg each of La_2O_3 and Y_2O_3 and about 10 mg Fe_2O_3. The lanthanum and yttrium are the inactive carriers for monitoring the chemical yields and (along with the iron) act as effective carriers for the subsequent precipitations.

5) Transfer the solution to a 40-ml centrifuge tube and precipitate the hydroxide group by addition of ammonium chloride and excess ammonia. Centrifuge, and after separating and discarding supernate, wash precipitate twice with ammonium chloride wash solution.

6) Dissolve precipitate in about 5 ml of 2 N nitric acid, stir in a little filter paper pulp, and centrifuge. Add supernatant solution drop by drop to a 40-ml "Lusteroid" tube containing 2 ml of conc. hydrofluoric acid (40%). Wash the paper pulp in the first tube with about 3 ml of 2 N nitric acid and add washings to the "Lusteroid" tube. The final concentration of hydrofluoric acid should be about 4 M for the precipitation of the rare earth fluorides. After leaving aside for about 15 mins., centrifuge, discard supernate, and wash precipitate twice with 5 M hydrofluoric acid.

7) Dissolve precipitate in a few ml of a mixture of equal quantities of saturated boric acid and 2 N nitric acid. Transfer the solution to a 40 ml glass centrifuge tube, dilute with water and precipitate the hydroxides of the rare earths by addition of ammonia. Centrifuge, discard supernate, and wash precipitate twice with ammonium chloride wash solution.

8) Dissolve precipitate in 1 ml of 2N hydrochloric acid and dilute to 5 ml with water. Precipitate the oxalates of the rare earths by addition of 5 ml of saturated oxalic acid solution. Allow to stand for 20 to 30 minutes, and centrifuge. Discard

supernate, and wash the precipitate twice with oxalic acid wash solution.

9) To the precipitate add EDTA in equimolar ratio with the total lanthanum and yttrium present (2 ml of EDTA solution B), and make alkaline by addition of ammonia. Dissolve the precipitate by stirring (and, if necessary, warming), add a small quantity of glacial acetic acid to act as buffer, and adjust the pH to 5, using bromo-cresol green as indicator. Dilute solution to 10 ml, heat in water-bath at 90°C, and add about 1 ml of saturated ammonium oxalate solution. To the solution maintained at the temperature of the water-bath, now add dropwise and with continuous stirring, an amount of the standard copper solution equivalent to 80 per cent. of the lanthanum carrier. Leave for a further 5 minutes with occasional stirring and remove from water-bath. Centrifuge, and transfer supernate to a second 40 ml centrifuge tube before the temperature falls below about 60°C. Wash the precipitate with small quantities of water till it is free of excess ammonium oxalate (4 washings are adequate).

10) In a separate tube take a suitable aliquot of the irradiated lanthanum standard solution (Step 3). Add 5.0 mg. of inactive La_2O_3 carrier and an equivalent

amount of EDTA. Adjust pH of solution to 5, and precipitate lanthanum oxalate as in Step 9, but adding the full amount of copper. Allow to cool thoroughly before centrifuging and washing the precipitate free of excess oxalate.

11) Dissolve the lanthanum oxalate precipitates of sample and standard (from Steps 9 and 10) in small quantities of dilute sulphuric acid (1 + 14), warm to about 75°C in a water-bath and titrate with the standardised 0.01 N permanganate solution to obtain the chemical yields. Mount the solutions (or suitable aliquots) in polythene bottles and count over the 1.62 Mev ^{140}La photo-peak on a gamma scintillation spectrometer. For better comparison, and in order to minimise errors due to instability of spectrometer, count the standard both before and after the sample. A complete gamma-ray scan and decay measurements made over the lanthanum photo-peak, will, if necessary, prove the purity of the activity counted.

12) To the supernate from the lanthanum precipitate of Step 9, add a solution of EDTA equivalent to 5.2 mg of Nd_2O_3 (2 ml of EDTA solution A), warm in a water bath at about 90°C to dissolve any precipitate which may have separated, and add 2 ml of

neodymium carrier solution (5.2 mg Nd_2O_3). To the hot solution maintained in the water-bath now add the standard copper solution equivalent to all the neodymium carrier plus 20 per cent. of the lanthanum carrier originally present (deficiency of copper used for lanthanum precipitation in Step 9). The copper solution should be added as in Step 9, viz., drop by drop and with continuous stirring to minimise co-precipitation of yttrium. Cool the solution to room temperature with occasional stirring and allow to stand for one hour. Centrifuge, transfer to a clean tube, and discard precipitate.

13) Repeat Step 12, i.e., add EDTA and neodymium to the supernate, and precipitate neodymium oxalate by addition of copper equivalent to the neodymium plus 5 per cent. in excess. Cool and allow to stand overnight. Centrifuge, discard precipitate, and transfer supernate to a clean tube.

14) Warm the tube containing the supernate in the water-bath at 90°C and add a quantity of the standard copper solution equivalent with 75 per cent. of the yttrium carrier. Cool to room temperature with occasional stirring and leave for about half an hour. Centrifuge and discard supernate. Wash precipitate

with small quantities of water to free it from excess ammonium oxalate.

15) In a separate tube take a suitable aliquot of the irradiated yttrium standard solution (Step 3). Add 5.0 mg of inactive yttrium oxide carrier and an equivalent amount of EDTA. Adjust pH of solution to about 5 (with indicator paper), and precipitate yttrium oxalate as in Step 4, but using an amount of copper equivalent to the total yttrium present. Cool, and leave for about an hour. Centrifuge, discard supernate and wash precipitate with small quantities of water till it is free from ammonium oxalate.

16) Mount the yttrium oxalate precipitates of sample and standard (Steps 14 and 15) in separate aluminium trays. Count in the solid Geiger-Müller counter about 80 hours after "zero time" (time when irradiation was completed) through aluminium absorbers of thickness 750 mg/cm^2. Determine the gamma-ray background by counting through an absorber thickness of 1100 mg/cm^2 and subtract it from the count at 750 mg/cm^2.

17) Dissolve the yttrium precipitates from the aluminium trays in few mls of dilute sulphuric acid (1 + 14). Remove and rinse the trays with water.

Warm the solutions to about 75°C and titrate against the standardised 0.01 N permanganate solution to determine the chemical yields.

2.74 Modifications for Lanthanum-rich Minerals

2.741 In determination of lanthanum

When analysing minerals which are very rich in lanthanum as compared to yttrium (e.g. monazite), the determination of both elements on the same sample would entail an error in the chemical yield determination of the lanthanum fraction. Since the poor sensitivity of yttrium determination necessitates the use of a large sample for such minerals, lanthanum from the sample itself makes a significant addition to the total lanthanum carrier present. It is advisable, therefore, to start with a separate, smaller sample for the determination of lanthanum alone.

If, however, both elements must be determined on the same sample, a correction can be applied to the lanthanum chemical yield in the following way: From the first value for the lanthanum content of the sample, an approximate value for the total La_2O_3 present to begin with (La_2O_3 carrier + La_2O_3 from sample) can be

calculated. The true value for La_2O_3 in the sample can then be calculated by a method of successive approximations. Cerium, too, would cause a positive error in the chemical yield figure. The actual amount of cerium accompanying lanthanum can be readily determined by counting the 33 day ^{141}Ce activity over its 0.145 Mev photo-peak after the lapse of two weeks when all lanthanum and praseodymium activity has decayed. For a comparison standard a small quantity of 'Specpure' CeO_2 that has been irradiated along with the other samples would be used.

The lanthanum result for monazite oxides (av. 20.1%) reported in Table VIII has been obtained on small samples (0.05 mg). The lanthanum fraction from a larger (3 mg) sample taken for the determination of yttrium was found to contain about 0.7 mg CeO_2. The values for La_2O_3 content of the large sample after correction for CeO_2 content, and after successive approximations for the chemical yield are shown in Table XVII. The final value (19.7%) is in good agreement with the reported average value of 20.1 per cent.

Table XVII

Effect of Correcting Chemical Yield of Lanthanum by Successive Approximations in Analysis of Monazite

Stage of Successive Approximation	Calculated Chemical Yield %	Corresponding La_2O_3 value for Sample %
Uncorrected	92.5	15.0
Corrected for Cerium Co-precipitated	79.1	17.5
Corrected for Lanthanum from Sample 1st Approximation	71.5	19.4
Corrected for Lanthanum from Sample 2nd Approximation	70.7	19.6
Corrected for Lanthanum from Sample, 3rd Approximation	70.5	19.7

2.742 In determination of yttrium

As shown in Section 2.425, 0.1% of praseodymium originally present accompanies the yttrium fraction. In a mineral like monazite where the ratio of praseodymium oxide to yttrium oxide is of the order of 5:2, this would cause a positive error of about 3 per cent. in the yttrium count taken at the recommended time. This can be reduced to less than 0.5% by introducing a third neodymium scavenging step before precipitation of yttrium. But this would further reduce the yield of yttrium. An alternative modification to the general procedure is, therefore, recommended, which was found to reduce the error from praseodymium to about +1 per cent., and which is as follows:

After separation of the lanthanum fraction as described in Step 9 of the procedure, the supernate is warmed on the water-bath, and the balance of copper (equivalent to 20 per cent. of the original lanthanum carrier) is added. The solution is cooled to room temperature, left for an hour and centrifuged. The neodymium scavenging operations of Steps 12 and 13 then follow, but with copper equivalent only to the neodymium being added in Step 12. The praseodymium left in solution with the yttrium is thus reduced to less than 0.05%

of that originally present, without affecting the yield of the yttrium fraction. The yttrium content of monazite oxides reported in Table XVIII was obtained in this way.

2.75 Determination of Lanthanum without Fractionation

Minerals or rock samples which are low in yttrium (< 60 ppm) would be beyond the scope of this method unless remote handling equipment and a laboratory fitted for processing high activities are available for handling large samples. In such instances it may be useful to have a knowledge of only the lanthanum content of the mineral, which can be determined on a much smaller sample.

The only elements of the rare earth group that can interfere in the gamma-counting of lanthanum (when no separations are made) over its 1.62 Mev photo-peak are praseodymium and holmium (see Sections 2.513 and 2.514). The contributions from these two elements to the lanthanum count if they were present in the same proportion as in a "natural mixture" (see Table II) would be only about 0.2% for holmium and one per cent for praseodymium (see Section 2.514).

The errors involved in counting lanthanum

without separating it from the rest of the rare-earth group are thus small for samples low in yttrium. It is, therefore, possible to shorten the method for the determination of lanthanum alone by eliminating the EDTA-oxalate fractionations. The oxalates of the total rare earths obtained in Step 8 of the procedure are washed free of oxalic acid, titrated against standard permanganate and counted. The rock samples "G-1" and "W-1" shown in Table XVIII were analysed by the shortened method.

2.8 RESULTS OF MINERAL ANALYSIS

2.81 Table of Results

The results of analysis of a variety of mineral samples by the recommended methods, and their comparison with results obtained by spectroscopic analysis are shown in Table XVIII.

2.82 Estimate of Precision

The precision of the method for the determination of lanthanum and yttrium was assessed from replicate results of analyses of some of the mineral samples. The results and the calculated coefficients of variations are shown in Tables XIX and XX. It can be seen

Table XVIII

Results of Analysis of Mineral Samples

Mineral	By Activation			By Spectroscopy†		
	La_2O_3 %	Y_2O_3 %	Ratio La_2O_3/Y_2O_3	La_2O_3 %	Y_2O_3 %	Ratio La_2O_3/Y_2O_3
Gadolinite	0.34	25.2	0.013	0.4	33	0.012
Tanteuxenite	0.06	11.1	0.0054	0.08	14	0.0057
Yttrotantalite	0.014	16.3	0.0009	<0.04	21	-
Yttrotungstite	0.49	8.0	0.061	0.24	8.7	0.028
* Samarskite	0.027	10.7	0.025	<0.02	13	-
* Lyndochite Oxides	1.4	13.6	0.103	-	-	-
* Monazite Oxides	20.1	1.9	10.6	23.2	2.1Ⓧ	11.0
* Davidite	3.0	2.7	1.11	3.7	2.5Ⓧ	1.48
* Granite	126 ppm	750 ppm	0.168	175 ppm	850 ppm	0.206
** Granite G-1	113 "	-	-	-	-	-
** Diabase W-1	13 "	-	-	-	-	-

* Replicate results are shown in Tables XIX and XX

**Analysed by shortened method for La determination

† By courtesy of Dr. J. R. Butler

Ⓧ By Fluorescent X-ray Spectroscopy

that the precision of the method is of the order of ± 5 per cent. for the determination of lanthanum and yttrium in the samples analysed.

Table XIX

Replicate Results of Analysis for Lanthanum

Sample	Monazite Oxides	Davidite	Lyndochite Oxides	Samarskite	Granite
% La_2O_3	19.7	2.80	1.39	0.028	125 ppm
	20.6	3.07	1.45	0.026	127 "
	20.4	2.96	1.44	0.026	
	19.9	2.91	1.32		
	19.6	2.93	1.44		
	20.2	3.08	1.44		
	20.0		1.37		
	20.9		1.41		
	20.2				
	19.7				
Average Value	20.1	2.96	1.41	0.027	126
Standard Deviation	±0.4	±0.10	±0.045	±0.001	±1
Coefficient of Variation	±2.0%	±3.4%	±3.2%	±3.8%	±0.8%

Table XX

Replicate Results of Analysis for Yttrium

Sample	Lyndochite Oxides	Davidite	Tanteuxenite
% Y_2O_3	14.04	2.56	11.46
	13.33	2.66	10.99
	13.45	2.60	10.90
	13.42	2.87	
Average Value	13.56	2.67	11.12
Standard Deviation	$\pm$ 0.28	$\pm$0.12	$\pm$ 0.24
Coefficient of Variation	$\pm$ 2.1%	$\pm$4.5%	$\pm$ 2.2%

3. DISCUSSION

3.1 ESTIMATE OF OVERALL ACCURACY AND PRECISION

From the results of mineral analysis it has been estimated that the overall precision of the method is of the order of $\pm$ 5 per cent. The individual steps of the procedure were investigated from the view-point of errors involved in them, and all factors that were considered liable to give appreciable errors were investigated in some detail. These were: (i) effect of self-shielding during irradiation, (ii) variation in stability of counter, (iii) interference of Pr and Ho in lanthanum measurements; and of Ho, Eu and Pr in yttrium measurements, (iv) errors in the method of yield determination and (v) effect of co-precipitation of Nd with yttrium. Of all these determinate errors the one associated with the determination of the chemical yield was found to be the largest (coeff. of variation $\pm$ 1.7 per cent.). In the case of yttrium there would be an additional error in the yield of $\pm$ 0.4% from the correction for neodymium co-precipitation. The errors involved in each of the other steps of the procedure were estimated to be of the order of $\pm$ 1% or lower. It appears, therefore, that the reproducibility of yield determination

is the limitation on the overall precision of the method. If required, the yield can be more accurately determined by the gravimetric oxides method as described in Section 2.62; but this will involve an additional step which will lengthen the procedure. Similarly, instead of applying an estimated correction for neodymium co-precipitated with the yttrium fraction, the amount of neodymium can be determined spectrophotometrically.[49, 50]

In the absence of a standard sample for comparison of results it is not possible to determine the overall accuracy of the method exactly, but an estimate can be made from a comparison with the results of analysis by spectroscopy. The spectroscopic value of yttrium in monazite oxides (Table XVIII) was obtained by fluorescent X-ray spectroscopy, which is considered to be a more accurate method for the determination of this element than optical spectroscopy.[95] The accuracy of results (by spectroscopy) for both lanthanum and yttrium in this sample is considered to be within $\pm$ 10 per cent.[95] If this is so, the overall accuracy of the activation method appears to be within about $\pm$ 10 per cent. also, and the other values recorded in Table XVIII, except those which are near the limits of determination by the spectroscopic methods, tend to confirm

this estimate.

It does appear that the values by activation tend to be lower than those obtained by spectroscopy. If the spectroscopic results are accepted, they would rule out the possibility of incomplete radiochemical purification in the activation method, as the results would then be higher. Three possibilities that would tend to give lower results by the activation method are: (i) loss of sample, e.g. during transfer from ampoules, before the addition of inactive carriers, (ii) self-shielding effects during irradiation, and (iii) positive errors in the determination of chemical yield. All these points have been investigated. Ignition of the sample ampoule avoids transferring of sample to the crucible. There is very little possibility, therefore, of a serious error from loss of sample. There was no evidence of self-shielding for the samples which were investigated from this aspect (Table III). A systematic positive error in the determination of chemical yield was possible only in the case of yttrium, and the suggested correction compensates it. None of the above factors, therefore, appear to give a systematic bias (of greater than 1 per cent.) to the results of analysis by activation.

The two reference silicates G-1 and W-1 have been analysed by activation and found to contain 96 and 11 p.p.m. of La respectively (single determinations). It is of interest to compare these values with the results that have been reported so far on these samples. In their report on the trace constituents of these samples, Ahrens and Fleischer[105] have reported 13 determinations on G-1 by spectroscopic methods by various laboratories. The results show a spread of values from 60 to 430 p.p.m., and these authors recommend an average value of 150 p.p.m., "but with reservation because of the considerable spread of values". For the lanthanum content of W-1 they state that the average of 30 p.p.m. of 3 determinations may serve as a magnitude only. The fourth value reported by them (and which was probably considered unreliable) for this sample was < 5 p.p.m. Hamaguchi *et al.*[106] have reported results of lanthanum determination by neutron activation of G-1 and W-1 as 122 and 27 p.p.m. respectively, but no details of the method or estimates of accuracy are given. The value for W-1 is a single determination and that for G-1 an average of 3 determinations with a spread of values from 95 to 150 p.p.m.

3.2 LIMITS OF SENSITIVITY

The limits of sensitivity of the measurements (for a count of 100 per min.) are 0.04 μg La_2O_3 and 3 μg of Y_2O_3, for an irradiation time of 60 hours in a flux of 10^{12} neutrons/sq.cm./sec. These are for the counting conditions described in Sections 2.514 and 2.524 and the counting time of 40 hours. after irradiation for lanthanum, and 80 hrs. for yttrium. Using 100 mg samples and with yields of about 70 per cent. for lanthanum and 45 per cent. for yttrium, this would permit the determination of 0.5 p.p.m. of La_2O_3 and 60 p.p.m. of Y_2O_3.

The sensitivity is sufficient for the determination of lanthanum in practically all mineral samples; but it might be desirable to have greater sensitivity for the determination of yttrium in some samples. Improved sensitivity may be had by using a higher neutron flux, irradiating to saturation activity, and by using a larger sample. But in this case, greater health precautions would need to be taken. The sensitivity of yttrium counting can also be improved by counting through thinner absorber (see Section 2.525); but this should be done with discretion because of the likely interference from other rare earth elements such as holmium.

3.3 POSSIBLE APPLICATIONS OF THE METHOD FOR THE DETERMINATION OF OTHER RARE EARTH ELEMENTS

Tracer experiments have shown that the fractional oxalate precipitation method is capable of dividing the rare earth elements roughly into four fractions, viz. (i) lanthanum and the elements nearest to it in EDTA complex stability, e.g. Ce and Pr; (ii) the neodymium fraction which probably consists of Sm, Eu and Gd, besides Nd itself; (iii) the elements of ionic size close to that of yttrium, such as Tb, Dy and Ho, which are carried by the yttrium precipitate; and (iv) the elements from Tm to Lu, and Sc if present, which should be in the mother liquor from the yttrium precipitate. Two of these fractions only have been studied in detail during the present work. Further work might reveal ways of utilising the two discarded fractions for obtaining useful information on other rare earth elements. For example, it would appear from the nuclear properties of rare earth isotopes formed by (n, γ) reactions (Table II), that it might be possible to determine europium in the neodymium fraction and scandium from the discarded mother liquor from yttrium.

The present method was developed with the object of utilising it for the geochemical investigation

of variations in the abundance pattern of the rare earth group of elements caused by the variation in their ionic radii. A rapid method for investigating problems connected with the other aspect of selective migration of rare earth elements due to variable valency (such as variations in the Ce/Eu ratios) would also be very useful to geochemistry. By an extension of the methods described in the present work it might be possible to achieve a rapid radiochemical separation of the 9 hr. ^{152m}Eu, It might thus be possible to determine the element more rapidly and with greater sensitivity than by the method[82] based on the long lived ^{154}Eu. Similarly, a method for the determination of cerium would be useful to study the problem of selective migration of quadrivalent cerium. Although this has long been suspected,[1b] only a few minerals are known in which cerium is deficient. The almost complete absence of this element in Rhabdophane has been commented upon (p. 4). In such a mineral which is almost devoid of natural cerium but which still retains its lanthanum content, the cerium present should consist mostly of ^{138}Ce, the daughter product formed from the naturally radioactive isotope ^{138}La ($t_{\frac{1}{2}}$ 2 x 10^{11} years). It should be practicable to determine the amount of ^{138}Ce

by measuring the activity of 140 day ^{139}Ce formed after irradiation. Thus, assuming a constant abundance of $^{138}La/^{139}La$, a determination of the La/Ce ratio by neutron activation analysis could afford a method for the determination of the point in geological time at which the naturally occurring cerium was oxidised and removed from the mineral.

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Short Communication

Determination of traces of nickel in uranium

A rapid method was required for the determination of microgram amounts of nickel in uranium. Dimethylglyoxime in ammoniacal solution has long been used for the determination of small amounts of nickel[1,2] but none of the reported methods[2-4] is satisfactory for the direct determination of nickel in uranium. The method proposed here uses an elevated pH (11.5 ± 0.5)[5,6] in order to obtain a stable colour. This high pH could be attained without precipitation of uranium, thorium, iron, etc., by using ammonium carbonate and ammonium citrate as the complexing agent. The limit of determination is 5 μg nickel per gram of U_3O_8; this can be extended to 1 p.p.m. by using a 5-cm absorption cell.

PROCEDURE

Two 1-g samples were weighed into 100-ml beakers, dissolved in nitric acid and the solutions evaporated to dryness. The residue was taken up with 1 ml of 1:1 sulphuric acid and diluted to 20 ml with water. 2 ml of saturated bromine water were added and the solution set aside for 5 min, after which ammonia (1:1) was added dropwise to destroy the excess of bromine and to form a permanent precipitate of ammonium diuranate. 10 ml of 25% (w/v) ammonium carbonate solution and 2 ml of 25% (w/v) ammonium citrate solution were then added and the solution cooled to about 20°. 8 ml of 25% (w/v) sodium hydroxide solution were added dropwise with stirring and the pH adjusted to 11.5 ± 0.5 by addition of a few drops of sodium hydroxide solution. 2 ml of dimethylglyoxime reagent (1% in alcohol) were added to one of the beakers, the other solution serving as the reference blank. The solutions were made up to 50 ml in volumetric flasks and set aside for 30 min for full colour development. After this time, the colour was stable for at least 24 h. The absorbancy of the solution was measured on a spectrophotometer at 530 mμ and the nickel concentration determined by reference to a standard curve prepared by taking between 5 and 100 μg of nickel in the presence of 1 g of U_3O_8 and following the same procedure. 50 μg Ni in a 1-cm cell at 530 mμ showed an optical density of 0.15.

TABLE I

Interfering metal	*Amount added* μg	*Ni added* μg	*Ni found* μg
Copper(II)	50	10.0	10.0
	100	10.0	10.0
	50	30.0	30.0
	100	30.0	29.5
Cobalt(II)	50	10.0	10.0
	100	10.0	11.5
	50	30.0	30.0
	100	30.0	31.5
Chromium(III)	50	10.0	10.0
	100	10.0	11.5
	50	30.0	30.0
	100	30.0	31.0

Copper(II), cobalt(II), and chromium(III) are the only interfering metals but their colours with dimethylglyoxime are much weaker than the nickel colour[1]; the

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effects of these elements are shown in Table 1. No interference occurs if the amounts in the sample aliquot are 50 μg or less; the interference is slight if the amount of the interfering metal is 100 μg.

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THE SEPARATION OF BERYLLIUM FROM IRON, ALUMINIUM AND TITANIUM BY ION EXCHANGE, AND ITS APPLICATION TO THE ANALYSIS OF BERYL

by

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Ion exchange methods have been applied for the isolation and estimation of beryllium from biological samples[1] and alloys[2] but not for estimation of beryllium in minerals and ores.

The beryllium complex of ethylene diamine tetraacetic acid (EDTA) at a pH of about 4, is much weaker than the corresponding complexes of iron and aluminium. It was, therefore, considered possible to effect a complete separation of beryllium from iron and aluminium on a cation exchange resin, making use of this difference in stabilities of the EDTA complexes, especially where beryllium has to be separated from large amounts of aluminium as in the analysis of beryls.

EDTA has been used as a complexing agent in the analysis of beryllium minerals in the following three methods: (i) the precipitation of beryllium as beryllium ammonium phosphate, after complexing interfering elements with EDTA, and its ignition to the pyrophosphate[3]; (ii) the precipitation of beryllium as beryllium ammonium phosphate in the presence of EDTA, and its volumetric estimation[4]; (iii) the precipitation of beryllium hydroxide, using EDTA as complexing agent for the interfering elements, and its ignition to the oxide[5]. In the last method phosphate interferes because it accompanies the hydroxide precipitate. Moreover, because the titanium complex of EDTA is weak, this element is also liable to contaminate the beryllium precipitate.

In the present method interference from titanium as well as phosphate has been eliminated.

EXPERIMENTAL

Apparatus and reagents

Ion exchange column: The common type of ion exchange column was used. The main column consisted of a pyrex glass tube 1.8 cm in diameter and 20 cm long. A 125-ml separating funnel was fitted over the tube for holding the solutions.

Ion exchange resin: Amberlite IR-120, 0.4-0.6 mm, filled to a height of 12 cm in the column.

Reagents: All reagents used were of C.P. grade.

General procedure

To the solution containing beryllium, aluminium, etc., a solution of EDTA (disodium salt) was added and the required pH was adjusted. This solution was then passed through the column containing the resin in the sodium form. After passing the entire solution, the column was washed with 0.5% EDTA solution and later with distilled water. The adsorbed beryllium was then recovered by eluting with 3*N* hydrochloric acid and estimated gravimetrically after precipitation as hydroxide.

The sodium form of the resin was used because the hydrogen form disturbed the pH of the solution and had a tendency to cause precipitation of the EDTA owing to the low solubility of the acid.

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Rate of flow

The rate of flow during the sorption step was first studied and the results are shown in Table I. It is seen that with a flow rate of 10 ml/min and above, the beryllium is not quantitatively held up by the resin column. In order to have a wide margin of safety a flow rate of about 5 to 6 ml/min (approx. 2 ml sq.cm^{-1}min^{-1}) was maintained for all further experiments. The same rate was maintained for the washing and elution steps also.

TABLE I

RATE OF FLOW

Rate ml/min	*BeO taken mg*	*BeO found mg*
5	51.0	51.2
10	51.0	50.4
15	51.0	40.6

Elution with acid

In order to establish the volume of 3*N* hydrochloric acid necessary for completely eluting out the beryllium, the column was eluted with different volumes of the acid after the sorption and washing stage. After passing the acid, the column was rinsed with 100 ml of distilled water in each case. 150 ml of the acid were considered necessary for this step, although the results (Table II) indicate that all beryllium is eluted by 100 ml of the acid.

TABLE II

ELUTION

3N HCl ml	*BeO taken mg*	*BeO found mg*
50	52.5	44.4
100	52.5	52.7
150	52.5	52.6

Effect of pH

Since the stabilities of the EDTA complexes vary with pH, it was to be expected that change of pH would have considerable effect on the separation of beryllium from aluminium and iron. It is seen from the results in Table III that below a pH of 2 a considerable quantity of alumina accompanies the BeO precipitate owing to the comparative weakness of the aluminium complex at this pH. Between pH 2.5 and 4.5 the separation was quantitative. The BeO precipitate was in each case tested with oxine for its purity. A pH of about 3.5 was considered most suitable as the stabilities of the iron and aluminium complexes are highest at about this pH. Moreover beryllium starts precipitating as phosphate at a pH of about four in the event of phosphate being present.

Separation from common ions

The ion exchange separation of beryllium was undertaken with a view to adopting it for the estimation of BeO in beryl. The minerals likely to be associated with beryl are quartz, felspar, apatite and mica. In addition to cations present in these minerals it was

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TABLE III

EFFECT OF PH

pH	*BeO taken mg*	*Total R_2O_3 found mg*
1.5	64.5	98.1
2.0	52.5	58.7
2.5	64.5	64.3*
3.5	56.5	56.2*
4.5	64.4	64.5*

(Approximately 6-8 mg Fe_2O_3 and 70-80 mg Al_2O_3 were taken along with the beryllium).
*Precipitate tested with oxine and found free from Fe and Al.

considered necessary to pay special attention to small amounts of titanium which is likely to be present, particularly because it also forms a weak complex with EDTA. Results of separation of common cations in artificial mixtures are given in Table IV. Whenever titanium was added it was complexed by means of hydrogen peroxide before the sorption step. The titanium was found to pass into the effluent quantitatively as an anion. According to SAMUELSON[6], phosphoric acid is adsorbed to a certain extent by cation exchange resins, and the adsorbed acid can be quantitatively removed by using a sufficiency of water during the washing process. Whenever phosphate was added, therefore, a larger amount of water was used for washing, and this was found to eliminate phosphate quantitatively. The BeO precipitate obtained finally was tested for the respective impurities added in each case. These were found to be either completely absent or present in such minute traces as not to affect the results. Apart from the purity of the beryllium separated, Table IV shows a complete separation from Fe, Al, Ti, Ca and P_2O_5.

TABLE IV

ANALYSIS OF SYNTHETIC MIXTURES

BeO taken mg	*Al_2O_3 added mg*	*Fe_2O_3 added mg*	*TiO_2 added mg*	*CaO added mg*	*P_2O_5 added mg*	*BeO found mg*	*Difference mg*
66.3	87.5	8.0	4.1	—	—	66.9	+ 0.6
52.5	75.0	—	—	—	—	52.5	nil
10.5	75.0	—	—	—	—	10.7	+ 0.2
78.8	75.0	—	—	—	—	78.7	— 0.1
52.5	—	16.0	10.0	—	—	52.6	+ 0.1
52.5	—	16.0	—	56.0	50.0	52.7	+ 0.2
52.5	50.0	16.0	—	28.0	25.0	52.8	+ 0.3

Analysis of beryl

The following procedure was used for the analysis of beryls: 0.5 g of the ground sample was weighed into a platinum crucible and fused for about 10 min with 2 g of sodium fluoride. After cooling, 5 ml of 1 : 1 H_2SO_4 were added and the covered crucible heated slowly on the sand bath. After the evolution of fluosilicic and hydrofluoric acids had ceased, the crucible was opened and heated more strongly till the evolution of SO_3 fumes started. The crucible was then heated over a direct flame until a clear melt was obtained. After cooling the contents of the crucible were extracted in 150-200 ml of water in a 600 ml beaker, when a clear solution was obtained. To this solution were added 20 ml of a 10% solution of the disodium salt of EDTA and the volume made to approximately 400 ml. The pH was adjusted to 3.5 by means of a 10% solution of sodium hydroxide, and 1 ml of hydrogen peroxide (100 vols.) was added when the solution was ready for the ion exchange column. (In case titanium was known to be absent in the sample, the addition of peroxide was not made.)

The resin was first converted to the sodium form by passing 100 ml of a 10% solution of sodium chloride and washing with about 150 ml of distilled water. The solution to be analysed was then

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passed through the column at a rate of about 5 to 6 ml per minute. The column was next washed with 150 ml of a 0.5% EDTA solution of pH 3.5, followed by 200 ml of distilled water. (When phosphate was known to be absent only 100 ml of water was used for this step.)

The adsorbed beryllium was recovered by eluting with 150 ml of 3*N* hydrochloric acid followed by 100 ml of water, and estimated gravimetrically by igniting to BeO after double precipitation as hydroxide with ammonia with usual precautions.

Table V shows the results of analysis of a number of beryl samples analysed by the present method as compared with analyses by the standard gravimetric method[7], and the volumetric method recommended by DAS AND ATHAVALE[4]. It is seen that the results compare well. Experiment 9 in the table is with a mixture of 0.25 g of a previously analysed beryl with 0.25 g of calcium phosphate. The mixture after fusion with sodium fluoride and subsequent fuming with sulphuric acid did not give a clear solution owing to the low solubility of calcium sulphate. This was dissolved by the addition of about 5 ml conc. HCl, and the third group elements precipitated by ammonia. The precipitate was redissolved in dil. HCl containing 5 ml of the concentrated acid, and the solution used for the analysis.

TABLE V

ANALYSIS OF BERYL SAMPLES

Serial no.	% *BeO*		
	Gravimetric	*Volumetric*	*Ion exchange*
1	12.88	12.88	12.90
2	11.80	12.03	11.76
3	12.00	11.98	11.80
4	—	8.80	8.90
5	—	12.43	12.54
6	11.30	11.19	11.24
7	10.38	10.50	10.58
8	—	1.90	1.98
9	6.44	6.44	6.45

Experiment 8 shows that the method also works in cases where the BeO content of the sample is very low.

Further work is in progress to adapt this method for the recovery and analysis of beryllium in materials containing microgram quantities of the element.

SUMMARY

A new ion exchange method is proposed for the separation of Be from Al, Fe, Ti, Ca and phosphate, by preferentially adsorbing it on cation exchange resin Amberlite IR-120, after complexing the other ions with EDTA and H_2O_2. The successful application of the method to the analysis of beryls is demonstrated.

RÉSUMÉ

Une nouvelle méthode par échange d'ions est proposée pour la séparation de Be d'avec Al, Fe, Ti, Ca et phosphate, en adsorbant de préférence sur la résine Amberlite IR-120, pour échange de cations; on complexe au préalable les autres ions avec EDTA et H_2O_2. Cette méthode a été appliquée avec succès à l'analyse des béryls.

ZUSAMMENFASSUNG

Eine neue Methode zur Trennung des Be von Al, Fe, Ti, Ca und Phosphat durch dessen bevorzugte Adsorption an dem Kationenaustauscherharz Amberlite IR-120, nach Komplexierung der anderen Ionen mit EDTA und H_2O_2 wird beschrieben. Die erfolgreiche Anwendung der Methode auf die Analyse des Berylls wird bewiesen.

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DETERMINATION OF MICROGRAM QUANTITIES OF URANIUM IN THORIUM

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In the analysis of thorium of nuclear purity, a method was required for the determination of uranium in thorium at a level of about 1 p.p.m. Several methods have been reported for the separation and determination of uranium in thorium. WILLIAMS[1] used an alumina-cellulose chromatographic column and extracted uranium with ether containing 1% nitric acid. The uranium was then determined either spectrophotometrically or fluorimetrically. The method is satisfactory above 50 p.p.m. of uranium; at lower concentrations all reagents (particularly alumina) have to be first washed thoroughly with ether. EBERLE AND LERNER[2] separated uranium from thorium by extraction with tributyl phosphate (TBP); for a good separation, the organic phase containing the extracted uranium must be washed many times, first with hydrochloric acid and then with nitric acid. CLINCH AND GUY[3] extracted uranium as the thiocyanate complex into TBP, using EDTA to prevent the extraction of iron and some other elements. However, they recommend a preliminary separation of the uranium by ether extraction before applying the method to thoria samples; at low levels of uranium, the accuracy is not satisfactory. HARDWICK AND MORETON-SMITH[4] have recently reported a method for the separation of ^{233}U from irradiated thorium by extraction of the diethyl dithiocarbamate complex of uranium with hexone. The method was improved[5] by extraction of the oxine complex of uranium with chloroform in the presence of EDTA. In either method the ^{233}U is determined by α-counting.

The most sensitive method for the determination of microgram quantities of natural uranium is by measurement of its fluorescence in fused sodium fluoride melts[6]. Uranium must be in a fairly pure form because most other elements, including thorium, have a quenching effect on the fluorescence. This paper presents a method of separating uranium from thorium by means of TBP in the presence of EDTA as complexing agent. Although CLAYTON *et al.*[5] have reported that this extraction of uranium is not satisfactory, their conditions of pH, etc. were not described. The recovery of uranium by the proposed method was found to be quantitative within the limits of accuracy of the fluorimetric method of determination. The method was satisfactory for thoria samples having an uranium content of as low as 0.4 p.p.m. and it may be possible to extend it to other ranges by suitable adjustment of sample size.

EXPERIMENTAL

Apparatus

1. Fluorimeter, A.E.R.E., Harwell, Model 1080A; 2. pH meter; 3. separatory funnels, Squibb pear-shaped, 125-ml and 250-ml capacity.

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Reagents

1. EDTA, disodium salt, A.R. Grade; 2. calcium nitrate, crystalline, A.R. Grade; 3. nitric acid, A.R. Grade; 4. ammonium hydroxide, liquor ammonia, A.R. Grade, diluted 1:1; 5. ammonium nitrate solution. Saturated aqueous solution of ammonium nitrate (A.R. Grade) adjusted to pH 2.5 with dilute nitric acid; 6. ammonium carbonate solution. 5% (W/V) Aqueous solution of ammonium carbonate, A.R. Grade; 7. tributyl phosphate, 5% solution. The commercial TBP was washed with a 5% solution of sodium carbonate to remove any mono- or di-butyl phosphate present, and then several times with distilled water to remove the carbonate. It was then diluted with kerosene or white spirit to give a 5% (V/V) solution. This solution was equilibrated with an equal volume of dilute nitric acid of pH 2.5, and was, after separation, ready for use.

Principle of the method

To the thorium in the form of a nitrate solution, EDTA is added in slight excess over the equimolecular ratio and the pH is adjusted. Salting agent is added and the uranium extracted with 5% TBP solution. The organic layer is scrubbed with saturated ammonium nitrate solution and the uranium back-extracted into 5% ammonium carbonate solution. Uranium is then determined fluorimetrically.

Salting agent

Various salting agents have been recommended[7] to assist the extraction of uranyl nitrate by TBP. Sodium, calcium and aluminium nitrates were studied for their salting effect in the present method. The extraction in the presence of sodium nitrate was not quite satisfactory, whereas aluminium nitrate caused the extraction of thorium into TBP, even when EDTA was present. Calcium nitrate was found to be satisfactory. It is considered that calcium nitrate not only acts as a salting agent, but also associates with the excess EDTA and thus helps in the extraction of uranium. For quantitative recovery it was necessary almost to saturate the aqueous phase with calcium nitrate and to carry out 5 successive extractions with TBP using a volume almost equal to that of the aqueous phase each time.

Effect of pH

CABELL[8] has reported that uranium forms complexes with EDTA at a pH of about 3 to 5, although these may be weak. It was, therefore, expected that the pH of the aqueous phase would have a considerable effect on the extraction of uranium. The effect of pH was studied over the range 1–4, and it was found that the recovery of uranium was quantitative between pH 2 and 3.5. Below pH 2 considerable quantities of thorium ($>$ 0.5 mg) were extracted owing to the instability of the thorium–EDTA complex. For all further work the pH was adjusted to approximately 2.5 by means of indicator paper. At this pH the amount of thorium extracted was only about 2 μg, which did not interfere in the final fluorimetric determination.

Interferences

The interferences of several common cations and anions were investigated. The ions were added as shown in Table I; no interference was observed. Much greater amounts of these impurities could probably be tolerated.

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TABLE I

INTERFERENCES STUDIED

Ion	*Quantity added* μg	*Ion*	*Quantity added* μg
Fe^{+3}	400	Cr^{+3}	40
Al^{+3}	200	Ni^{+2}	100
Ce^{+4}	100	Co^{+2}	40
Ti^{+4}	40	Mg^{+2}	200
Cu^{+2}	200	SO_4^{-2}	500
Zn^{+2}	100	PO_4^{-3}	500
Cd^{+2}	40	F^-	500
Pb^{+2}	200	MoO_4^{-2}	100
Sn^{+2}	100	VO_3^-	40
Bi^{+3}	40		

PROCEDURE

An aliquot of the sample was taken containing about 1 g of ThO_2 as the nitrate. If the sample contained organic matter it was evaporated in a platinum dish and ignited in a furnace at 600° to destroy all organic matter. The residue was dissolved in nitric acid with a few drops of dilute hydrofluoric acid (2%) and the solution was evaporated to dryness. The residue was then taken up with a few ml of nitric acid and again evaporated to dryness.

The dried residue was dissolved in 5 ml of water, 1.6 of EDTA was added and the pH of the solution adjusted to 2.5 with the help of indicator paper. Dry crystalline calcium nitrate (16 g) was added and the volume adjusted to 25 ml with water. The solution was then transferred to a 125-ml separatory funnel and 20 ml of equilibrated 5% TBP were added after rinsing the beaker with the same TBP. The funnel was shaken vigorously for one min, and the two layers allowed to separate. The aqueous layer was drawn off into the original beaker and the organic layer transferred to a 250-ml separatory funnel using a few ml of TBP solution to rinse the funnel stem. The extraction procedure was repeated four times and the TBP layers combined in the second separatory funnel. The combined organic phase was then scrubbed with saturated ammonium nitrate (adjusted to pH 2.5) three times to remove the small quantities of aqueous phase mechanically carried over. The uranium was stripped from the TBP extract with one 10-ml portion of distilled water, one 10-ml portion of 5% (W/V) solution of ammonium carbonate and finally with two 10-ml portions of water containing 1 ml of ammonium carbonate solution. All the uranium strippings were collected in a porcelain dish, acidified with nitric acid, and evaporated to dryness slowly over a burner. The dried residue was then ignited at 600° in a muffle furnace. The residue was taken up with dilute nitric acid, transferred to a 5-ml volumetric flask and the volume made up. Uranium was then determined fluorimetrically.

Results on synthetic samples are shown in Table II. Various quantities of uranium in the range 1 to 10 μg were added to aliquots of thorium nitrate solution containing approximately 1 g ThO_2, and the uranium content determined. A blank was run on all the reagents used, and amounted to 0.32 μg uranium. In experiment 7, 2.5 g of

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ThO_2 were taken, thus extending the limit of determination to 0.4 p.p.m. of uranium in ThO_2.

TABLE II

ANALYSIS OF SYNTHETIC SAMPLES

Sr.No.	*Uranium added* μg	*Uranium found* μg	*Difference* μg
1	1.00	1.08	+ 0.08
2	2.00	1.88	— 0.12
3	3.00	2.98	— 0.02
4	5.00	5.05	+ 0.05
5	7.00	7.08	+ 0.08
6	10.00	10.13	+ 0.13
7	1.00	1.09	+ 0.09

SUMMARY

Uranium present in micro amounts in thorium is extracted with 5% tributyl phosphate in presence of EDTA at pH 2.5. Calcium nitrate is used as salting agent. Uranium is back-extracted with ammonium carbonate and determined fluorimetrically. Thoria samples containing as little as 0.4 p.p.m. of uranium have been analysed.

RÉSUMÉ

Une méthode est décrite pour le dosage de l'uranium, en faibles teneurs, dans le thorium. On procède par extraction; l'uranium est finalement dosé par fluorimétrie.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von kleinen Mengen Uran in Thorium nach dem Extraktionsverfahren mit anschliessender fluorimetrischer Bestimmung des Urans.

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STUDIES OF GALLIC ACID COMPLEXES WITH METALS AND THEIR ANALYTICAL APPLICATIONS

Part II. A Spectrophotometric Study of Molybdenum Complexes

By

M. S. Varde and V. T. Athavale

Experimental

Apparatus and Reagents

Instruments.—pH measurements were made on a Marconi pH meter, type TF 511 D. Spectrophotometric measurements were done on a Beckman Model DU Quartz Spectrophotometer using 1 cm. quartz absorption cells.

Gallic acid.—E. Merck, G. R. recrystallised and dried at 120° C. Fresh solutions were prepared when required.

Sodium molybdate.—B.D.H. Analar molybdic acid dissolved in a little more than the stoichiometric quantity of sodium hydroxide solution (from E. Merck, G.R. grade) and standardised by gravimetric estimation as lead molybdate.

Sodium acetate.—E. Merck, G.R. grade.

Sulphuric acid.—E. Merck, G.R. grade.

Absorption Spectra

The absorption spectra of the two reactants, *viz.*, sodium molybdate in $2{\cdot}8 \times 10^{-5}$ M concentration, gallic acid in $1{\cdot}5 \times 10^{-4}$ M concentration and of the complex formed by mixing these, all at a pH of 4·2, are presented in Fig. 1. The optical density values for the complex have been obtained after allowing for the absorption due to the two reactants. The curve shows a single absorption peak at 305 mμ.

Absorption measurements were also carried out with more concentrated solutions in the region of 300–600 mμ using ratios of molybdic acid: gallic acid as 1 : 1, 1 : 4 and 1 : 10·5. No characteristic absorption was observed in any case as seen from Fig. 2 (plotted up to 500 mμ only).

Effect of pH

Preliminary experiments had shown that the formation of the molybdenum-gallic acid colour was extremely sensitive to hydrogen-ion concentration and showed maximum absorption in the pH range of 4–4·5 beyond which a sharp decrease in the absorption was noticed. The results obtained at 320 mμ are shown in Fig. 3. As the absorption of gallic acid is affected by the change in pH,[4, 5] this effect was obviated by taking gallic acid solutions of corresponding pH as blanks.

The same effect was observed in the absorption spectra in the region of 250–375 mμ by taking molybdic acid and gallic acid in the ratio of 1 : 4 and changing the pH (Fig. 4).

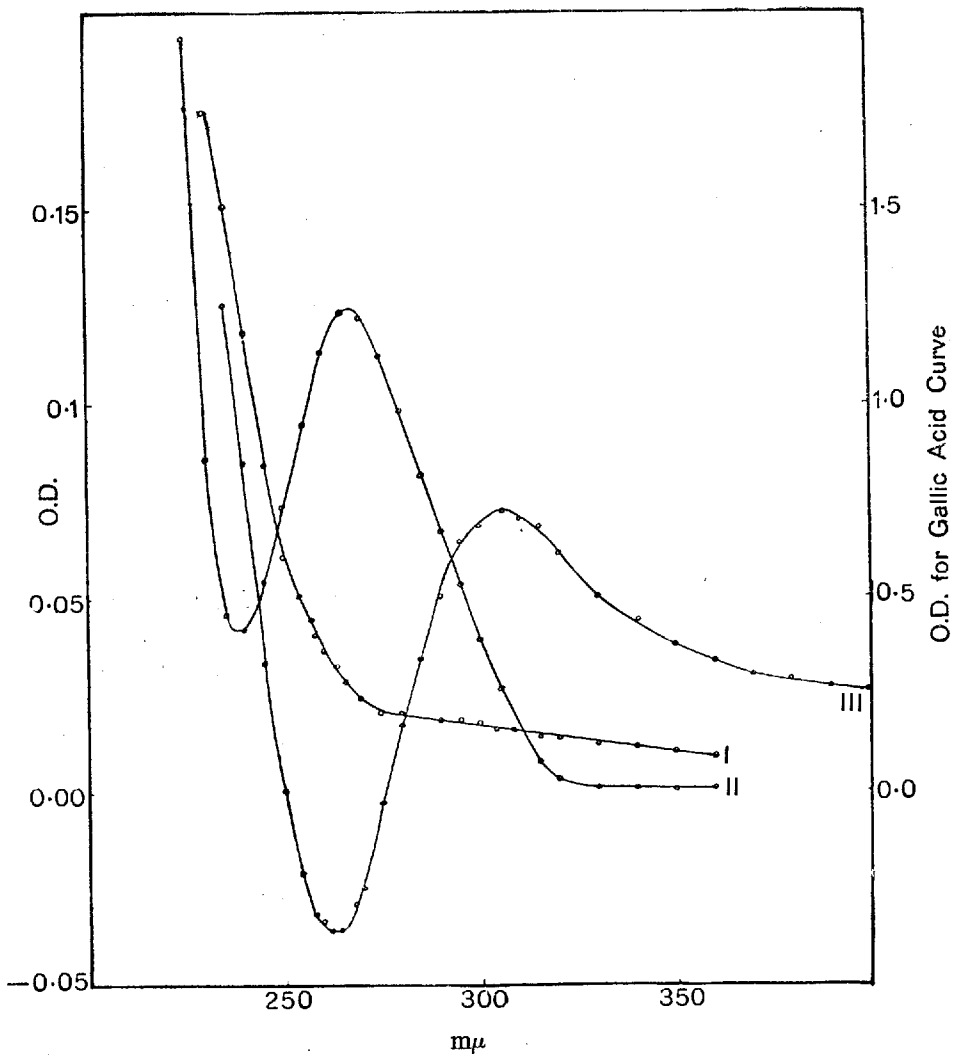


FIG. 1. Absorption Spectra:—Curve I: $2{\cdot}8\times10^{-5}$ M. Molybdate.
,, II: $1{\cdot}5\times10^{-4}$ M. Gallic Acid.
,, III: Complex, $2{\cdot}8\times10^{-5}$ M. in Molybdate and $1{\cdot}5\times10^{-4}$ M. in Gallic Acid (all at pH 4·2)

In all further experiments therefore the pH was adjusted to 4·2.

COMPOSITION OF THE COMPLEX

The ratio of Mo to gallic acid in the complex or complexes was investigated by three different methods, *viz.*, (*a*) method of continuous variations,[6,7] (*b*) the molar ratio method[8] and (*c*) the modified slope ratio method.[9,10]

Since molybdenum is stated to form more than one complex with gallic acid it was necessary to find out suitable wavelengths at which measurements for the various complexes could be made.

Absorption spectra of the solutions were first obtained where molar ratios of Mo to gallic acid were varied. These absorption curves above the wavelength of 300 mμ are shown in Fig. 2. Owing to high absorption of

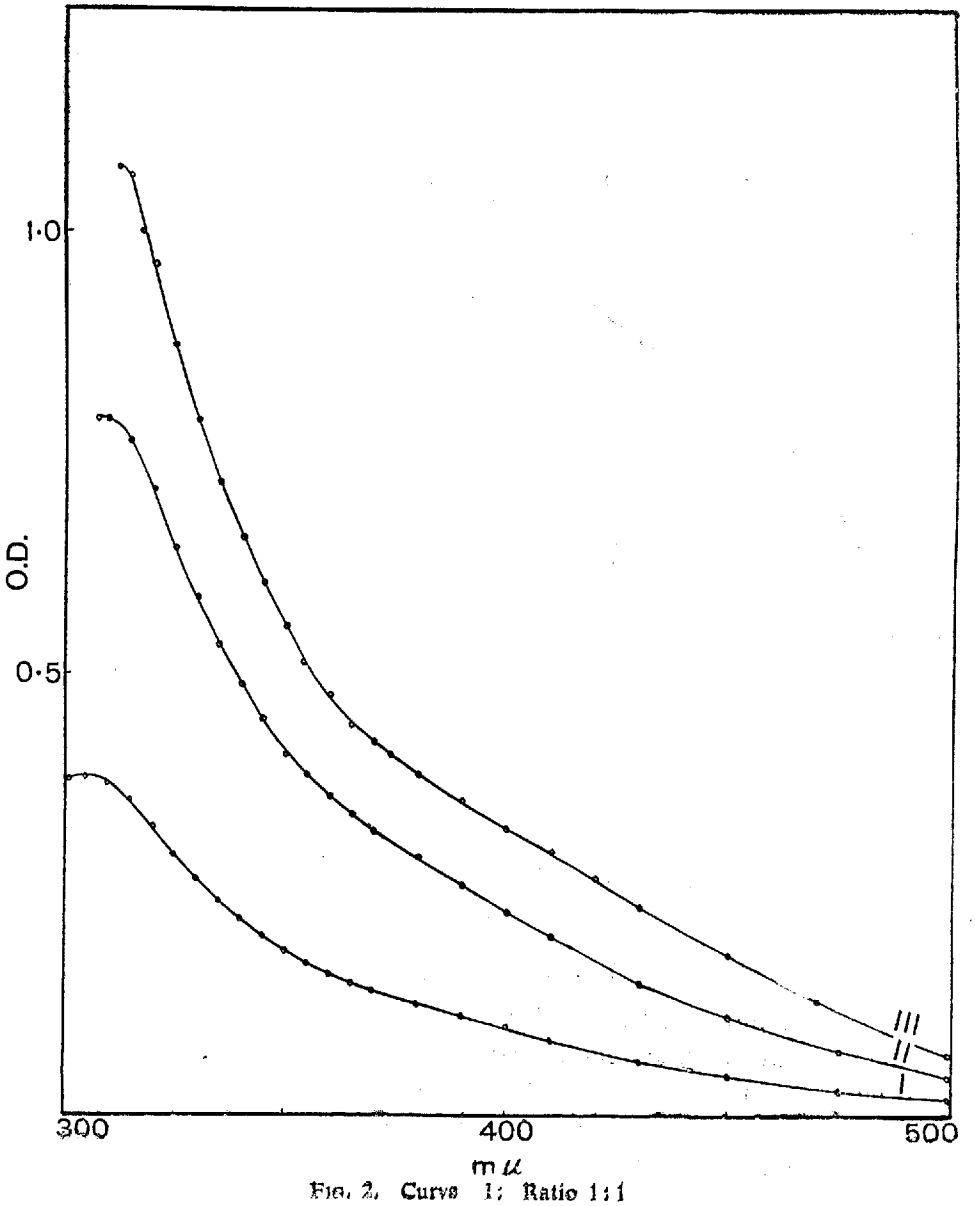


Fig. 2. Curve I: Ratio 1:1
" II: " 1:4
" III: " 1:10·5

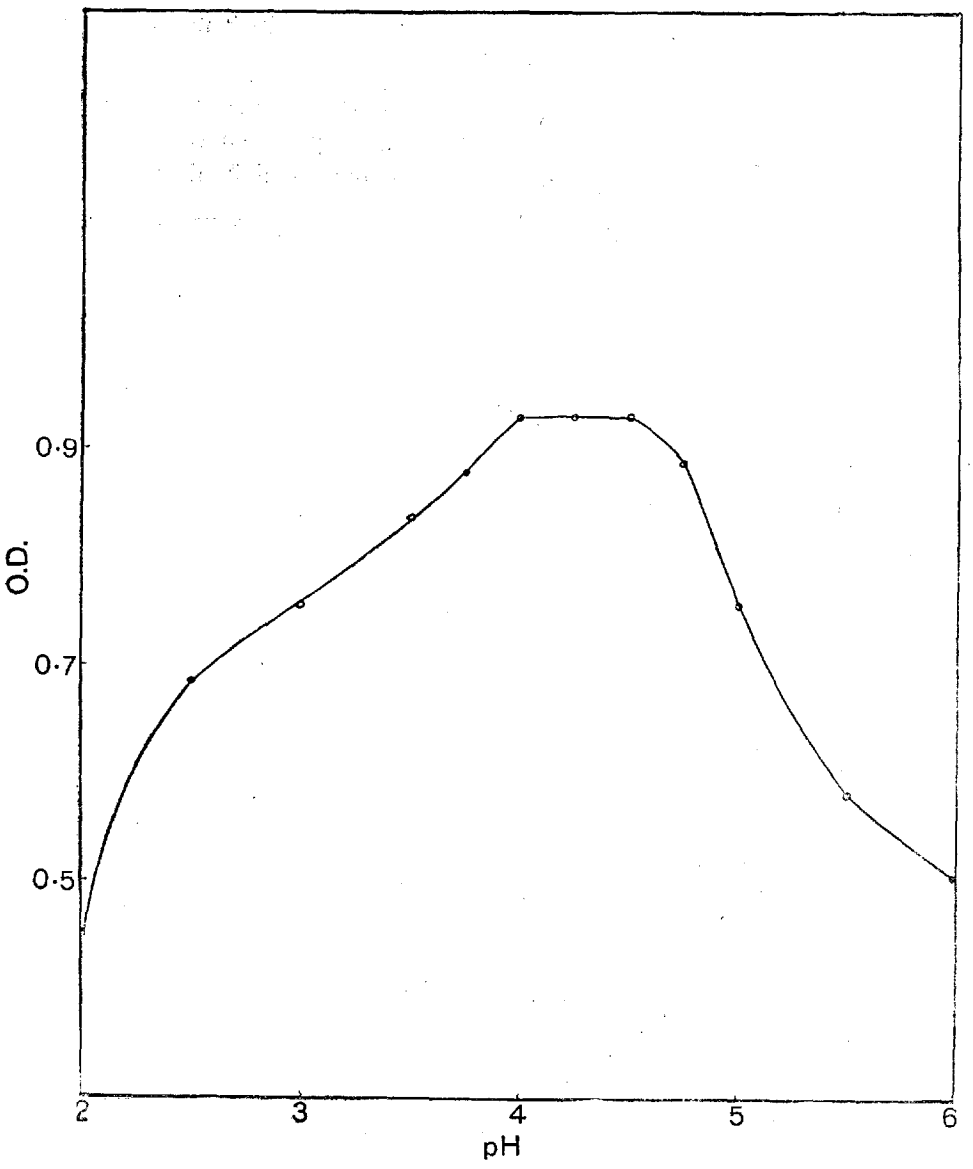


FIG. 3. Effect of pH,

gallic acid in the ultraviolet region it was not possible to make measurements in the region lower than 300 mμ for solutions containing high ratio of gallic acid to molybdenum. Similarly curves II and IV of Fig. 4 show the absorption spectra of solutions containing molybdenum: gallic acid in the ratios of 1:4 and 1:1 respectively all the other conditions being constant.

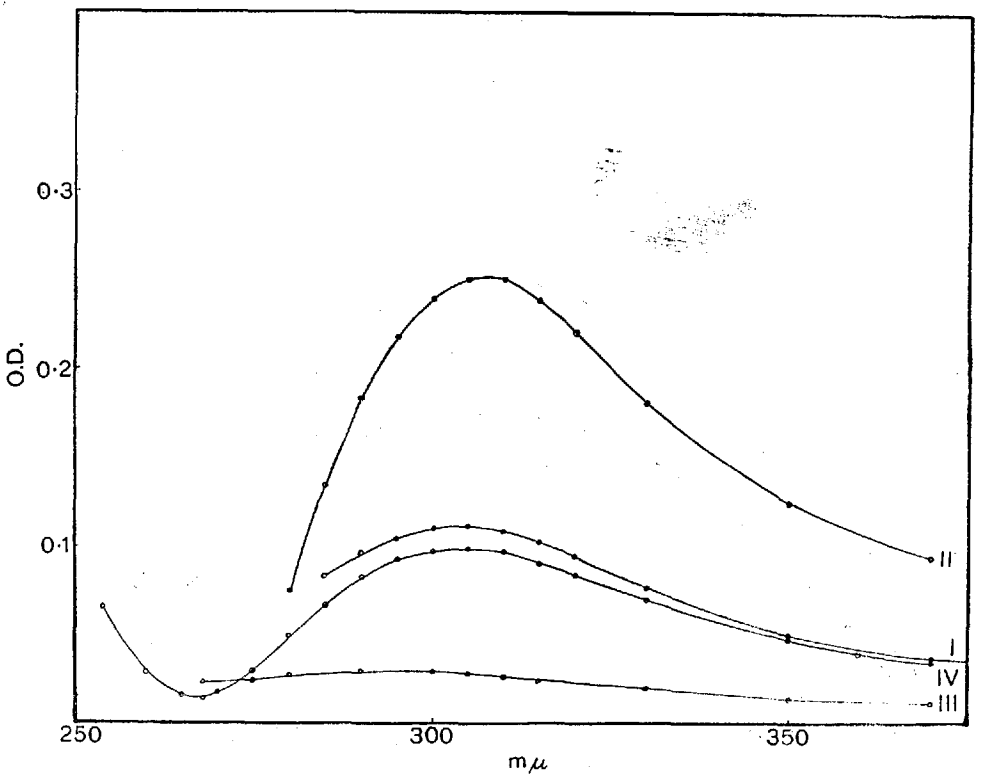


FIG. 4. Curve I: pH 2·5; Ratio 1:4.
„ II: „ 4·2; „ 1:4.
„ III: „ 6·0; „ 1:4.
„ IV: „ 4·2; „ 1:1.

The spectral data does not in the least indicate the formation of more than one complex in the solutions or alternately if more complexes do exist they have similar absorption characteristics.

(*a*) *Method of Continuous Variations*

In the absence of any characteristic wavelengths of absorption for different complexes, if at all they are present, the study of the system by the method of continuous variation was made at three wavelengths, *viz.*, 300 and 315 mμ which are near the maximum absorption wavelength of the complex and at 360 mμ where the reactants themselves will have a very low absorption.

A series of solutions was prepared in which the ratios of molybdenum to gallic acid was varied but the total molarity of the two was constant, the pH also being kept constant at 4·2, and their optical densities were measured. Fig. 5 shows the results obtained at wavelengths of 300, 315 and 360 mμ

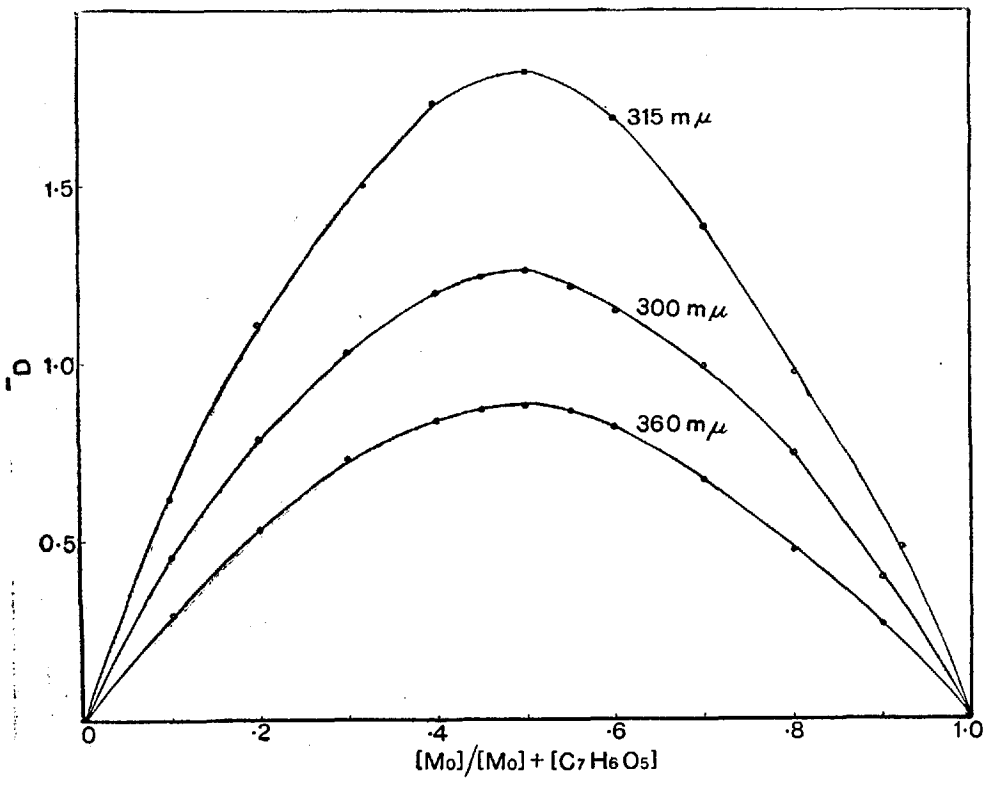


FIG. 5. Continuous Variations.

where the difference (D) between the observed optical density of each solution and that calculated on the assumption that there is no reaction between the two reagents have been plotted against the ratio [Mo]/[Mo] + $[C_7H_6O_5]$. For convenience of representation the values of $\overline{D}$ for the wavelength of 300 mμ have been multiplied by a constant factor in Fig. 5.

In all the three curves the maximum absorption occurs when the relative proportion of gallic acid to molybdenum is 1 : 1 forming a complex which from the nature of the graphs indicates that it is highly dissociating in solution.

(*b*) *Molar Ratio Method*

Fig. 6 shows the effect of increasing the molar concentration of one of the reagents at a fixed concentration of the other, the measurements being made at 380 mμ. Owing to the high dissociation of the complex the curves do not show any sharp break. Attempts were made to get a sharp break in the curve by increasing the ionic concentration of the solutions by addition

of potassium chloride. A slight increase in the optical densities was observed but the increase was so slight as not to be of any consequence.

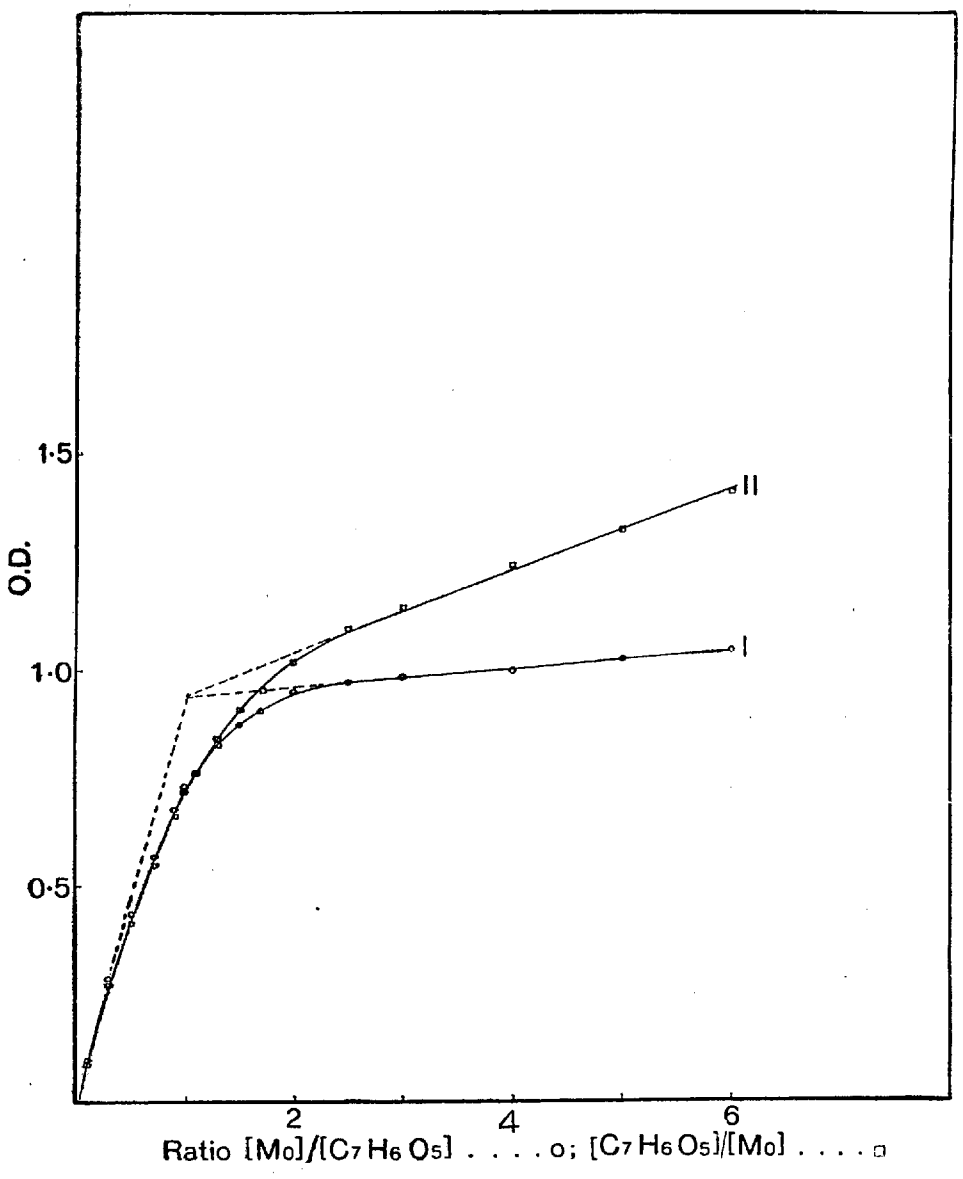


FIG. 6. Molar Ratio.

The dotted lines in the figure are expected to present the true curves on the assumption that there was no dissociation of the complex in which case

the point of intersection corresponds to a molar ratio of molybdenum: gallic acid as 1 : 1.

Further it may be noted that curve I (Fig. 6) in which the concentration of molybdenum is varied with respect to a constant concentration of gallic acid levels off to a reasonably constant optical density, whereas in curve Ii the optical density was still found to be rising even at a molybdenum: gallic acid ratio of 1 : 6. In fact increasing the ratio of molybdenum: gallic acid up to 1 : 50 still showed increasing values in optical density. This may possibly be due to the formation of only 1 : 1 complex in the former case while in the latter case the second complex of molybdenum (Mo : gallic acid :: 1 : 2 as previously reported) is probably formed as more and more gallic acid is made available. No direct evidence for the formation of the molybdenum: gallic acid :: 1 : 2 complex was however obtained.

(*c*) *Modified Slope Ratio Method*

Raghava Rao and co-workers[9, 10] have used a modified slope ratio method in which they plot the optical densities *versus* the concentration of the variable components from either end of the X-axis, thus giving two plots which intersect at a point corresponding to the composition of the complex, the assumption being that only one complex is formed.

In the discussion under " Molar ratio method " it has been shown that a large excess of gallic acid increases the optical density of the solutions continuously. Restricting therefore to molar ratio of one reactant up to 2 with respect to 1 mole of the other a plot is obtained as given in Fig. 7, which once again gives the ratio of molybdenum: gallic acid in the complex as 1 : 1.

DISSOCIATION CONSTANT

The dissociation constant of the complex was calculated by the method described by Anderson and co-workers.[11, 12] Assuming that the extreme end of curve I of Fig. 6 represents complete colour saturation for the quantity of gallic acid used (0·0005 gramme moles in one litre), the molar extinction coefficient of the complex was calculated. From the absorbancy values and the known concentrations of the two reactants, the equilibrium concentrations of the complex and the two reactants were calculated. From these the dissociation constant (K) was calculated. The average value for

$$K = \frac{[Mo]\,[R]}{[MoR]} = 0{\cdot}6 \times 10^{-4} \pm 0{\cdot}1 \times 10^{-4}$$

where R represents gallic acid.

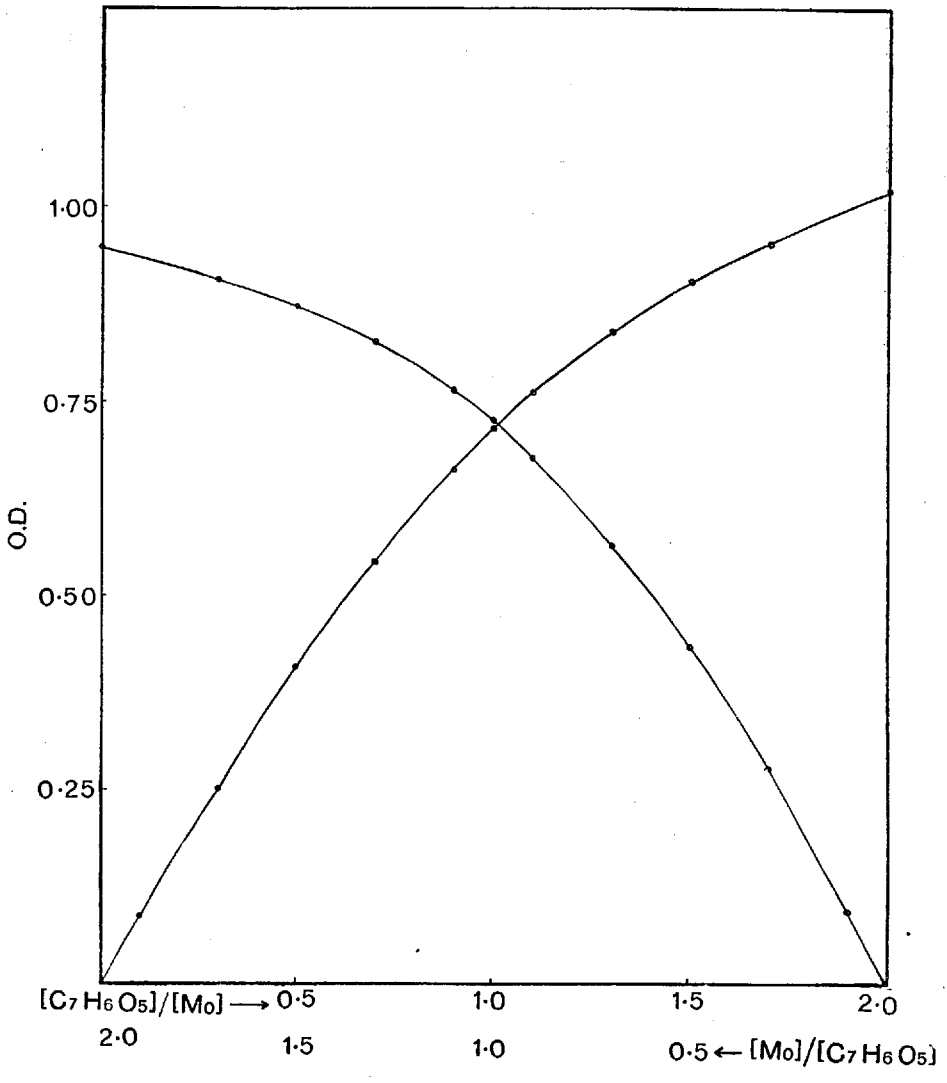


FIG. 7. Modified Slope Ratio.

ESTIMATION OF MOLYBDENUM

Contrary to the observations of Pozzi-Escot[3] it was found that by maintaining pH constant at 4·2 Beer's law was valid for the ranges studied, *viz.*, 0·01 to 0·10 mg. and 0·10 to 1 mg. of molybdenum per 100 c.c. of solution in the presence of 15 mg. and 150 mg. respectively of gallic acid. Measurements were preferably taken at wavelengths of 330 mμ and above as

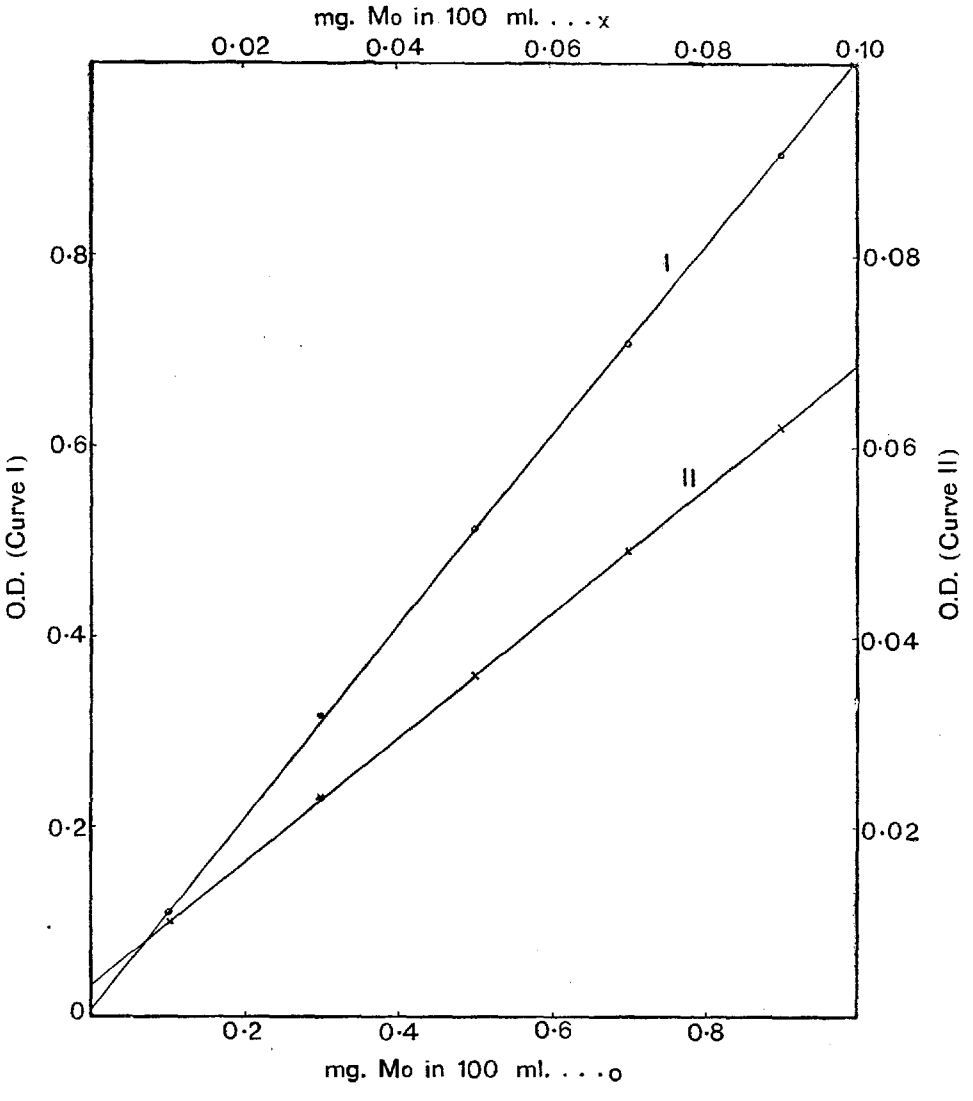


FIG. 8. Beer's Law Curves (330 mμ).

the absorbancy due to gallic acid is low in this region. The colours are developed immediately and were found to be stable up to 24 hours.

The graphs as given in Fig. 8 for the two ranges of molybdenum concentration studied show different slopes. It may be remembered however that the excess of gallic acid used in the two sets is very much different.

Interferences

A number of metal ions such as Fe, Ti, V, W, etc., interfered in the estimation. This interference could not be easily removed. Addition of complexing agents like tartaric and oxalic acid or E.D.T.A. either diminished the molybdenum colour or destroyed it completely. It is therefore necessary to isolate the molyebdnum before developing the colour.

Sensitivity

Rice and Yerkes[13] have reported the sensitivities of various reagents used for molybdenum estimation. A comparison of these with the present method is given below:—

Reagent	Sensitivity in g. of Mo per litre
Potassium ferrocyanide	0·1
Sodium thiosulphate	0·04
Phenyl hydrazine	0·006
Potassium xanthate	0·004
Butyl xanthate	0·004
Amyl xanthate	0·004
Pentasol xanthate	0·004
Potassium ethyl xanthate (colour extracted with ether)	0·0004
Gallic acid	0·0001 (O.D. = 0·01)
Ammonium thiocyanate-stannous chloride (colour extracted with ether)	0·00002

Summary

Spectrophotometric study of the molybdenum-gallic acid system showed the formation of a yellow complex of the empirical formula MoR which shows an absorption maximum at 305 mμ. The complex dissociates appreciably in solution and gave the value for K, the dissociation constant as $0{\cdot}6 \times 10^{-4} \pm 0{\cdot}1 \times 10^{-4}$. Beer's law was found to hold good for concentrations up to 1 mg. Mo per 100 c.c. and quantitative estimations could be made after isolation of Mo from interfering elemcnts.

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STUDIES OF GALLIC ACID COMPLEXES WITH METALS AND THEIR ANALYTICAL APPLICATIONS

Part II. A Spectrophotometric Study of Molybdenum Complexes

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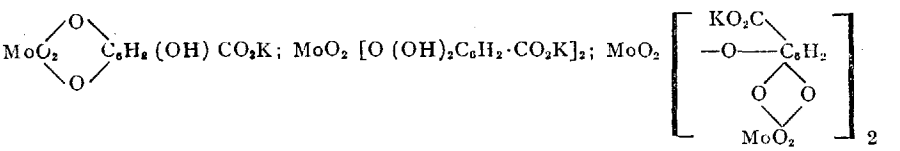
(Chemistry Division, Atomic Energy Establishment, Bombay)

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INTRODUCTION

FERNANDES[1] has reported the preparation of numerous compounds of various hydroxy organic acids with molybdic and tungstic acids and has mentioned three distinct complexes of molybdic oxide with potassium gallate in the ratio 1, 2 and 0·66 moles of gallate per mole of MoO_3 to which the following formulæ have been assigned respectively:—



(i) (ii) (iii)

These were obtained by treating solutions of potassium gallate with calculated quantities of the molybdenum oxide and concentrating the solutions when the compounds crystallised out. However in a subsequent communication[2] on the complexes of other hydroxyacids with MoO_3, WO_3 and UO_3 it has also been stated that in aqueous solutions compounds of the first type, *viz.*, 1 : 1 complexes, are normally obtained but a very large excess of the phenol is required to give complexes of the second type.

Pozzi-Escot[3] has utilised the yellow to orange colour given by molybdates in presence of polyphenols, such as gallic and pyrogallic acids, for the detection of molybdenum.

The work presented in this paper was undertaken firstly to find out by spectrophotometric method, under controlled conditions of pH, etc., the evidence for the formation of the various compounds reported and secondly to find out the feasibility of utilising the colour formation for the quantitative estimation of molybdenum.