Radiochemical studies of the fission of heavy elements by fast neutrons

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"RADIOCHEMICAL STUDIES OF THE FISSION OF HEAVY ELEMENTS BY FAST NEUTRONS"

THESIS

Presented in candidature for the degree of

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in the

UNIVERSITY OF DURHAM

by

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MEMORANDUM

The work described in this Thesis was carried out partly in the Londonderry Laboratory for Radiochemistry, Durham University and partly in the University Chemical Laboratory, Canterbury, Kent, between September 1962 and May 1965, under the supervision of Dr. S.J. Lyle, Lecturer in Radiochemistry.

The results presented in the thesis contain some original research by the author and no part of the material offered has previously been submitted by the candidate for a degree in this or any other University. Where use has been made of the results and conclusions of other authors in relevent studies, care has been taken to ensure that the source of information is always clearly indicated, unless it is of such general nature that indication is impracticable.

M.S.M. Rahman.

ABSTRACT

The relative yields of 8 mass chains both in the fission of Th^{232} by 3- and 14-Mev. neutrons have been measured radiochemically. The measured relative yields were corrected to total chain yields by applying the equal charge displacement hypothesis. The relative yields were converted to absolute yields by imposing the condition that the sum of all the fission products must be 200%.

Use has been made of the measured relative yields of near complementary fragments to determine the number of secondary neutrons emitted by a few fragment pairs. The number of secondary neutrons emitted by mass number 145 and its complementary fragment in 14-Mev neutron fission was found to be 4.04 and by mass number 132 and its complementary fragment in 3-Mev neutron fission to be 2.30.

The mass yield curves obtained in the present investigations showed the predominence of asymmetric fission at the lower excitation energy. The maxima of the peaks for 14-Mev fission were at mass numbers 91.00 and 137.96, while those for 3-Mev neutron fission were at mass numbers 91.35 and 139.28. An explanation of the relative change of the peak maxima at different energies has been put forward.

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CHAPTER I

INTRODUCTION

1. Nuclear Fission:

Shortly after the discovery of the neutrons in 1932, Fermi[1] in Italy bombarded uranium with neutrons in an effort to produce elements beyond uranium in the periodic table. He observed that the bombarded uranium gave rise to several β-active products and that half-lives of these radioactive nuclides did not correspond to half-lives of any known heavy element. He, therefore, concluded that the activities in question should be attributed to transuranic elements having atomic number 93 or higher, produced by β-emission from uranium nuclei following the capture of neutrons.

In order to investigate more fully the nature of the radio-nuclides formed during such neutron irradiation of uranium (and of thorium) Curie and Savitch[2,3], in France and Hahn, Strassman and Meitner[4] in Germany chemically separated the radio-nuclides from uranium. They showed that some of the activities formed during the bombardment of uranium were due to radioactive barium or lanthanum. At this stage, Meitner and Frisch[5] gave the correct explanation of the experimental data, namely that instead of forming a transuranic element, the uranium nucleus split into two fragments of unequal masses.

This process of splitting of a heavy nucleus into two parts they termed "fission". Shortly afterwards, Bohr and Wheeler[6] predicted on theoretical grounds that it is the isotope U^{235} which undergoes fission as a result of the capture of the slow neutrons. The phenomenon was confirmed experimentally by Frisch[7] and Joliot[8] who measured the ionization produced by the fission products.

The term "fission product" is used to refer to and include the "fission fragments" as well as their radioactive decay products. The fission fragments are generally unstable and an understanding of their instability may be obtained from their neutron-proton ratios immediately after fission. The neutron-proton ratio of the compound nucleus undergoing fission is considerably greater than the corresponding ratios of stable nuclides formed during fission. Although a number of neutrons may also be released at the instant of fission, the main fragment generally retain approximately the same neutron-proton ratio as the fissioning nucleus. Such neutron-excess fission fragments decay by a series of successive β-emissions to produce nuclides which are increasingly close to the neutron-proton nuclear stability limit. β-emission may leave the fission product in an excited state. γ-rays are then emitted from such a fission product to remove this excess energy. The resultant isobaric sequence of fission product decay is called a "fission chain". A large number of fission chains have already been identified in fission products. Some typical examples of such chains are given below:

$$\begin{tikzcd}
 & & & 6h\ Te^{99} \arrow[dd, "\gamma"] & \\
33s\ Zr^{99} \arrow[r, "\beta^-"] & 2.4m\ Nb^{99} \arrow[r, "\beta^-"] & 66h\ Mo^{99} \arrow[ur, "\beta^-"] \arrow[dr, "\beta^-"] & & Ru^{99}(stable) \\
 & & & 2.1 \times 10^{5}y\ Te^{99} \arrow[ur, "\beta^-"] &
\end{tikzcd}$$

$$2.6m\ Sn^{130} \xrightarrow{\beta^-} 7.1m\ Sb^{130} \xrightarrow{\beta^-} Te^{130}\ (stable)$$

$$\begin{tikzcd}
69s\ Se^{83m} \arrow[dd, dashed] \arrow[dr, "\beta^-"] & & 114m\ Kr^{83m} \arrow[dd, "\gamma"] \\
 & 2.4h\ Br^{83} \arrow[ur, "\beta^-"] & \\
25m\ Se^{83} \arrow[ur, "\beta^-"] & & Kr83\ (stable)
\end{tikzcd}$$

The independent fission-yield of a nuclide is the fraction or percentage of the total number of fissions in which that nuclide is formed as an initial fragment. Because of the rapid decay of many of these fragments, the experimental determination of the independent yield of a given mass-chain is difficult. Again, after sufficient time has elapsed for complete decay of its β-active precursors, by measuring the yield of any nuclide in a mass-chain, one can determine the cumulative yield and this does not include the contribution of the latter members of the mass-chain.

However, the independent yields of fission product members of various mass-chains, especially yields of shielded nuclei have been determined and correlated to give the charge distribution in fission.

Measurements of such independent yields have shown that the nuclear charge for any given mass, Z_A, is usually distributed about the most probable charge Z_P. For low and medium energy fission this distribution is best accounted for by the hypothesis of '<u>Equal Charge Displacement</u>'[10] which may be written as

$$^{*}\ (Z_A - Z_P)_L = (Z_A - Z_P)_H$$

For high energy fission, results are best fitted by the concept of an "<u>Unchanged Charge Distribution</u>"[11] i.e.

$$\left(\frac{Z}{A}\right)\text{ fission products} = \left(\frac{Z}{A}\right)\text{ fissioning nucleus}$$

From these hypotheses it is possible to obtain a value for the independent yield for any nuclide of mass A as a fraction of the cumulative yield for the chain.

For a better understanding of the fission process, mass yields are needed to determine the mass distribution in fission

---

* Where, L and H refers to light and heavy fragment respectively.

and independent yields are needed to determine the charge distribution in fission. In either case, absolute yields are required to find the formation cross-section of a particular mass chain or a particular isotope. A direct determination of the absolute yield of a given nuclide requires knowledge of (i) the total number of fission events occurring in the sample considered and (ii) the total number of nuclei of that species which had resulted from the measured number of fissions. Since the direct measurement of absolute fission yield is rather difficult, in general, yields are determined relative to a reference nuclide. These relative yields are then made absolute by applying the consideration that since each fissioning nucleus gives two main fragments the sum of all the fission yields must equal 200%.

Although the initial radiochemical work related to the identification of the nuclides and their radioactive decay characteristic, the emphasis of such work is now concerned with measurement of quantitative cumulative yields of fission chains and where possible the independent yields of individual fission product isotopes. It follows, therefore, that the determination of cross-section of nuclear reactions and nuclear fission, and the determination of the number of prompt and delayed neutrons on fission come under the domain of radiochemistry. The fission product yields also can be determined mass-spectrometrically with considerable accuracy, but such determinations are possible only where sufficient atoms are produced for mass-spectrometer sources. On the contrary, such cases in addition to those in which the number of fissions produced are too low to produce a sufficient ion-current for mass-spectrometric studies, fission yields can be determined by the radiochemical technique. In spite of the difficulties of determining the absolute disintegration rates, the accuracy of this method is now within 10%.

2. Mass-Distribution.

Though the main products of the fission of heavy nuclei lie between mass numbers 72 and 162 and between atomic numbers 30 and 65, their individual yields differ to a great extent. As stated earlier, a series of products with the same mass number A is called a fission product chain and one of the main goals of radiochemistry is to measure quantitatively the yield of individual fission chain and where possible, the independent yield of individual fission product isotopes. The cumulative chain yield Y(A) is defined as

$$Y(A) = \frac{(\text{Number of product nuclei of mass no. A}) \times 100\%}{(\text{Number of fissioned nuclei})}$$

A plot of chain yield against mass number is called a fission yield curve. This concept of fission yield curve is due to

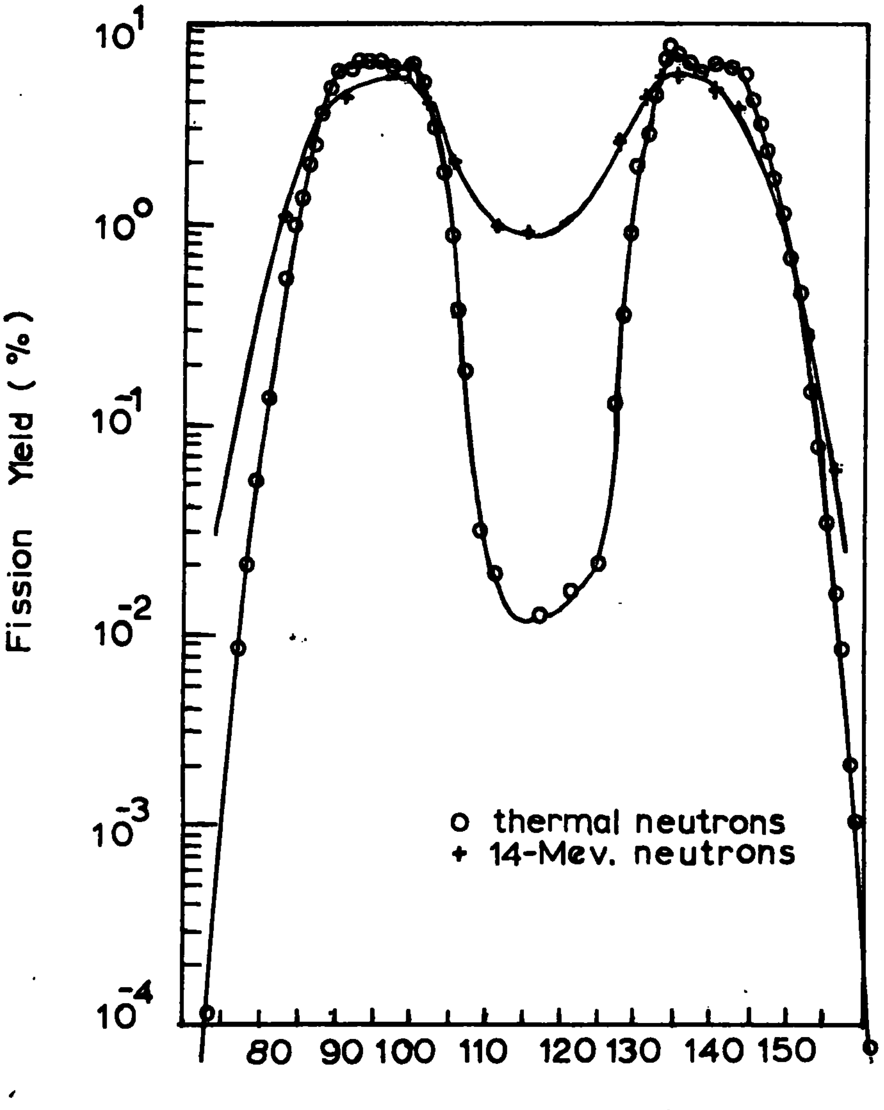

Fig. 1. The mass distribution of U^{235} fission products

Fermi and his co-workers[12] and has subsequently developed into mass-yield distribution curve for fission.

Splitting of U^{235} with thermal as well as fast neutrons is one of the most interesting and one of the most extensively studied phenomenon of nuclear fission. This mass-yield distribution is shown in Fig. 1.[13] This is a result of radiochemical and mass spectrometric investigations made over a range of 90 mass units and 35 charge units and represents the mass distribution of fission products after neutron emission.

The most striking feature of the curve is the presence of two large maxima with a very deep minimum between them. The minimum occurs at mass numbers corresponding to symmetric fission, which is thus seen to be very unlikely to occur. The most probable division, as the positions of the maxima show, is into fragments of unequal masses i.e. unsymmetric fission. Measurement of mass distribution from kinetic energy measurements of fission fragments confirms also this sort of asymmetric fission.[14] It is of interest to note that though symmetric fission is far less probable than asymmetric fission, a very asymmetric fission is much less probable than the symmetric one.

Another feature of the mass yield distribution is the relative change in symmetric and asymme tric fission with excitation energy. The mass yield curves obtained[15] for the spontaneous fission of U^{238}, Pu^{240}, Cm^{242} and Cf^{252} show an essentially undetermined valley. For thermal neutron induced fission of U^{235} the peak to valley ratio is in the region of a few hundred.[16] A compilation[17] of the peak to valley ratios in the fission of various target nuclei by different particles of various energies shows the general increase of the valley to peak ratio with increasing excitation energy. This pattern of fission product yield as a function of energy of bombarding particles seems to be largely independent of the target element or the bombarding particles. Associated with the increase in bombarding energy is an increase in the width of the mass yield distribution that is the twin peaked asymmetric mass yield distribution is narrower than the single peaked mass yield distribution.

Radiochemical and mass spectrometric analysis of fission product yield distribution has shown the existence of deviations from the smooth mass yield curve. Though the yield curve for the thermal neutron fission of U^{235} was originally drawn as a smooth curve,[18] with two peaks of asymmetric fission, mass spectrometric studies[19] of Kr and Xe fission isotopes showed the presence of fine structure in the yield curve with Kr^{85} and Xe^{134} yields about 35% too high to fit the smooth curve. According to Glendenin[20] this is due to 82 neutron closed shell causing cross-chain branching. To fit this postulate to other experimental results Pappas[21] extended the chain branching mechanism to include the 3rd, 5th and 7th neutrons in excess of the 82 neutron closed shell. Recent calculations by Terrell[22] offer an alternative explanation of the observed fine structure on the basis of the change of neutron emission probabilities from mass to mass.

3. Fission of Th^{232}.

The discovery of the fission of uranium immediately led to investigations to determine whether other nuclei are fissionable. Although neutron induced fission is still the most important, other particles with high energy such as protons, deutrons, alpha-particles etc. has been used and in fact, if the energy of the projectile is high enough, any heavy nucleus will undergo fission. From the industrial point of view, fission by thermal neutrons is at present by far the most important. This work has been largely confined to the heaviest nuclides. U^{235} is one of those which occur in nature in appreciable quantities and has been serving as the basis for practically the entire nuclear energy programme. Two other nuclides usable as fissionable material in nuclear power plant are U^{233} and Pu^{239}. Since they do not occur in nature, they are produced by suitable nuclear reactions from Th^{232} and U^{238} respectively. These latter materials which are not themselves fissionable by thermal neutrons, are known as fertile materials:

$$_{90}Th^{232} + _{0}n^{1} \longrightarrow _{90}Th^{233} \xrightarrow{\beta^-} _{91}Ph^{233} \xrightarrow{\beta^-} _{92}U^{233}$$

One of the problems now under critical study in commercial power production is the use of Th^{232} and U^{238} in breeder reactors in which it is hoped to produce more fissionable material than is consumed. Though Th^{232} does not undergo fission by thermal neutrons and hence has the possibility of being used in breeder reactors, it undergoes fission by fast neutrons. The study of the fission of Th^{232} received interest because of general curiosity and its possible use as breeder. Moreover, the knowledge of the yield and mode of thorium fission are needed to indicate such things as shielding, health hazard, decontamination problems and poisoning of the fission reaction.

Shortly after the neutron fission of uranium fission of Th was confirmed.[23] Other early experiments showed that thorium fission was asymmetric[24] with a cross-section of about $10^{-25}cm^2$.[25] and requiring fast (0.5 to 2.4 -Mev) neutrons.[26] Ballou and his co-workers[27] did some work on the fission of thorium for the Manhattan Project, but most work on thorium was temporarily postponed because of the more promising potentialities of U^{235} during the 1939-44 War.

Since the mass yield curve of U^{235} for its thermal neutron fission was determined, the mass yield curves of various other target nuclei have been determined using increasingly energetic bombarding particles. A radiochemical study of Th^{232} with pile-neutrons of estimated effective energy of 2.6-Mev was published by Turkevitch and Niday[28] in 1951. This was followed by a similar investigation in which Turkevitch et al[29] bombarded Li with 7.6-Mev deutron to obtain neutrons with a maximum energy of 21-Mev. Their calculations indicated that most of the neutrons had energies less than 14 Mev, that the majority of the fission events were caused by neutrons with energies between 6 to 14-Mev and that 10% of the fission events were induced by neutrons with energies greater than 14-Mev. Their error was about 20% and they could not indicate any fine structure in the yield curve. The valley-to-peak ratio of the yield curve was 0.1 in contrast to about 0.01 obtained in the pile neutron fission of Th^{232}. Using this valley to peak ratio as a measure of symmetric to asymmetric fission, they decided that this ratio increases with increasing fissioning energy. Alexander and Coryell[30] used 0 to 19 Mev neutrons from beryllium-deutron reaction to bombard Th^{232} with similar results. A recent publication of Lyle et al[31] has shown that for the monoenergetic 14.7 Mev neutrons induced fission of Th^{232} the valley to peak ratio is about 0.19.

Another study[32] of Th^{232} using 14.9-Mev neutrons gives an estimated valley to peak ratio of about 0.17.

In the fission of somewhat lighter elements, for example the fission of Bi^{209} with 42-Mev alpha-particles only a single narrow peak appears. In the intermediate nucleus Ra^{226} bombardment with 30.8- and 38.7-Mev alpha particles give a fission yield curve with three peaks whereas bombardment of U^{238} with 29.4- and 42.0-Mev neutrons produces yield curves with only two peaks.[33] The possibility of a third peak in the trough region of neutron induced fission of Th^{232} is not ruled out by the results of Turkevitch and Niday[28] on the pile neutron fission or even by those of Turkevitch et al[29] on the Li+D-neutron fission of Th^{232}. The results of the recent calculations by Newson[34] shows a third peak for the fission of Th^{232} by 2.8-Mev neutrons. The investigation of Iyre et al[35] indicated the presence of a small third peak in the pile neutron fission of Th^{232} in the symmetric region of the mass yield curve, whereas the results of some other investigations[31,36,37] were inconclusive.

Radiochemical and mass spectrometric analysis of fission product yields have demonstrated the existence of deviations from the smooth mass yield curve. This is particularly true in the region of masses 100 and 135 for the fission of U^{235} by thermal neutrons.[19,38,39] Fine structure of the mass yield curve of several other heavy elements has also been observed by many investigators.[40,41,42] Such fine structure has recently been observed in the fast neutron fission of Th^{232} by Kennett et al[43] and in the 14.8- and 2.95-Mev neutron fission by Broom.[36] Other works[31,35] could not produce any evidence for fine structure in the pile as well as monokinetic neutron induced fission of Th^{232}.

It has been observed that as the mass of the compound fissioning nucleus is increased the fission product mass distribution exhibits a shift of the light mass peak towards greater masses but the heavy peak remains essentially the same. On the other hand for the same fissioning nucleus, it appears that with the increasing excitation energy the light peak remains fixed whilst the heavy peak tends to move towards lighter masses. This effect has already been observed with both U^{235} and U^{238}.[44]

In the case of Th^{232} fission starting from pile up to 14-Mev neutrons, the position of the mass no. at the maximum of light peak lies at 91 ± 1, whereas the position of the mass no. at the maximum of the heavy peak does not seem to follow any regularity.[28,29,35,36,31,32]

The number of prompt neutrons emitted in nuclear fission is of utmost practical importance in the application of nuclear chain reactions in nuclear reactors or explosions.

The measurement of neutron emission probabilities is of particular interest, since it provides a measure of the excitation energies of the fission fragments at the time of scission and since the knowledge of the magnitude and dependence on fission mode of these energies is basic to a description of the fission process. A number of measurements[45,46,47] have been made for $\bar{v}$, the average number of prompt neutrons emitted per fission from 3.5- to 14.9-Mev neutron induced fission of Th^{232} and a linear relationship has been obtained for $\bar{v}$ against energy of the fissioning neutrons.[48] In most of these works the technique used was to detect and measure fission fragments and prompt neutrons simultaneously.

Recently there has been experimental evidence that the neutron yield from fission fragments is not simply equally divided between light and heavy fragments, but is a more complicated function of fragment mass. This strong variation of neutron yield with fragment mass was first reported by Fraser and Milton[49] for the thermal neutron fission of U^{233}. Stein and Whetstone[50] also reported how the total number of prompt neutrons emitted in spontaneous fission of Cf^{252} is affected by the division of the mass between fragments and by the amount of energy going into kinetic energy of the fragments. Whetstone's[51] results for the spontaneous fission of Cf^{252} give a clear indication that prompt neutrons are emitted preferentially by the heaviest light fragments and the heaviest heavy fragments. A recent experiment on the neutron fission of U^{235} has also shown that the number of neutrons emitted from individual fragments varies with the mass number of the emitting fragments. No such measurements appear to have been made for Th^{232} fission induced by neutrons.

Purpose of the Present Work:

The purpose of the present investigation was firstly to determine precisely the relative fission yields of a few selected nuclides produced during the 3- and 14-Mev. neutron induced fission of Th^{232} in an effort to find out some information about the emission of secondary neutrons during such fissions, and secondly to use the measured relative yields to draw mass-yield curves to examine the effect of the energy of the bombarding neutron on the positions of the peak-maxima.

CHAPTER II

1. Introduction

The determination of relative mass yield requires four main operations -- the production of fission in Th^{232} by neutrons, separation and purification of a particular isotope, the determination of the number of atoms of this isotope relative to the reference isotope and the correlation of the results thus obtained.

To avoid possible contribution to some fission products by daughter activities initially present, the thorium sample to be irradiated was purified when necessary before irradiation. Thorium nitrate or where initial purification was necessary, thorium-hydroxide was irradiated with 14- and 3- Mev. neutrons produced by the D + T and D + D reactions respectively. To make allowance for the effect of fluctuation of the neutron flux on the yield of different nuclides the neutron yield was monitored throughout the irradiation.

The gross separation of an isotope is performed chemically aided by the addition of a carrier. After irradiation the target material is dissolved and carriers added for the fission products to be separated. To reduce errors due to adsorption of fission products on glassware etc. and to maintain the yields as high as possible, carriers were added to the whole of the solution, thus restricting the choice of elements to be separated from an irradiated sample by the compatability of the added carriers and the requirements pertaining to the chemistry needed for the separation of each element.

Isotopic exchange between the inactive carrier and the active fission products is ensured by recommended procedures such as stirring, digestion or redox cycles etc. The gross separation and purification of an isotope is done chemically through repeated cycles of chemical operations designed to reduce contamination by other fission products. The methods used in the present investigation are based upon published radiochemical procedures for the isolation of fission products with suitable modifications taking into account the chemistry of Th in the solution and the presence of an need for separating other elements. Reference to such procedures for individual fission products is quoted in appropriate section of the thesis. In order to inter-relate the results of various runs, 17.0 hr. Zr^{97} produced during the fission was chosen as the reference element and the yields of all other nuclides are determined relative to that of Zr^{97}.

The determination of the number of atoms of the separated and purified isotopes has been done by counting with an end-window gas-flow β-proportional counter. This was done by calibrating it against a 4π gas-flow β-proportional counter. Where such calibration was not possible due to short half-life of the species counted, either extrapolation was made from other calibration curves taking account of the -energies of the species concerned and the electron density of the source or using other radioisotopes of comparable decay scheme and energies.

4π -proportional counters can be used to determine the fission yields.[52] The main advantage of this method is the elimination of many correction factors required in the end-window counter method. But this method requires more sensitive determination of carriers. It also involves a tedious method of production of 4π sources after each irradiation. Use of an end-window proportional counter facilitates rapid exchange of sources when several sources are counted and absolute disintegration rates of the sources are obtained by once calibrating the counter for each nuclide against 4π counter. Each sample is counted long enough to keep statistical error as small as possible and till the decay is complete.

The gas-flow end-window proportional counter does not directly determine the mass number or atomic number of the detected activity, but because of the extensive work that has been done on many isotopes[53] there is usually little doubt as to which isotope is being counted. The genetics of the fission product decay chain in the fast neutron fission of Th^{232} are assumed to be the same as those of thermal neutron induced fission of U^{235}.[54] Detailed information of the decay systematics of specific nuclides was obtained from 'Nuclear Data Sheets'.[55]

2. Neutron Sources

(a) 14-Mev Neutrons: A deutron beam of suitable energy was available in the Londonderry Laboratory for Radiochemistry, Durham from the Cockroft-Walton accelerator for producing a high flux of essentially monoenergetic neutrons by the following reaction;

$$^{2}D + {}^{3}T \longrightarrow {}^{4}He + {}^{1}n + 17.6 \text{ Mev.}$$

The reaction has a high broad resonance for deutrons of 100 Kev striking a thin target of tritium; 14.7 ± 0.2 Mev neutrons are produced by this machine.

The tritium targets as described by Wilson and Evans[56] were supplied by A.E.R.E. Harwell. Each disc contains about one to three curies of tritium which was absorbed on a thin film of metallic zirconium or titanium: The zirconium or titanium film is soldered on a copper blocking to a copper foil, which is, in turn, well soldered to the copper target block of the accelerator with Wood's metal. The target block is water cooled during irradiation to take away the considerable amount of heat dissipated in it during irradiation and thus preventing the loss of tritium by "boiling off" due to heating of the target.

During normal irradiation the deutron beam current was maintained in the region of about 200 μa. and a neutron flux of about 2 x 10^9 neutrons/sec was obtained. Though the life of a target was about a thousand-μa-hour bombardment, the neutron yield normally drops during the course of bombardment. This is due to loss of tritium from the heated area of the target and deposition of pump oil on it.[56]

For the irradiation the sample was held to the bottom of the target block by rubber bands. The energy of the neutrons varies to some extent with the angle of emission with respect to the bombarding beam. However, for the over all solid angle within which the thorium samples were irradiated, the variation amounts to less than 3% and indicates no significant variation of the relative fission product yields with the variation of neutron energy within that limit.[31]

(b) <u>3-Mev Neutrons</u>: For 3-Mev neutrons the newly built Van-de-Graaff type Electrostatic Rotary Generator at the

Chemical Laboratory, University of Kent at Canterbury, was used to obtain a deuteron beam of energy 400 Kev. for the reaction:-

$$D^2 + D^2 \longrightarrow He^3 + N^1 + 3.28 \text{ Mev.}$$

A good neutron yield can be obtained with deutrons of this energy and the neutrons are obtained with a well defined narrow energy range.

The target used is a copper disc coated with titanium metal. Deuterium is adsorbed in the thin (about 1 mg./cm^2) titanium layer. The disc which is 1.1 inches in diameter and about 1 mm thickness is divided into four segments and one segment at a time is fitted into a target block designed by Societe Anonyme de Machines Electrostatiques, Grenoble, France -- the maker of the accelerator. The cooling water for the target block passes directly over the back surface of the target disc for good cooling efficiency, since at maximum beam current about 400 watts will be dissipated at the target.

During a normal irradiation, the beam current is maintained at about 700 μa and the accelerating voltage is 400 Kev. The total neutron yield obtained was about 5 x 10^8 neutrons/sec. The neutron yield remained fairly constant throughout the irradiation, sometimes increasing slightly due to build up of deuterium in the target.

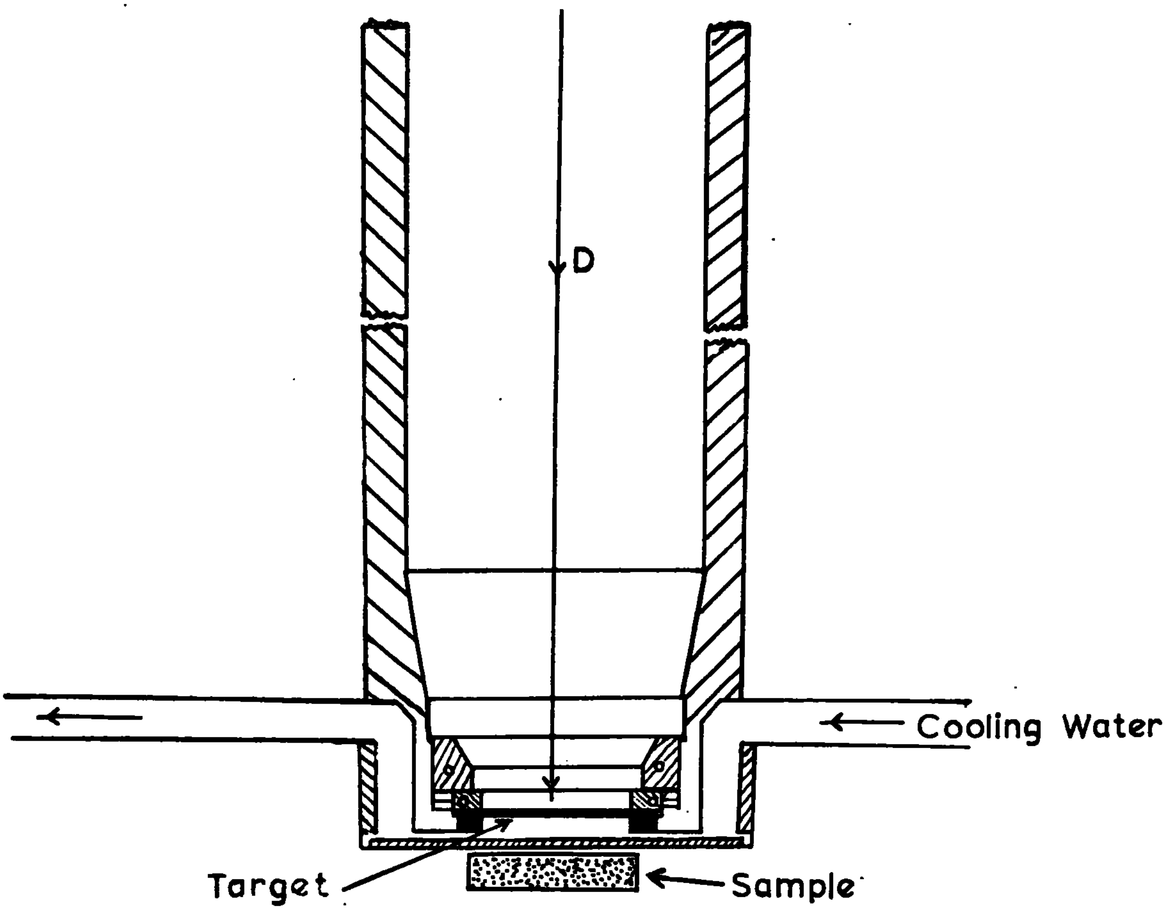

Fig. 2 Target Assembly

Due to the thickness of the metal and of cooling water behind the target disc, it was not possible to put the sample very close to the target for irradiation. This reduces the neutron flux at the sample. The target assembly is illustrated in Fig. 2. The energy of the neutrons under the irradiation conditions was estimated to be 3.0 ± 0.4 Mev.[57]

3. General Method for calculating Relative Yields:

It has been stated earlier that the 14-Mev neutron generator does not produce a steady neutron flux. An allowance must be made for this on the rate of production of each fission product nuclide studied, in addition to correcting for radioactive decay over the duration of the irradiation.

Let us consider an irradiation of duration T, and suppose that a nuclide 1 is isolated at time t' after the end of the irradiation.

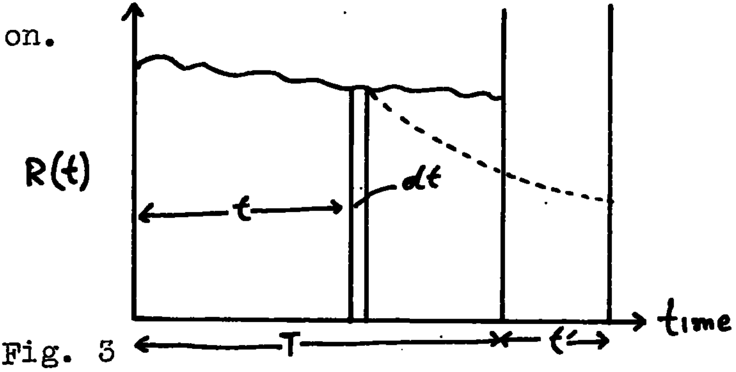

Fig. 3

(a) Suppose that the precursors of the nuclide I in the chain:

$$\longrightarrow 1 \xrightarrow{\lambda_1} 2 \text{ (stable)}$$

are short lived compared with T and t'. Throughout the irradiation the nuclide 1 is produced at an irregular rate R(t). During the short time interval dt the number of nuclei of 1 which are produced will be

$$dN_1 = R(t).dt$$

and these will decay exponentially, so that at the time of isolation (t') the number remaining will be

$$dN_1(t') = R(t).e^{-\lambda_1 \left[t'+(T-t) \right]}.dt$$

$$= e^{-\lambda_1 t'}.R(t).\ e^{-\lambda_1 (T-t)}.dt$$

The total number of nuclei of the species 1 remaining at the time of isolation will be

$$N_1(t') = e^{-\lambda_1 t'} \int_{t=0}^{t=T} R(t).\ e^{-\lambda_1 (T-t)}.dt$$

Now the rate of production of nuclide 1 is given by

$$R(t) = B.\ \sigma_f\ Y_1\ \phi\ (t)$$

where, B = a constant depending on the quantity of fissionable material irradiated,

σ_f = fission cross-section of the irradiated nuclei,

Y_1 = fission-yield of nuclide 1,

$\phi(t)$ = neutron flux through the irradiated sample.

The counting rate of the neutron monitor, $I(t)$, which was recorded, is directly proportional to the neutron flux, and hence proportional to $R(t)$

$$R(t) = B.\ \sigma_f.\ Y_1.\ I(t)\ /\theta$$

where θ= efficiency of the neutron monitor.

Thus,

$$N_1(t') = \frac{B.\ \sigma_f.\ Y_1.}{\theta}\ e^{-\lambda_1 t'} \int_{t=0}^{t=T} I(t).e^{-}\ 1^{(T-t)}dt.$$

The integral can be replaced by the summation:-

$$S_1 = \sum(\ Ie^{-\lambda_1(T-t)}.\ \delta t$$

Provided δt intervals taken are very much shorter than the half-lives of the species concerned. Thus,

$$N_1(t') = \frac{B.\ \sigma_f.\ Y_1}{\theta}\ .\ e^{-\lambda_1 t'}\ S_1$$

Similarly, if a reference nuclide r is isolated at a time t", we have:

$$N_r(t'') = \frac{B.\ \sigma_f.\ Y_r}{\theta}\ .\ e^{-\lambda_r t''}.\ S_r.$$

Thus,

$$\frac{N_1(t')}{N_r(t'')} = \frac{Y_1.e^{-\lambda_1 t'}.\ S_1}{Y_r.e^{-\lambda_r t''}.\ S_r}$$

By extrapolation of the decay curves the activities of the isolated species at the end of the irradiation, A^o, can be determined. Then since $A^o = N^o.\lambda.\eta.$; we have,

$$\frac{A_1^o}{A_r^o} = \frac{Y_1.S_1.\lambda_1.\eta_r.}{Y_r.s_r.\lambda_r.\eta_r.}$$

η_1, η_r = efficiencies of the end window counter for the nuclides concerned.

or, $$\frac{Y_1}{Y_r} = \frac{A^o{}_1.\Upsilon_1.s_r.\eta_r.}{A_r^o.\Upsilon_r.s_1.\eta_1.} \qquad \text{.......(1)}$$

where Υ_1 = half-life of the nuclide 1,

Υ_r = half-life of the nuclide r,

The above equation was used in calculating the relative yields of fission products of thorium measured in the current investigation. The values of S_1 and S_r were calculated from the readings of the neutron monitor during the irradiation. Values for A^o were obtained by extrapolating the decay curves of the fission product sources counted to the time of the end of irradiation and applying correction for chemical yield. Values for η_1 and η_r were obtained from the counter efficiency curves.

(b) Where the half-life of the immediate precursor of the isolated fission product is not negligible compared with that of its daughter, an account must be taken of this in calculating the relative yields.

Let us consider the chain:-

$$\text{(short)} \longrightarrow 1 \xrightarrow{\lambda_1} 2 \xrightarrow{\lambda_2} 3 \text{ (stable)}$$

in which λ_1 and λ_2 are comparable and the species 2 is isolated at a time t' after the irradiation. Using the same notation as above,

$$N_2(t') = \frac{\lambda_1}{\lambda_2 - \lambda_1} \cdot e^{-\lambda_1 t'} \int_{t=0}^{t=T} R(t) e^{-\lambda_1 (T-t)} dt$$

$$dt = e^{-\lambda_2 t'} \int_{t=0}^{t=T} R(t) e^{-\ \ {}_2 (T-t)} dt.$$

and also

$$N_2(t') = \frac{B\ \sigma_f\ Y_1}{\theta} \cdot \frac{\lambda_1}{\lambda_1 - \lambda_2} \left(e^{\lambda_1 t'} S_1 - e^{\lambda_2 t'} S_2\right)$$

If t' is long enough compared with the half-life of the species 1,

$$N_2^0 = \frac{N_2(t')}{e^{-\ \ {}_1 t'}} = \frac{B \cdot \sigma_f \cdot Y_1}{\theta} . \quad \frac{\lambda_1}{\lambda_1 - \lambda_2} \cdot S_2$$

Since $A^0 = {}_2 N^0{}_2 / h_2$ the value of the activity of the species 2 in equation (1) must be multiplied by the factor $\dfrac{\lambda_1 - \lambda_2}{\lambda_1}$ to allow for the effect of the comparative half-lives of species 1 and 2.

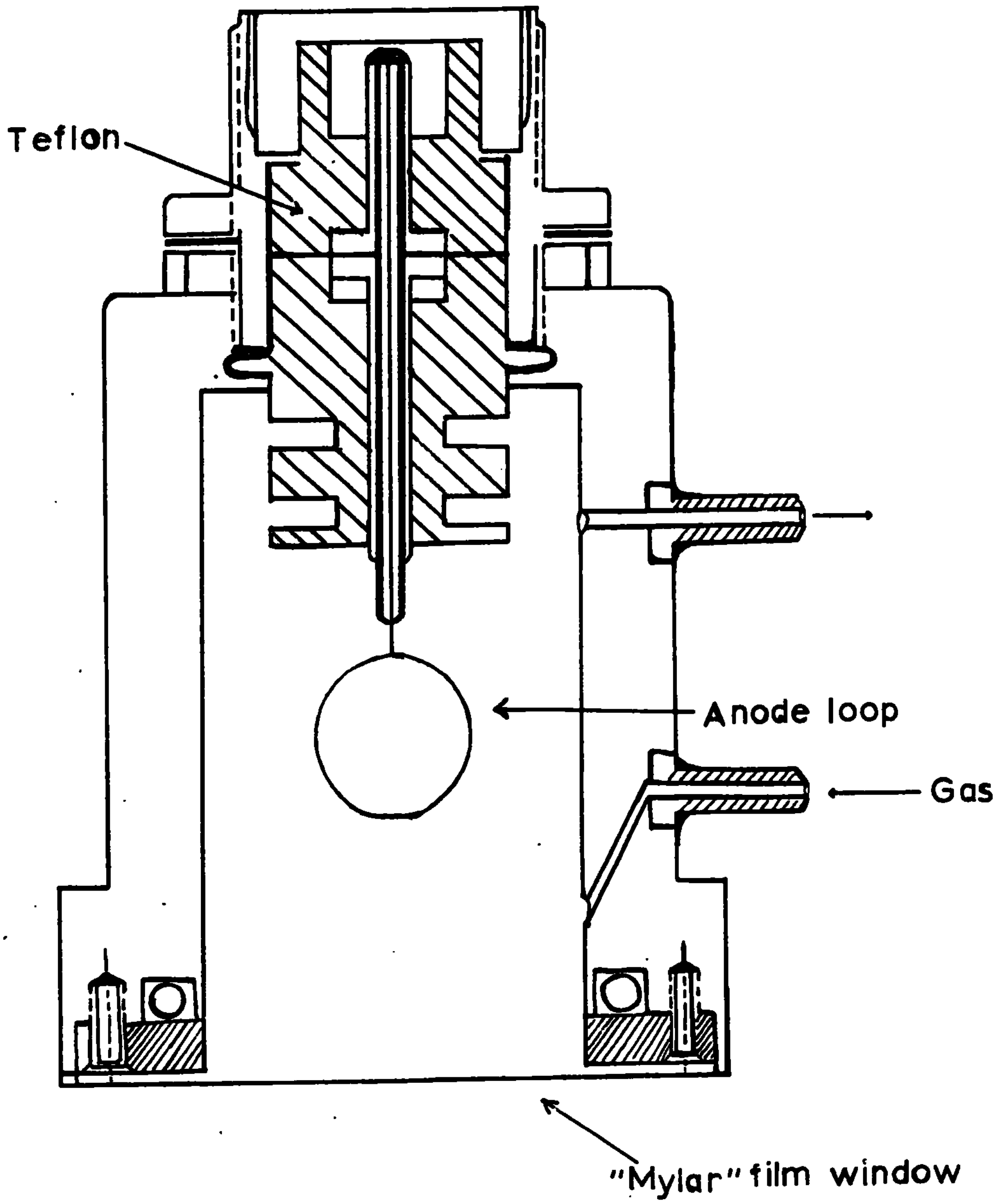

Fig. 4— End-window Gas-flow β-proportional Counter

4. The End-window Gas-flow β-proportional Counter:

For counting the activity of the separated and purified isotopes the end-window gas-flow proportional counter is used. The counter which is cylindrical in shape is constructed mainly of brass. The anode is a circular loop of 10 cm diameter constantan wire of 0.001 inch in diameter. This is soldered to the terminal of a nickel tube which is supported by a single teflon insulator in the top of the counter. (Fig. 4) The window of the counter is 2.6 cm in diameter and is made of thin (1 mgm/cm^2) 'Melinex Film'. The film is supported on a brass ring of appropriate size that can be screwed to the end of the counter tube. The window is gold coated on its interior side in order to conserve a uniform electric field inside the counter.

The counter tube is fixed on a stand with a standardised shelving arrangement for placing the solid source on aluminium planchets for counting. The counter together with the stand is housed inside a lead castle to keep external interference to a minimum.

The E. H. T. supply which is obtained from a filtered 2 kV line is connected to the anode through a high resistance of 1.5 megohms. via a potentiometer.

The pulses from the counter are first passed to a

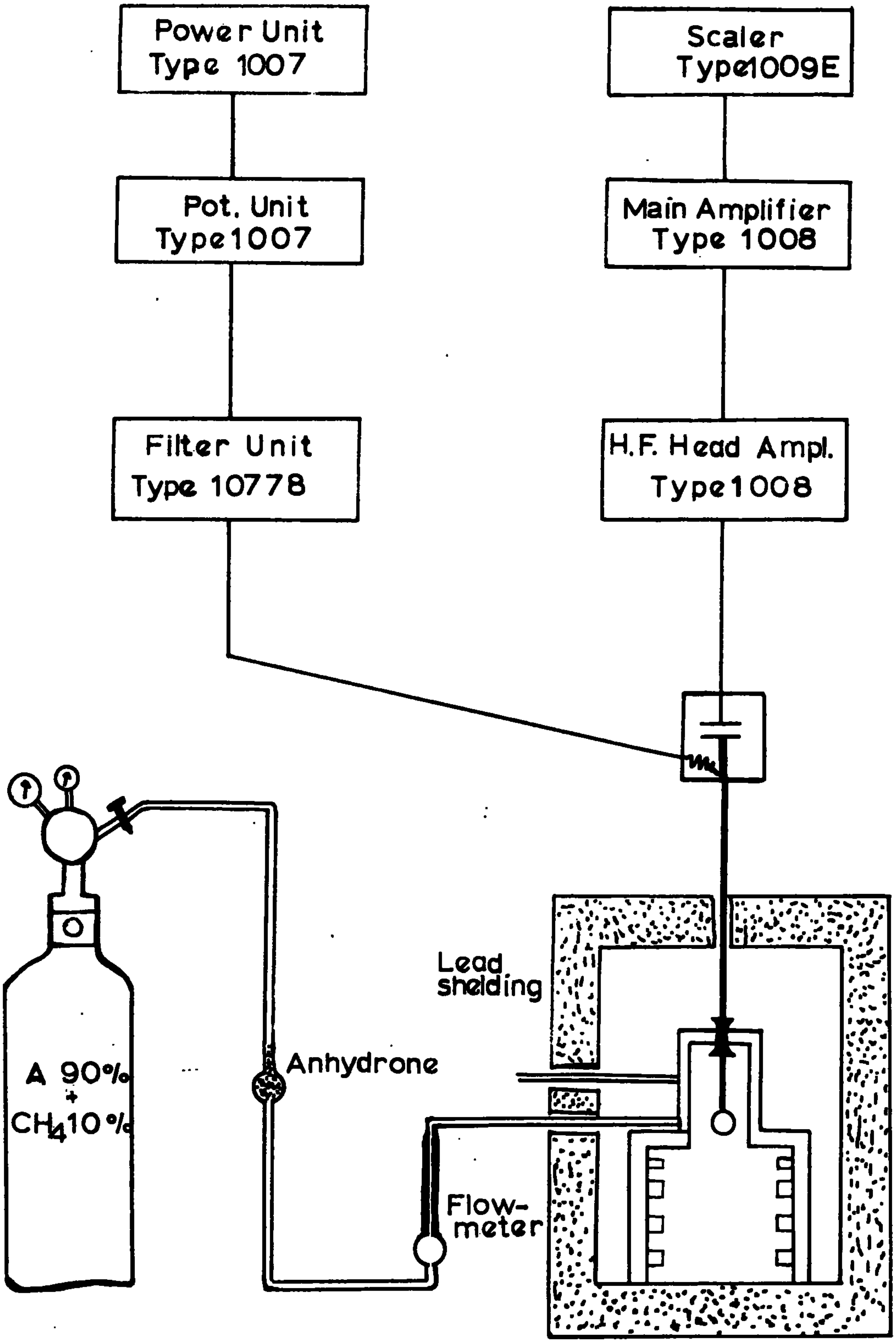

Fig. 5. Gas-flow system and electronics for the end-window β-proportional counter.

pre-amplified and then to the main amplified. The overall amplification is ~~of~~ about 5 x 10^6. Pulses thus amplified are passed through a discriminator so as to eliminate the smaller noise pulses from the amplifiers. The output pulses from the discriminator are finally fed into a scaling unit for electromechanical registering. A block diagram of the system is given in Fig. 5.

The optimum working conditions for the particular counter used are tabulated below:

H.F. Head Amplifier Type 1008.
Main Amplifier Type 1008.

Differentiation Time = μ0.4 sec.
Integration time = μ0.4 sec.
Attenuation = 10 db.

Scaler Type 1009E.
Paralysis time = 50μsec.
Disc. Bias =15volts.

E.H.T. for counting = 1.85 kV.

With the above setting a pleateau of about 250 volts was obtained with slope of less than 5%/100 volts. The background counts varied from 10-17 per minute. The reproducibility of the counting measurements were frequently checked by counting a standard source. The standard count was found to vary within the range of ± 1.5% of the counting rate of 8500 c.p.m. for a 5 minute counting interval.

Occasional sources of spurious pulses in the counter were due to electrical breakdown of the counter insulation, due to humidity or faulty connections. Breakdown due to humidity was got rid of by washing with methanol and drying the teflon part of the counter and their associated connections using a hot air drier. When needed, different parts of the counting system were isolated to find the faulty connections and were replaced.

In ~~the~~ following the decay of any long-lived nuclide, the sample was counted at reasonable intervals for a sufficient time to keep the standard deviation to a minimum. For short lived species the counting was continuous till the decay was almost complete. In the latter case, the output from the scaler was transfered to a device which recorded a preset number of counts and time intervals in minutes on a paper tape. Appropriate decay curves were drawn from the recordings on the tape.

5. The 4π-proportional Counter:

In order to determine the absolute disintegration rates of the samples counted in the end-window counter, a calibration is required and this was done using a 4π-proportional counter. The 4π-counter used in the present investigation is of the type described by Hawkins

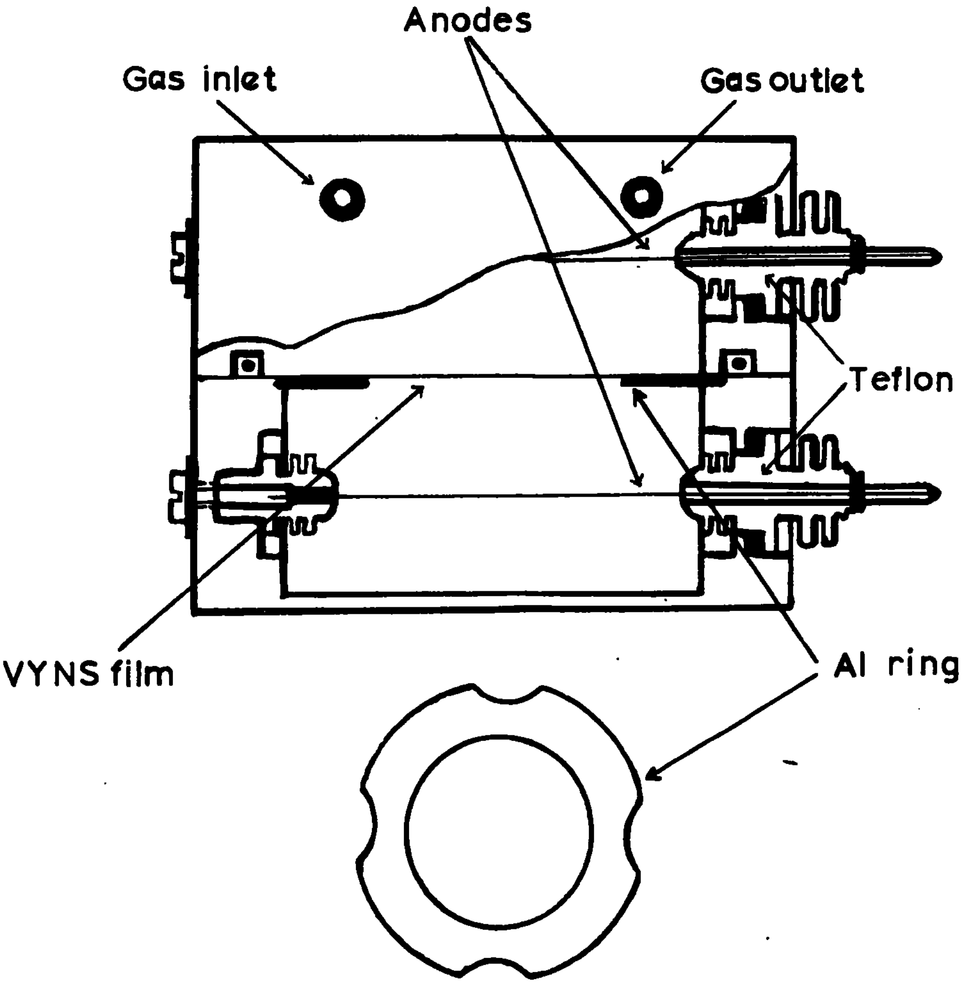

Fig. 6. 4π-Counter

and illustrated in Fig. 6. The 4π geometry is achieved by mounting the source on a thin film which becomes the partition between two counters. The source supports consist of thin VYNS films supported on aluminium rings which fitted in sandwich fashion between the counters. The gas flow system and the electronics used for 4π-counting were identical to those associated with end-window counting.

6. Source preparation for end-window counting:

The conventional procedure for determining the activity due to a particular isotope in a sample consists in adding a known amount of an inactive isotopic carrier, ensuring that isotopic exchange has been effected between the active and the inactive materials, and separating the carrier together with its radioactive species by conventional chemical methods. After suitable purification the amount of inactive carrier surviving the purification scheme is determined and it is assumed that the same proportion of the radioactive species is also carried through. The final step is to precipitate the element in a suitable gravimetric form for chemical yield determination and counting. Where it is not possible to obtain such a stoichimmetric chemical compound for gravimetric determination the yield may be determined by analysing the source after counting is completed. This will be discussed in detail in connection with the chemical yield determination of the rare-earths.

About 10 mg. of the carriers were used and the final purified material was precipitated in a suitable insoluble form. The precipitate was transferred to a weighed Whatman GF/A, 2.1 cm diameter filter disc. Before using these glass fibre discs for collecting the precipitate they were subjected to the same treatment as was used for washing and drying the precipitate. During filtration the disc was supported on a sintered polythene support in a demountable filter stick. The precipitate in the form of slurry was filtered through it whereby a circular disc of reproducible geometry of the precipitate could be obtained. After washing the precipitate with aqueous wash-solution, alcohol and ether in turn, the disc with the precipitate was removed from the filter stick and placed flat on an aluminium planchet. It was then dried in a vacuum desiccator and weighed accurately to the nearest 0.01 mg. for chemical yield determination. For counting the sources prepared as above, they were placed flat on aluminium planchets with a slightly raised rim (internal diameter $\sim$2.2 cm.) and weighing about 80 mg/ cm^2. An investigation into

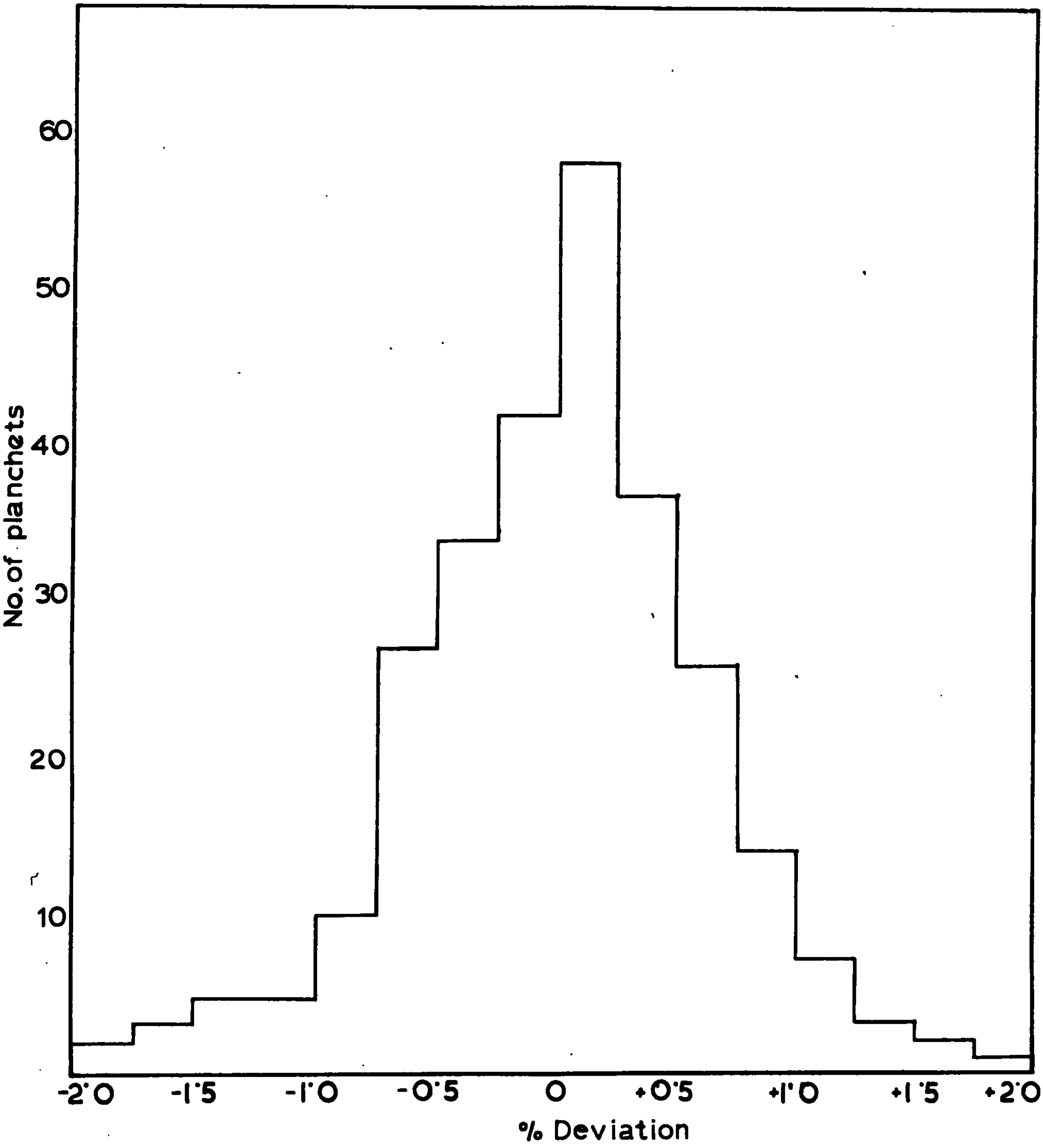

Fig. 7. Histogram of standard deviation from the mean counting rates of a P^{32} source counted on a series of Al planchets

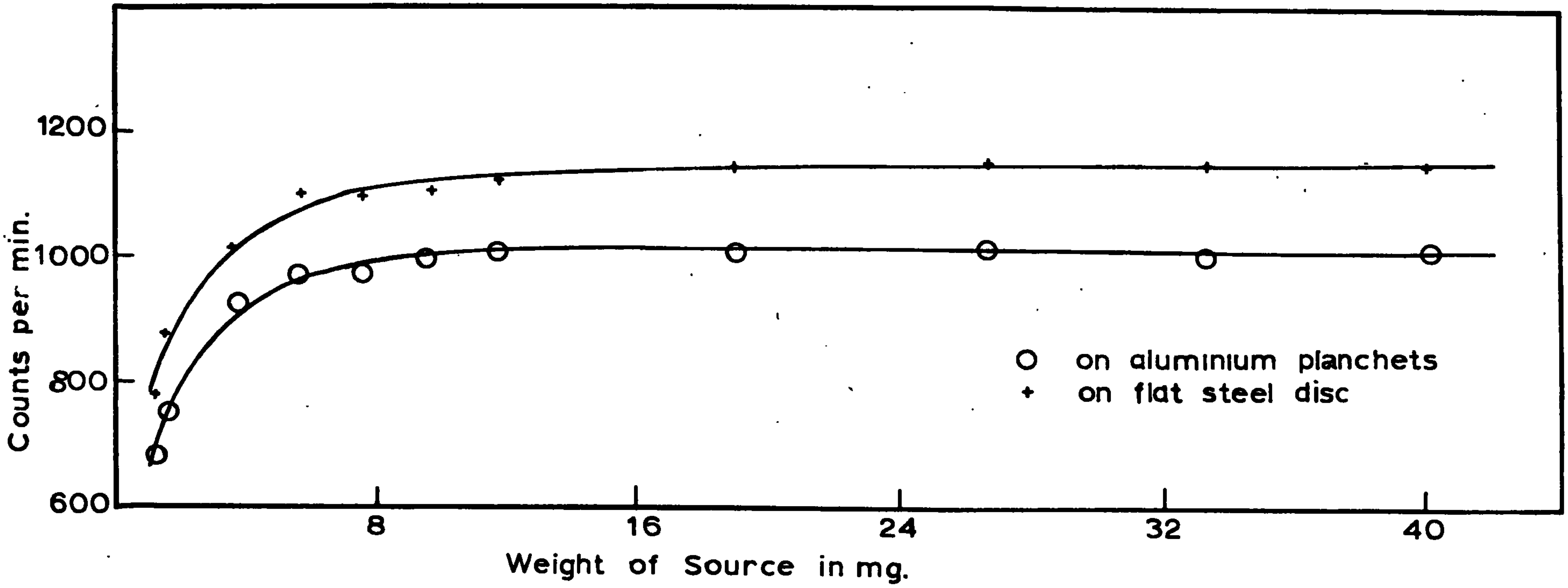

Fig.8. Counting rate as function of source weight mounted on different source supports.

of counts with the weight of the precipitate in both cases was identical. (Fig. 8). The higher counting rates for sources mounted on flat discs are due to the decrease of distance between the source and counter window. On the other hand, the fixing of sources on the flat discs with reproducible geometry was very inconvenient and time consuming. Again while flat discs might be convenient for micro-gram amounts of carrier, for handling 5 to 10 mg. of carrier materials, aluminium planchets have advantages over the flat discs. Another major requirement and hence a disadvantage of the thin source type measurement is the need for individual methods of analysis suitable for the accurate determination of very small amounts of material for chemical yield determination.

7. Calibration of the end-window counter

The procedures to obtain calibration curves for the end-window counter were as follows:-

Solutions of high specific activities of the nuclides for which the counter requires to be calibrated were obtained either from mixed fission products, by (n,γ) reaction or directly purchased from the Radiochemical Centre, Amersham, U.K.

Standards from this carrier free solution were mounted on VYNS films as described by Pate and Yaffe.[59] The films were about 20 $\mu g/cm^2$ thick and coated by an evaporation procedure with about 5 $\mu g/cm^2$ of gold on their lower surface. A few drops of dilute insulin solution were evaporated on the upper surface of the films to facilitate an even spreading of the active solution. Weighed amount of the carrier free solution was then put on the film and dried under an infra red lamp. They were counted in the 4 π-proportional counter.

A known amount of the standardized carrier free solution is added to a known amount of carrier solution of the element concerned and steps are taken to ensure complete isotopic exchange between the inactive carrier and the active species. The carrier was then precipitated in a suitable form for yield determination, thick sources of varying weights were prepared in the standard way, dried, mounted and counted.

Since the specific activity of the source is known by comparison with the standard on VYNS, the counting correction or efficiency was obtained by dividing the observed counting rate in the end-window counter by the absolute disintegration rate obtained from 4 π -counting. A calibration curve is thus plotted for efficiencies measured against source weight. In cases where the nuclide has a short lived daughter, necessary corrections are applied for the contribution of the daughter to the total counting rates of the 4π sources to eliminate the daughter count. Methods for such calculations will be presented for individual cases where appropriate. Both the 4π and solid sources were counted long enough to obtain complete decay curves for resolution.

8. Standardization of rare-earth carriers:*

The radiochemical analysis of a mixture of radioactive materials such as fission products normally involves the addition to the sample a known amount of carriers for the radioactive nuclides to be determined and the determination of the chemical yield of the recovered carriers after radiochemical separation and purification. In most of these procedures, the weight of the carrier added is 10 to 20 mg. and the chemical yield is determined gravemetrically, the final precipitate being collected and mounted in a suitable form for weighing and counting. Though chemical yield determination involves purely relative measurements and

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* This portion has been published in the form of a paper.[60]

hence absolute standardisation of the carrier may not be necessary, it is desirable that carrier concentration should be known to at least within 1%, as this enables a constant check to be maintained on the functioning of the method.

For the standardisation of the rare-earth carriers to be used in the present investigation, a suitable method applicable to most of the rare-earths was looked for. A survey of the literature revealed that complexones, especially ethylenediamine tetra acetic acid (EDTA) and its salts have been widely applied for the titrimetric determination of yttrium and the rare-earths using visual internal indicators, Methods which have been recommended can be divided into two groups; direct titration and back-titration. The direct titration has obvious advantages but the accuracy attainable in such procedures is not always appreciated and the back-titration procedures are sometimes recommended or used where they need not be. Moreover, the direct methods have not been reviewed critically, and adequate grounds for making a satisfactory choice of a method for a particular purpose are often lacking. An attempt was, therefore, made to compare a number of indicators and buffer systems previously recommended by different authors for such titrations. Relevent information pertaining to these systems is collected and summarised in Table 1.

All the indicators referred in the table were examined except Naphthyl Azoxine S, (7-(6-sulpho-2-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid), and Snazoxs, (7-(4-sulpho-1-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid). From the account in the original papers, these indicators are used and behave in exactly the same way as does Naphthyl Azoxine, 7-(1-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid, which was therefore selected to represent methods 5, 6 and 7 in the investigation.

Preliminary titrimetric work showed that Arsenazo, 3—(2-arsonophenylazo)4,5-dihydroxy-2,7-naphthalene disulphonic acid, trisodium salt and Bromopyrogallol Red, dibromopyrogallolsulphonephthalein were decidedly less satisfactory as indicators than the others referred to in Table I. Arsenazo was found to be very pH sensitive end-points were somewhat erratic at constant pH, and the colour change left much to be desired. With Bromopyrogallol Red the colour contrast was rather poor, and end-points were somewhat unpredictable and sluggish, particularly at metal ion concentrations greater than about 5 x 10^{-4}M. End-points were sluggish irrespective of whether titrations were performed into hot or cold solutions. The relatively poor performance of this indicator has previously been commented upon by Asensi Mora[72] who suggested Pyrocatechol Green (3,6-dihydroxy-9-o-sulphophenylfluorene-4,5-quinone) instead. Because of the considerable errors quoted for light lanthanon determinations using the latter indicator, no attempt was made here to compare it with other indicators.

Cerium, yttrium and ytterbium were selected to represent the main groups of rare earths (excluding scandium), and a study was made of the indicator colour change at the end-point, precision, accuracy, buffering

TABLE I.- Summary of Methods Previously Recommended for the Direct Titration of Yttrium and the Lanthanons.

	Indicator	Titration conditions	Colour change	Refs.
1.	Alizarin Red S (C.I. 1034) screened with Methylene Blue	pH 4, CH_3COONH_4 buffered in hot solution	red→ grey→ green	61, 62
2.	Arsenazo	pH 5.0-6.5 pyridine buffer in hot solution	violet→ orange — red	63

TABLE I.- (continued)

	Indicator	Titration conditions	Colour change	Refs.
3.	Bromopyrogallol Red	CH_3COONH_4 buffer in the cold	blue→ red	64
4.	Eriochrome Black T (Solochrome Black T; C.I. 203)	(a) pH 8-9 in boiling tartrate or citrate soln.	red→ blue	65
		(b) TEA at pH 7		65, 66
5.	Naphthyl Azoxine	pH 5.5-6.5 with Cu present; CH_3COONH_4 or pyridine buffer	yellow→ red	67
6.	Naphthyl Azoxine S	As for 5	as for 5	68
7.	SNAZOXS	pH 6 with Cu present; pyridine buffer	yellow→ red	69
8.	Xylenol Orange*	(a) Acetate buffer pH 5 + 1 drop pyridine	red→ yellow	70
		(b) pH 4.5-6 with hexamine buffer		

* 3,3'-bis N,N-di(carboxymethyl)-aminomethyl -o-cresolsulphonephthalein.

and working pH range applicable to each of the remaining methods (1, 4, 5 and 8) in Table I.

Experimental

Standard solutions

Cerium^{III}: A 0.05 M solution was prepared by dissolving 27.4 g of analytical-grade ammonium nitratocerate IV in water, reducing with hydroxylamine hydrochloride and diluting to 1 litre with water and a little nitric acid. It was standardised by precipitating as cerium^{III} oxalate, igniting and weighing as CeO_2.[73]

Yttrium and ytterbium: 0.05000 M solutions were prepared by dissolving 5.646 and 9.852 g of their respective trioxides (from L. Light and Co., England, 99.9% pure) in separate 20 ml. portions of concentrated hydrochloric acid and diluting each to 1 litre with water.

Standard 0.01 M solutions of cerium^{III}, yttrium and ytterbium were prepared by dilution of the above solution.

Zinc: A 0.1 M solution was prepared from a weighed quantity of analytical-grade granulated zinc dissolved in a slight excess of dilute hydrochloric acid. Before weighing, the zinc was stirred with very dilute hydrochloric acid to remove surface oxide, washed well with water, alcohol and ether and dried at 50°.

Copper^{II}: A 0.005 M copper nitrate solution was prepared from analytical-grade hydrated copper^{II} nitrate in water.

EDTA: A 0.1M solution was prepared by dissolving about 37 g. of analytical-grade $C_{10}H_{14}O_8N_2Na_2.2H_2O$ in 1 litre of water. It was shown to be 0.1005M by standardising against the 0.1M zinc solution using Zincon, (2-carboxy-2'-hydroxy-5'-sulphoformazylbenzene), as indicator.[74] 0.01M EDTA solutions used in the titrimetric work were prepared by diluting this stock solution with water.

Buffer solutions

For pH values within the range 4.5-6.5, 0.2M acetic acid and 0.2M sodium acetate solutions were mixed in the calculated ratios. For values within the range 6.5-8.0 a 10% solution of hexamethylenetetramine was added in the appropriate amount to the solution to be titrated. In titrations with Eriochrome Black T, triethanolamine (TEA) was used to raise the pH initially, and ammonium acetate was added for additional buffering as required. Buffer pH 10 was made from 570 ml. of aqueous ammonia (sp. gr. 0.88) and 70 g. of ammonium chloride made up to 1 litre with water.

Indicators

Chemical indicators were obtained either from

British Drug Houses, England (B.D.H.) or Hopkin and Williams, England (H.W.) and were used as supplied.

Alizarin Red S screened with Methylene Blue (H.W.): 45 ml. of 0.5% ammonium alizarin sulphonate were mixed with 15 ml. of 0.1% methylene blue in water.

Arsenazo (B.D.H.): 0.5% in water.

Bromopyrogallol Red (B.D.H.): 0.05% in 1:1(v/v) ethanol-water mixture.

Eriochrome Black T (B.D.H.): (a) 1% in 1:1 (v/v) ethanol-triethanolamine mixture, or (b) 0.5 g. of indicator and 4.5 g. of hydroxylamine hydrochloride made up to 100 ml. in ethanol.

Naphthyl Azoxine (H.W.): 1% in dimethylformamide.

Xylenol Orange (B.D.H.): 0.1% in 1:1 (v/v) ethanol-water mixture.

Zincon (H.W.): 0.13 g. of indicator dissolved in 2 ml. of 0.1M sodium hydroxide and diluted to 100 ml. with water.

Selection of optimum titration conditions

Five-ml samples of the standard 0.01M rare earth solutions, under varying buffer conditions and in a final volume of about 50 ml. were titrated with 0.01M EDTA. Approximate upper and lower pH limits within which the indicator could be expected to function were determined by taking a titrated metal-containing sample and with the aid of a pH meter noting the values when the indicator showed a significant pH response on raising or lowering the pH. pH values of solutions to be titrated were set with the appropriate buffers around the crude limits thus obtained, and titrations were performed, end-points and colour changes being noted. In this way pH ranges were established within which the titration could be carried out with little uncertainty about the end-point, although colour changes might not be the best attainable with the indicator. Optimum conditions of pH were then determined by performing titrations within the range. All pH measurements were made at 20 to 25°.

Tests on the precision and accuracy of the various methods were made by carrying out replicate titrations (10 for each method with each metal ion) on 25-ml. portions of 0.01M metal solutions in a total volume of 250 ml. under optimum pH conditions. As a measure of the dispersion of titre values about the mean for each series, the standard deviation was determined. The mean titres were compared with the required calculated titres. The same burette and pipette (both grade A) were used throughout in these titrations. Dilutions of stock rare earth and EDTA solutions were made with the pipette mentioned, and with two standard flasks, all three of which were intercalibrated.

In all titrations involving cerium, a reducing agent was present. Hydroxylamine hydrochloride and ascorbic acid were equally satisfactory for this purpose.

Results and Discussion

Working and optimum pH ranges are recorded in Table II for each of the three metal ions, with each of the four indicators and buffering systems compared. The pH ranges applicable to a particular indicator do not vary greatly from metal to metal titrated, a fact of use in determining mixed rare earths, excluding scandium. Table III permits comparison between required and experimental titres, and of standard deviations. It will be seen that all of the four methods are, in general, capable of giving quite precise and accurate results.

Alizarin S screened with methylene blue is quite satisfactory for light and middle lanthanon fractions, but the results presented here suggest that it would give slightly early end-points in the titration of heavy rare earths. The titration is best performed in near boiling solution, otherwise the end-point approach is quite slow. Eriochrome Black T should be suitable for titrating the lanthanons and yttrium in the pH range indicated in Table II with reliable results. If required, the pH can be adjusted by adding 1 drop of 1% methyl red indicator to the metal solution and raising the pH to the colour change with TEA before adding the metal indicator. Ammonium acetate may be added for additional buffering.

TABLE II.- Working and "Optimum" (in Parenthesis) pH Ranges for Titrations

Indicator	pH Range Ce^{III}	Y	Yb
Screened Alizarin Red S	4.5-5.5 (4.7-5.3)	4.6-5.5 (4.7-5.3)	4.6-5.5 (4.7-5.4)
Eriochrome Black T	6.5-7.5 (6.7-7.2)	6.5-7.5 (6.7-7.2)	6.5-7.5 (6.7-7.2)
Naphthyl Azoxine	5.4-7.6 (5.5-6.0)	5.3-7.6 (5.5-6.0)	5.4-7.6 (5.5-6.0)
Xylenol Orange	5.0-6.5 (5.8-6.4)	5.1-6.5 (5.8-6.4)	5.1-6.6 (5.8-6.4)

The colour change is then from red to greenish-blue. There is no advantage in performing titrations in hot rather than cold solution. The end-point reading should be taken when all reddishness has just permanently disappeared from the solution. Although Eriochrome Black T can be used up to about pH 9.3, end-points are attained only very slowly about pH 8 in hot solution with TEA, citrate or tartrate being present to prevent hydrolysis of the metal ions. In titrations with Naphthyl Azoxine, end-point detection results from indicator-copper-EDTA interaction. The standard deviation is caused by a combination of the dispersions in the lanthanon + copper titre and the copper titre alone. The necessity for a blank titration on the copper alone makes this method little more attractive than a back-titration. An advantage of this method is that titrations are performed in the cold. The indicator is quite sensitive, but, however the colour contrast is not all that might be desired. Better end-points are also obtained by adding the copper towards the end of the titration rather than just before the beginning.

As is seen from Table III, Xylenol Orange gives accurate, and also very precise, titres. Of the indicators examined for the direct titration it is, in our opinion, the most satisfactory. The titration can be performed in the cold, but the end-point can be approached more quickly in warm solution. Preliminary pH adjustment of acid solutions can be made by adding 1 drop of 0.1% Thymol Blue indicator, then aqueous ammonia until the indicator is about to change to yellow. Addition of buffer then gives optimum titrating conditions. Care is needed when hexamethylenetetramine is used as buffering agent, because addition of too much will raise the pH about the titration range. It may also be noted that there is a discrepancy between the previously recommended pH range for this titration (Table I) and the range found to be satisfactory in this work (Table II). Of the commoner anions, chloride, nitrate, perchlorate and sulphate (at least up to 1M) do not interfere in these methods, but acetate interferes in concentrations about 1M, and solutions containing oxalate cannot be titrated satisfactorily by direct methods. In standardising the rare-earth carriers, xylanol orange was therefore used as an indicator in the present work.

TABLE III.- "Required" and Mean Titres Obtained Under "Optimum" pH Conditions on Titrating 25 ml. of Standard 0.01M Metal Ion with 0.01005M EDTA (Standard Deviations in Parentheses)

	Titre, ml. of 0.01005M EDTA					
Indicator	Ce^{III}		Y		Yb	
	Reqd.	Found	Reqd.	Found	Reqd.	Found
Screened Alizarin Red S	24.82	24.82 (0.02)	24.88	24.88 (0.02)	24.88	24.83 (0.02)
Eriochrome Black T	24.82	24.83 (0.02)	24.88	24.91 (0.02)	24.88	24.86 (0.03)
Naphthyl Azoxine	24.82	24.83 (0.02)	24.88	24.89 (0.02)	24.88	24.87 (0.03)
Xylenol Orange	24.82	24.82 (0.01)	24.88	24.90 (0.01)	24.88	24.87 (0.01)

9. Analysis of rare-earth oxalate sources for chemical yield determination*

In radiochemical analysis oxalic acid is commonly used to precipitate yttrium and the lanthanons from acid solution, for source preparation and chemical yield determination. Because of the variable composition of the product, it is usual in classical quantitative analysis to ignite the resulting precipitate to the metal oxide or to determine the metal indirectly by permanganate titration of the oxalate.[75,76] The former method is slow, and the latter depends on being able to obtain a constant and known ratio of metal to oxalate in the precipitate; in any case, it cannot be used satisfactorily for cerium without prior separation of the metal.[77]

For isotope-dilution analysis, particularly of fission-product yttrium and lanthanons, using an end-window proportional or Geiger-Müller counter, Ballou[78] showed that chemical yields could be measured to within a few per cent by direct weighing of the metal oxalate, precipitated and dried under carefully controlled conditions. However, with demands for improved accuracy, and accumulation of information on the thermal stability[79] of the hydrates of these metal

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*This portion has been published in the form of a paper.[60]

oxalates, it is more recent practice to ignite the oxalate to the oxide, and from this to prepare a solid radioactive source for counting.[80,81] The last-mentioned operation is not without its difficulties if a uniform source of moderate thickness, reproducible geometry and known composition is to be obtained from the oxide. Oxalate is the most frequently used precipitant for yttrium and the lanthanons and, gives a deposit which, apart from its composition, is satisfactory. (For example, 8-hydroxyquinoline gives gelantinous deposits which shrink and crack excessively during the drying process). It is not expected that the variation in composition (amounting to perhaps 5% in terms of metal present) encountered in these oxalate precipitates will affect corrections for self-absorption of radioactivity, but in order to measure chemical yields a simple and reliable method is desirable for determining the metal content directly. Such a "direct" method would also have advantages in determining rare earth contents of oxalate precipitates generally.

Complexometric titration offers considerable scope for performing such analyses. Because oxalate interferes in the direct titration of yttrium and the lanthanons with EDTA, it must be destroyed or otherwise removed before the titration. This can be done by wet-oxidation methods; or by decomposition with alkali[82] and separation by filtration;

the latter is a process too slow to merit serious consideration for routine purposes. An alternative method is that described by Misumi and Taketatsu,[83] in which the precipitate is dissolved in an excess of EDTA and the excess is back-titrated with magnesium at pH 10.2-10.5. In the work to be described, both approaches have been used; and in addition the use of zinc in place of magnesium in the back-titration is investigated. Another back-titration method, previously used[84] in the absence of oxalate, in which the excess EDTA is back-titrated at pH 8-9 with lanthanum and Arsenazo indicator, has been examined for determinations in the presence of oxalate. Some oxalates have been prepared, and the metal contents have been determined.

EXPERIMENTAL

Reagents

Magnesium: A 0.01M solution was prepared from analytical-grade $MgSO_4.7H_2O$, and was standardised with EDTA using Eriochrome Black T indicator.[85]

Lanthanum: A 0.01M solution was prepared from reagent-grade hydrated lanthanum chloride (British Drug Houses, England), and was standardised with EDTA, using Xylenol Orange indicator.

Praseodymium: A 0.01M solution was prepared by weighing out an appropriate quantity of the trioxide

(L. Light & Co., England, 99.9% pure) and dissolving in a minimum of hydrochloric acid.

All other reagent solutions were prepared as described previously (see page 40).

Titration of yttrium and lanthanon oxalates without prior removal of oxalate

To a 5 ml portion of each metal in solution a measured excess of standard EDTA (10 ml) was added, and the excess was determined by titrating in a total volume of 50 ml with either 0.01M magnesium or 0.01M zinc solution to a colour change from blue to red with Eriochrome Black T indicator. The titrations were repeated with the addition of an amount of oxalate calculated to be sufficient for precipitation of all of the metal ion. As recommended in the original procedure for magnesium, the solution to be titrated was buffered between pH 10.2 and 10.5, using buffer pH 10 and aqueous ammonia, and with the assistance of a pH meter. Buffer pH 10 provides adequate buffering and control of pH for titrations with zinc.

When lanthanum was used as back-titrant in conjunction with Arsenazo as indicator, the pH was adjusted using ammonium chloride and buffer pH 10, with the aid of a pH meter or phenolphthalein indicator as recommended by Wolfsberg. The solution, total volume about 50 ml, is brought almost to boiling and titrated with lanthanum until the indicator changes from pink to violet.

For freshly prepared oxalate precipitates addition of buffer and the excess EDTA is sufficient to cause rapid solution. However, precipitates filtered off, dried by the method described by Ballou or above 100°, and kept for some time, are somewhat more resistant to dissolution. Such "aged" precipitates are conveniently dissolved by first treating with a little dilute perchloric or hydrochloric acid, adding the EDTA, neutralising with aqueous ammonia, then buffering as required.

Analysis of weighed oxalate samples

Using Ballou's method[78] suitably scaled up, batches of about 50 mg of each rare earth studied were precipitated as oxalate. The precipitate was split up into portions having weights ranging from about 5-65 mg, and each portion was collected on a glass-fibre disc (Whatman GF/A 2.1 cm. diameter) in a demountable filter stick, washed with water, ethanol and finally ether, and was then dried to constant weight in a vacuum desiccator (without desiccant) connected to a water-pump.

For wet oxidant, the weighed oxalate sample, together with the glass-fibre support, was transferred to a 250 ml conical flask and treated with 5 ml of 72% perchloric acid. The temperature was maintained at the decomposition point of the acid for 10-15 min, depending on the sample size. (The time required for oxidation of different sample weights is determined in trial runs by the method suggested by Smith.[86]) The flask was cooled, the contents were diluted to about 25 ml and the acid was neutralised with ammonia to the yellow colour change of thymol Blue. After buffering at pH 6 and addition of water to a final volume of about 150 ml, the contents of the flask were titrated with EDTA, using Xylenol Orange indicator.

Batches of metal oxalate prepared as described above were also analysed for metal content by the back-titration method without removal of oxalate, using zinc as titrant. About 5-10 ml of 0.01M EDTA in excess of that required to complex the metal ion was added before each titration.

RESULTS AND DISCUSSION

Table IV records results obtained on titrating known amounts of yttrium and various lanthanons by the methods which do not require removal of oxalate ion. They may be compared with results obtained by titrating directly with EDTA the same amounts of metal ion, in the abbence of oxalate, using Xylenol Orange indicator (column 2, Table IV). It will be seen that both magnesium and zinc as back-titrants give highly satisfactory results. On the other hand, the colour contrast with Arsenazo in back-titrations with

TABLE IV: Determination of Yttrium and some Lanthanons by Various Titration Procedures[a]

Element	Amount present[b] mg	Amount found by back-titration, mg		Back-titrant
		Oxalate absent	Oxalate present	
La	6.95	-	6.96 ± 0.02	Zn
Ce	6.94	6.95 ± 0.02	6.97 ± 0.02	Mg
		6.96 ± 0.02	6.96 ± 0.02	Zn
Pr	4.86	-	4.86 ± 0.02	Zn
Y	4.43	4.41 ± 0.02	4.39 ± 0.02	Mg
		4.43 ± 0.01	4.43 ± 0.01	Zn
Yb	8.65	8.63 ± 0.02	8.62 ± 0.02	Mg
		8.65 ± 0.01	8.64 ± 0.02	Zn
		-	8.58 ± 0.02	La

(a) In each case the mean value and standard deviation of 5 determinations.

(b) Determined by titration using Xylenol Orange at pH 6 in the absence of oxalate

lanthanum in the presence of oxalate is rather poor, and the end-point is sluggish and drawn out, making the true equivalence point somewhat difficult to determine. In addition, the titration is performed in very hot solution, whereas titration with mgnesium or zinc is carried out in the cold using Eriochrome Black T indicator. Of the two last mentioned titrants, zinc is preferred, because it can be used over a wide pH range (9 to 11) and the colour change is appreciably sharper. Although the relative stability constants[87] of the EDTA complexes of lanthanum and zinc are such that the former is a little less stable than the latter, results for lanthanum determination using zinc as titrant are not affected (Table IV).

In Table V, the percentage metal found in oxalate samples of different weights varies over a range of 2-3% for some batches of precipitate. This variation is probably largely associated with the washing, which is done on separate portions of the batch, and with the final drying. However, in rare earth oxalate precipitation many factors contribute to variable composition[88] and hence to the various hydrates reported by different investigators. The desirability of determining the metalcontent of an oxalate,

TABLE V: Analysis(a) of weighed oxalate samples for metal content(b)

1.	Wt. of sample, mg	Y found %,	2.	Wt. of sample, mg	Ce found, %
	14.41	29.4		10.91	39.5
	14.60	29.8		11.32	39.7
	17.63	29.8		23.24	39.4
	26.28	29.7		25.41	38.1
	32.42	29.7		27.20	38.3
	Mean	29.7		Mean	39.0

3.	Wt. of sample, mg	Ce found, %	4.	Wt. of sample, mg	Yb found, %
	4.53	38.2		14.73	51.3
	7.11	38.9		29.81	49.0
	8.71	38.4		30.30	49.5
	15.16	38.3		47.32	48.4
	21.93	39.0		63.66	50.0
	Mean	38.6		Mean	49.6

(a) Batches 1 and 2 were analysed by wet oxidation of the oxalate followed by direct titration with EDTA, 3 and 4 by adding excess EDTA and back-titrating with zinc.

(b) $Y_2(C_2O_4)_3.9H_2O$ requires 29.44% of Y.
$Ce_2(C_2O_4)_3.10H_2O$ requires 38.68% of Ce.
$Yb_2(C_2O_4)_2.5H_2O$ requires 49.42% of Yb.

rather than assuming a formula and calculating the content from the sample weight for the purpose of determining radiochemical yields, is thus obvious, because there may easily be a 5 or 6% variation in the amount of metal in the compound.

Both methods for which results are presented in Table V are satisfactory for the determination of yttrium and lanthanons in oxalate precipitates in the range 2-30 mg of metal; and with suitable scaling up they can be used equally satisfactorily on larger samples. However, oxidation of oxalate with perchloric acid requires nearly 20 min in all to complete a determination, compared to 3-5 min for the back-titration with zinc, all solutions and reagents being to hand. Other oxidants (nitric acid, aqua regia and alkaline hypochlorite or hypobromite) are somewhat less effective and slower than perchloric acid. Sulphuric acid could, however, probably replace the last mentioned oxidant without adding to the time required for complete oxidation. Addition of excess EDTA, and back-titration of the sample with zinc solution in the presence of oxalate ion, therefore has an appreciable advantage over complexometric titration methods requiring removal of oxalate.

The method described above was used in the present work for the determination of chemical yield in the rare-earth oxalate sources.

CHAPTER III

1(a) Initial purification of thorium nitrate for irradiation:

In preliminary investigations for separating added stable isotopes of the elements occurring as fission products from unirradiated thorium samples by following recommended radiochemical procedures it was found that in some cases the final solid source was contaminated by decay products from thorium. The procedures in which the separated elements were found to be contaminated were the rare-earths. In the separation procedure due to similar chemical properties Ac^{228} was found to be in present the separated rare-earths.

In such cases where the daughters of thorium were shown to follow fission products in their separation procedures, it was found more convenient to remove the daughter activities from thorium before irradiation than to separate the induced fission product activities from thorium daughters which followed them after irradiation. It becomes apparent from the thorium series that it is possible to remove the gross daughter activities by repeated scavenging for radium, actinium, lead and bismuth. The purification of thorium was carried out by the method described by Ballou.[89] It consists of scavinging precipitations of barium and lead sulphates to remove radium and lead, bismuth sulphide to remove bismuth and lanthanum carbonate, to remove actinium. The procedure in detail is given in the appendix. After initial purification, 'blank' separation of added carriers gave final sources essentially free from contamination.

(b) The Reference Element - Zirconium.

In the present investigation Zr^{97} was chosen as the reference element in order to correlate the relative yields measured in each experiment. In choosing this fission-product element as reference the following factors were taken into consideration. It is readily isolated from the irradiated thorium sample and its radiochemical purification is easily carried out. The fission yield of Zr^{97} is reasonably high and coupled with the activity of the niobium daughter this ensures adequate counting rates for satisfactory statistical accuracy. Its half-life is also suitable for the length of irradiation and time available for chemistry and counting. The reliability of Zr^{97} as reference element in the fission yield measurements of Th^{232} has been fully investigated by Whitley.[90]

The decay chain for mass 97 is:-

$$\begin{tikzcd}
 & \text{60 sec. } Nb^{97m} \arrow[d] & \\
\text{17 hr. } Zr^{97} \arrow[ur] \arrow[dr] & & Mo^{97} \text{ (stable)} \\
 & \text{73m } Nb^{97} \arrow[ur] &
\end{tikzcd}$$

Other isotopes of Zr produced during fission are either too long-lived or too short-lived to be detected in the sources prepared for the present work.

After each irradiation the sample (thorium nitrate or thorium hydroxide) was dissolved in acid and 10 mg. of the appropriate carriers of the elements (including zirconium) to be separated was added. After allowing sufficient time for the decay of the precursers of the elements to be separated, steps were taken to ensure complete isotopic exchange between the fission product species and the added carrier. Zr was separated at a convenient stage by precipitation with mandelic acid. It was then radiochemically purified by two lanthanum scavenges followed by several precipitations of barium zirconyl fluoride. It was finally precipitated as zirconium tetramandelate for source preparation, counting and chemical yield determination. The full radiochemical procedures for the above purification as described by Hahn and Skonieczny[91] is given in detail in the appendix. Solid sources thus prepared showed an initial growing in of activity due to Nb^{97} and then decayed with 17 hours half life. In each case the decay of the sources was followed for several days until the counting rates became comparable with the background rates.

Calibration of the End-window Counter for 17 hr. Zr^{97}.

For calibrating the counter for Zr^{97}, a solution of high specific activity was prepared by isolating Zr from a sample of pile irradiated uranium. The same chemical procedures as described above were used using 1 mg. amount of carrier and omitting the final precipitation step. After appropriate dilution weighed amounts of the diluted solution were dried on 4π films under an infra-red lamp. Each of these 4π sources was then counted until the counting rates were comparable to the background and decay curve for each source was obtained.

The contribution of Zr^{97} to the total counting rates of the 4π sources was calculated in the following way:-

(a) The efficiency of the 4π counter for the short lived Nb^{97} was estimated to be 2.3%. Thus for each Zr disintegration 1.023 counts were recorded.

(b) Considering Zr^{97}— Nb^{97m} and Nb^{97} in transient equilibrium; if Zr^{97}— $Nb^{97m} = 1$, and $Nb^{97} = 2$,

$$\frac{A_1}{A_2} = \frac{\lambda_2 - \lambda_1}{\lambda_2} \quad \frac{0.5640 - 0.0407}{0.5640} = 0.9278$$

Assuming equal detection of Zr^{97} and Nb^{97} in the 4π counter,

$$A = A_1 + A_2 = A_1 \left(1.023 + \frac{1}{0.9278}\right) = 2.10\ A_1$$

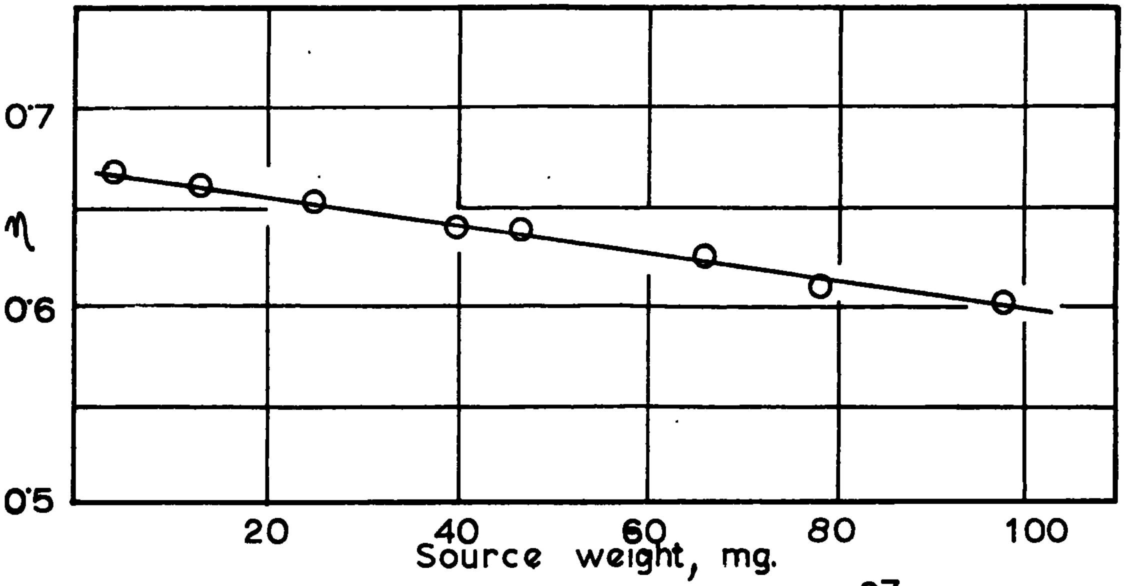

Fig.9. Counting-efficiency curve for 17h Zr^{97} as a function of source weight.

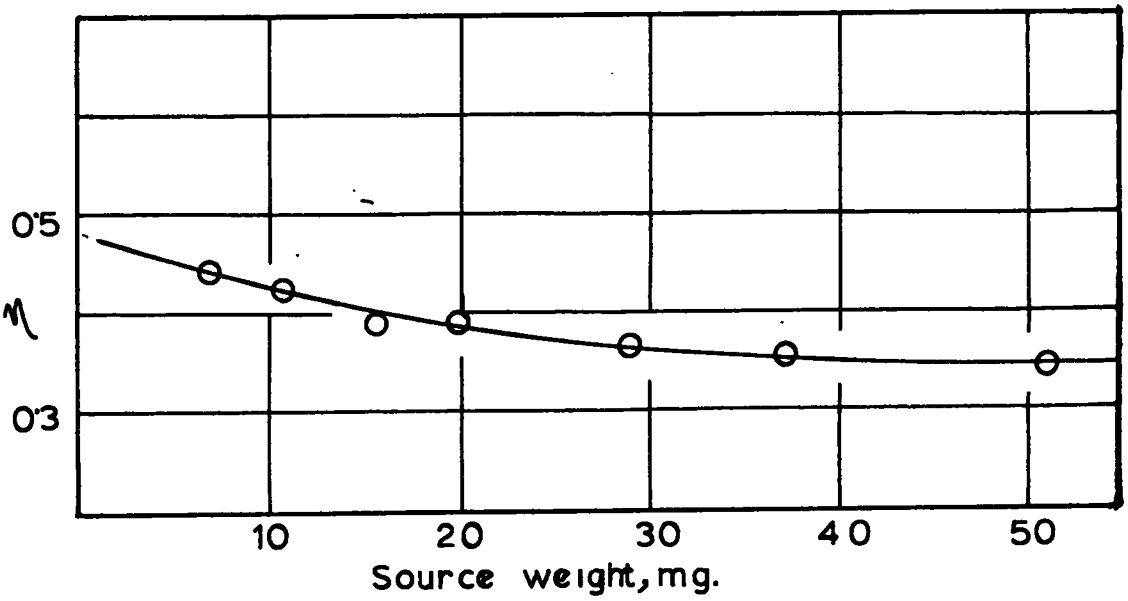

Fig. 12. Counting-efficiency curve for 66h Mo^{99} as a function of source weight.

TABLE VI

Run No.	Wt. of ppt.mg.	Chem. Yield %	A^{o}_{obs}	A^{o}	η_{Zr}	$S_{Zr} \times 10^{3}$
1	27.20	29.58	1,425	4,817	.643	2,314
2	29.55	32.11	1,150	3,581	.640	1,442
3	32.25	35.06	590	1,683	.639	677
4	33.08	35.97	625	1,738	.638	1,293
5	44.75	48.66	1,600	3,288	.627	324
6	49.96	54.32	570	1,049	.620	144
7	24.18	26.29	825	3,138	.648	264
8	48.25	52.47	7,500	14,293	.625	1,127
9	76.75	83.45	4,080	4,890	.592	505
10	33.50	36.43	5,0 7 5		.637	1,343
11	5,76	6.26	350	5,591	.667	981
12	75.85	82.46	6,600	$8,005_{4}$	.595	764
13	64.41	70.04	2,620	$3,742_{1}$	.605	701
14	48.16	52.38_{6}	4,300	8,214	.625	1,358
15	43.90	47.73	2,500	$5,239_{8}$	.628	1,389
16	69.65	75.73	5,700	7,527	.607	1,049
17	46.33	50.38_{7}	6,200	12,306	.629	1,773
18	55.50	60.35	19.000	31,483	.620	3,114
19*	34.52	88.78	1,400	1,577	.355	2,707
20*	20.80	53.50	500	935	.390	1,432
21*	12.56	32.30	800	929	.405	1,548
22*	22.00	56.58	320	566	.382	891

continued

*These data are for Mo^{99} when it was used as secondary reference for I^{131}.

TABLE VI (continued)

Run No.	Wt. of ppt. mg.	Chem. Yield %	A^{o}_{obs}	A^{o}	η_{Zr}	$S_{zr} \times 10^{3}$
23	65.20	70.89	1,500	2,116	.610	814
24	46.10	50.35	1,060	2,109	.629	730
25	55.80	60.67	1,720	2,838	.620	1,037
26	65.57	71.29	2,300	3,226	.610	943
27	62.80	68.28	1,425	2,087	.615	1,553
28	38.20	41.54	960	2,311	.637	1,385
29	24.00	26.10	360	1,379	.648	1,161
30	49.07	53.35	445	834	.620	177
31	40.22	43.73	1,290	2,930	.634	2,558
32	53.60	58.28	520	892	.620	369
33	44.26	48.12	150	312	.630	130
34	61.11	66.44	900	1,354	.615	466
35	39.15	42.57	225	529	.635	221
36	30.30	32.95	160	486	.643	200
37	85.86	93.36	730	782	.590	330
38	57.38	62.39	590	946	.618	381

or $$A_1 = \frac{A}{2.10}$$

Thus, the Zr^{97} activity used in the preparation of the solid sources for the end-window counter was obtained and the efficiency of the counter for sources of different weights found. In making solid sources for the end window counter a weighed quantity of the active solution was added to a solution containing 100 mgs. of Zr carrier and after digestion for a few minutes to facilitate complete isotopic exchange between the active species and the inactive carrier zirconium tetramandelate was precipitated. A batch of sources of different weights was then prepared from the precipitate, dried, mounted and counted. To eliminate the contribution of any contamination each of these solid sources was counted long enough to get a decay curve for resolution. The counting efficiency of the end-window counter for different sources was then obtained by dividing the counting rate of the solid source by the disintegration rate of the same source calculated as set out above. The results of the calibration are shown in Fig. 9.

Results of the measurements of Zr^{97} for the relative yield determinations of other Th fission products are given in Table VI. A^{o} was obtained by applying the appropriate correction for the chemical yield to A^{o}_{obs}. Values for η_{Zr} were obtained from the calibration curve in Fig. 9 and S_{Zr} were calculated from recordings of the neutron monitor throughout the irradiation.

2. 14-Mev Neutron Fission of Thorium.

(a) Bromine.

The relative fission yields of masses 83 and 84 were determined by radiochemical isolation and estimation of 2.4h Br^{83} and 31.8m Br^{84} respectively. The decay chain for these masses are:-

$$\begin{tikzcd}
\text{69s Se}^{83m} \arrow[dd, dashed] \arrow[dr] & & \text{114m Kr}^{83m} \arrow[dd] \\
& \text{2.4h Br}^{83} \arrow[ur] & \\
\text{25m Se}^{83} \arrow[ur] & & \text{Kr}^{83}\text{ (stable)}
\end{tikzcd}$$

$$\begin{tikzcd}
& \text{6.0m Br}^{84} \arrow[dr] & \\
& & \text{Kr}^{84}\text{ (stable)} \\
\text{3.3m Se}^{84} \arrow[r] & \text{31.8m Br}^{84} \arrow[ur] &
\end{tikzcd}$$

In order to allow sufficient time for the decay of the precursors in the case of Br^{83} separation procedures were not begun, until about 4 hours after the end of the irradiation; in the case of Br^{84} the time of 'cooling' was about half-an-hour. The time for irradiation was not the same in each case. The yield of 2.4h Br^{83} was determined after an irradiation of about an hour. The yield of 32m Br^{84} was determined after an irradiation of about half-an-hour using a new target to achieve maximum neutron flux.

Owing to the timing requirements, different chemical procedures was used for the different isotopes. For the separation of Br^{83} the procedure used was essentially that of Glendenin, Edwards and Gest[92] as modified by Ramaniah.[93] The irradiated thorium nitrate was dissolved in about 6 M nitric acid and 2 ml of bromide carrier were added to the solution. The bromide was oxidised to bromine with Ce^{IV}, extracted into carbon tetrachloride and then re-extracted into aqueous sodium bisulphite. After acidification of the aqueous bromide solution with nitric acid, active iodine was removed by oxidation of added iodide carrier with excess sodium nitrite and subsequent extraction into carbon tetrachloride. Finally the bromide was oxidised to bromine with excess potassium permanganate, extracted into carbon tetrachloride and re-extracted into aqueous sodium bisulphite. This was then acidified, boiled to expel sulpher dioxide and precipitated as silver bromide for source preparation and counting.

The separation of 32m Br^{84} was performed by the method of Strassmann and Hahn[94] as modified by Sattizahn, Knight and Kahn.[95] Irradiated thorium nitrate was placed in a distillation flask containing 2 ml of bromide carrier in 3 M hot nitric acid solution. After the irradiated sample had dissolved, the bromide was oxidised to bromine with Ce^{IV} and evolved gas was swept by nitrogen into a separatory funnel containing freshly prepared ferrous sulphate solution and a little iodide carrier. The iodide was oxidised to iodine by sodium nitrite and extracted into carbon tetrachloride and the bromide was precipitated as silver bromide for source preparation and counting. Full descriptions of both the radiochemical procedures are given in the appendix.

The Br^{83} sources were counted for about 48 hours and the Br^{84} ones for about 24 hours. The Br^{83} sources decayed rapidly in the beginning due to the presence of some 32m Br^{84} and then with the expected half-life of 2.4 hours. In the case of Br^{84} sources, although the separations were not begun until half-an-hour after the end of the irradiations, some short-lived activity was always found to be present in the freshly prepared samples. This was due to short-lived bromine isotopes from fission, especially 6.0m Br^{84}. The 32m Br^{84} sources also decayed with a long tail due to the presence of long-lived Br^{83} isotope from fission. However, the decay curves could always be resolved without difficulty.

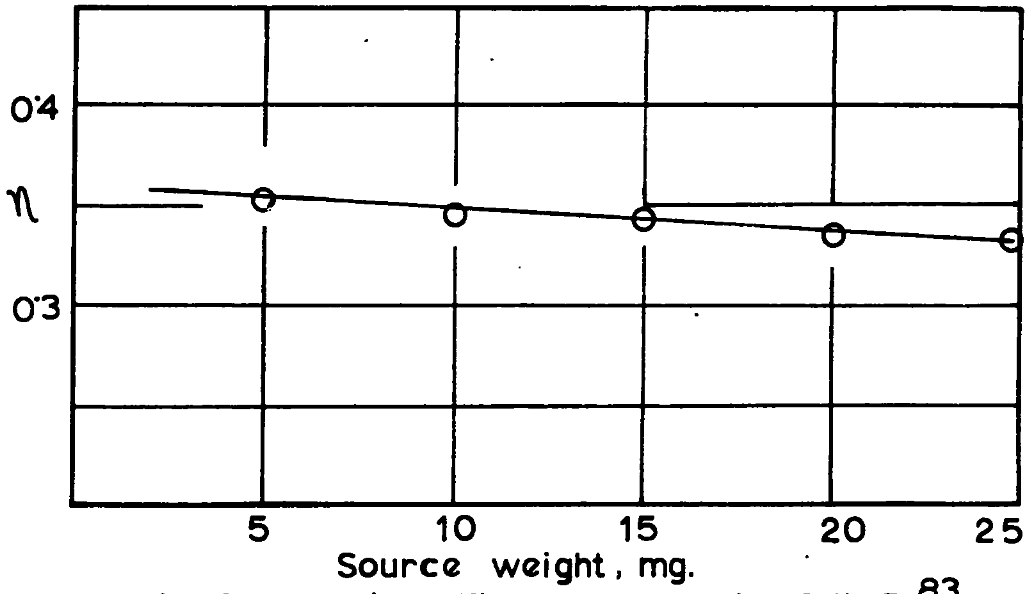

Fig. 10. Counting-efficiency curve for 2·4h Br^{83} as function of source weight

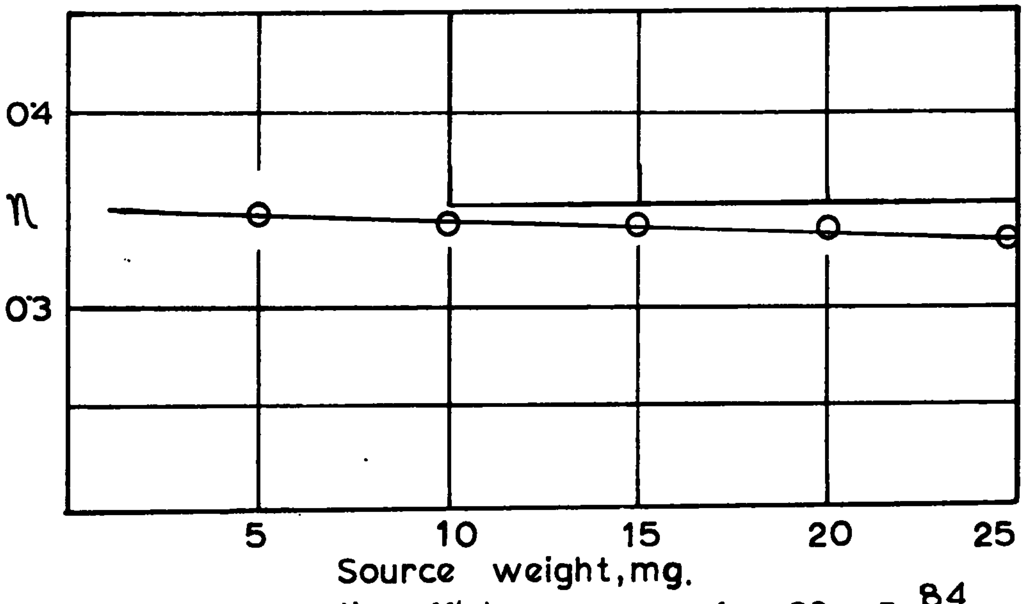

Fig. 11. Counting-efficicncy curve for 32m Br^{84} as function of source weight

Calibration of the proportional counter for bromine isotopes.

The method of calibrating the proportional counter for short-lived isotopes such as those of bromine becomes difficult and inconvenient by the method suggested by Steinberg, which entails plotting self-absorbtion curves for the isotopes. An alternative method, outlined by Bayhurst and Prestwood[96] was therefore used.

In this method a series of determinations of counting efficiencies is made using long-lived isotopes of convenient energies, and plotted in the form of counting efficiency, ϵ, against average β-energy $\bar{E}$, for each of a series of precipitate weights, ranging from about 5 mgms to 50 mgms. The plots are constructed from the self-absorbtion curves of the isotopes used, as calibrated by 4π counting. The self-absorbtion curve of any nuclide of known average β-energy, $\bar{E}$, can then be read off from the Bayhurst curves.

The average β-energy, $\bar{E}$, is calculated for β-emitters according to the prescription given by the authors in their original papers.[97] The calculation takes into account the maximum β-energy, the spectrum shape, the atomic number of the nuclide and whether it is a negatron or positron emitter. The counting efficiency of nuclides with complex β^--groups can also be calculated by weighting

TABLE VII

Results for 2.4h Br^{83}.

Run No.	Wt. of ppt. mg.	Chem. Yield %	A^{o} obs.	A^{o}	η_{Br}	$S_{Br} \times 10^{3}$	Relative yield
8	6.45	27.18	8,200	30,169	.350	1,011	.591
9	18.95	79.85	7,200	9,017	.342	448	.510
10	16.23	68.38	20,666	30,222	.344	1,190	.638
17	8.56	36.06	8,600	23,849	.348	1,577	.554
18	10.17	42.85	30,000	70,012	.347	2,782	.626

Relative yield of 2.4h Br^{83} = .583 ± .023

TABLE VIII

Results for 32 m Br^{84}

Run No.	Wt. of ppt. mg.	Chem. Yield %	A^o obs.	A^o	η_{Br}	$S_{Br} \times 10^3$	Relative yield
5	20.69	87.19	35,000	40,142	.340	270	.837
6	21.12	88.97	12,142	13,647	.340	133	.795
7	13.57	57.20	24,300	42,483	.342	241	.859
16	7.06	29.75	28,000	94,118	.345	858	.833

Relative yield of 32m Br^{84} = .831 ± .013

the efficiency of each group by its fractional abundance.

Thus to use the curve for a β-emitter whose counting efficiency is to be determined it is only necessary to calculate the average β-energy, $\bar{E}$, and read off the efficiency on the curves for each of the different source weights to construct a calibration curve.

The calibration curves for Br^{83} and Br^{84} obtained by the above method are given in Fig. 10 and Fig. 11 respectively.

The results of the relative yield measurements for Br^{83} are given in Table VII, and those for Br^{84} in Table VIII. The values for A^{0}_{Zr}, S_{Zr} and η_{Zr} are taken from Table VI and relative yields were calculated by applying the relative yield equation as deduced on page 25.

(b) Molybdenum.

The relative fission yield of mass number 99 was determined by means of 66h. Mo^{99}. The decay chain of this mass number is:

$$\begin{tikzcd}
 & & & 6hTe^{99m} \arrow[dd] & \\
30sZr^{99} \arrow[r] & 3mNb^{99} \arrow[r] & 66hMo^{99} \arrow[ur] \arrow[dr] & & \\
 & & & 2.1x10^{5}yTc^{99} \arrow[r] & Ru^{99}(stable)
\end{tikzcd}$$

The separation and radiochemical purification of the fission product Mo from the irradiated sample was based on the method as described by Scadden.[98] In brief, this method consists of the initial separation of the added Mo carrier as the α-benzoinoximate from the fission product mixture followed by two reprecipitations, destruction of the organic reagent with nitric-perchloric acid mixture, one scavenge with Fe^{3+} and a final precipitation of the Mo as lead-molybdate for source preparation, counting and chemical yield determination.

The fission product Mo sources were counted for a couple of weeks and they decayed with the expected half-life of 66 hours after an initial growing-in period of 6 hour technetium daughter.

In runs where Mo^{99} was used as a "secondary" reference for the relative yield determination of 8 days I^{131}, the irradiated samples were 'cooled' for about 200 hours to allow complete decay of I^{131} precursors. In such cases the Th samples were irradiated for 3 hours with the maximum obtainable neutron-flux and the Mo activity remaining after 'cooling' was sufficient for counting and extrapolation purposes. In other cases the duration of the irradiation was 2 hours and the chemistry started half-an-hour after the irradiation.

Calibration of the Counter for Mo^{99}

For calibration of the proportional counter for Mo^{99}

TABLE IX

Results for 66h Mo^{99}

Run No.	Wt. of ppt. mg.	Chem. Yield %	A^o obs.	A^o	η_{Mo}	S_{Sb} x 10^3	Relative yield
11	20.25	52.10	325	624	.385	997	.739
13	36.82	94.72	343	362	.350	712	.639
14	16.50	42.45	350	824	.390	1,377	.616
15	27.18	69.93	400	572	.365	1,409	.718
18	5.85	15.05	593	3,940	.440	3,114	.674

Relative yield of 66h Mo^{99} = .677 ± .023.

a solution of high specific activity containing micro gram amounts of the carrier was obtained by irradiating natural molybdenum (as oxide) with pile-neutrons, and separating Te from it by dry distillation immediately before taking the Mo into solution. A measured amount of the solution was dried on a 4π film and counted in a 4π counter for determining the disintegration rate. The growth of 6h Tc^{99} was observed in the 4π sources and the contribution of Mo^{99} to the total counting rates was calculated using standard methods.

A known weight of the standard active solution was added to a known amount of Mo carrier and a set of sources covering the required range of precipitate weights was prepared. The solid sources were counted with Tc^{99} in transient equilibrium with Mo^{99} and the activities extrapolated to the time of separation. Efficiency of the counter was then obtained by dividing the observed counting rate by the disintegration rate due to Mo^{99} in the solid sources and a calibration curve was obtained as shown in Fig. 12.

The results for the relative fission yield measurements are shown in Table IX.

(c) Antimony.

4.6h Sb^{129} was used to determine the relative fission yield of mass number 129. The decay chain for this mass number is:-

$$\begin{tikzcd}
 & 37\text{d } Te^{129m} \arrow[d] & & \\
4.6\text{h}Sb^{129} \arrow[ur, "36\%"] \arrow[dr, "64\%"'] & & 1.7\text{x}10^{7}\text{y } I^{129} \arrow[r] & Xe^{129}\text{(stable)} \\
 & 72\text{m } Te^{129} \arrow[ur] & &
\end{tikzcd}$$

The radiochemical procedure used for the separation of fission product antimony from irradiated thorium was based on the method described by Hagebø, Kjelberg and Pappas[99] with some modification to suit present conditions. The main steps involved in the method being the oxidation of added Sb^{III} carrier to Sb^{V} with bromine, to facilitate complete isotopic exchange, separation of antimony from other fission products by precipitating it as sulphide, extraction of Sb^{V} into di-isopropyl ether from concentrated hydrochloric acid, reduction and back extraction of antimony into 0.5M hydrochloric acid, one scavenging precipitation of Te and final precipitation of Sb as the n-propyl gallate for source preparation and chemical yield determination.

After an initial increase in activity, due to the growth of 72m Te^{129}, the antimony samples decayed with the 4.6 hour half-life of Sb^{129}. The decay of the samples were followed for about 2 days so that the small

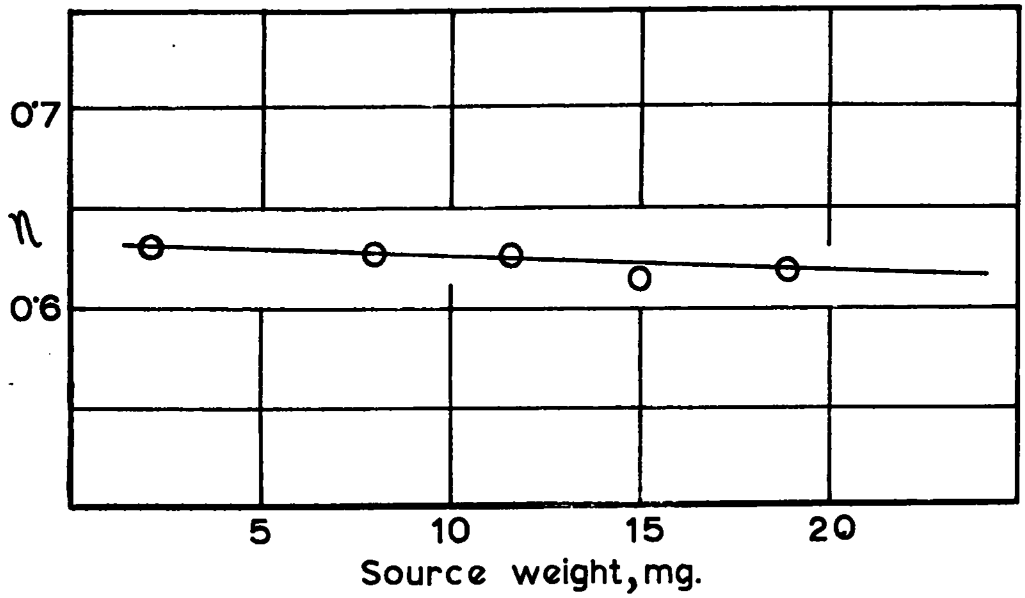

Fig.13. Countig efficiency curve for 4'6h Sb^{129} as function of source weight.

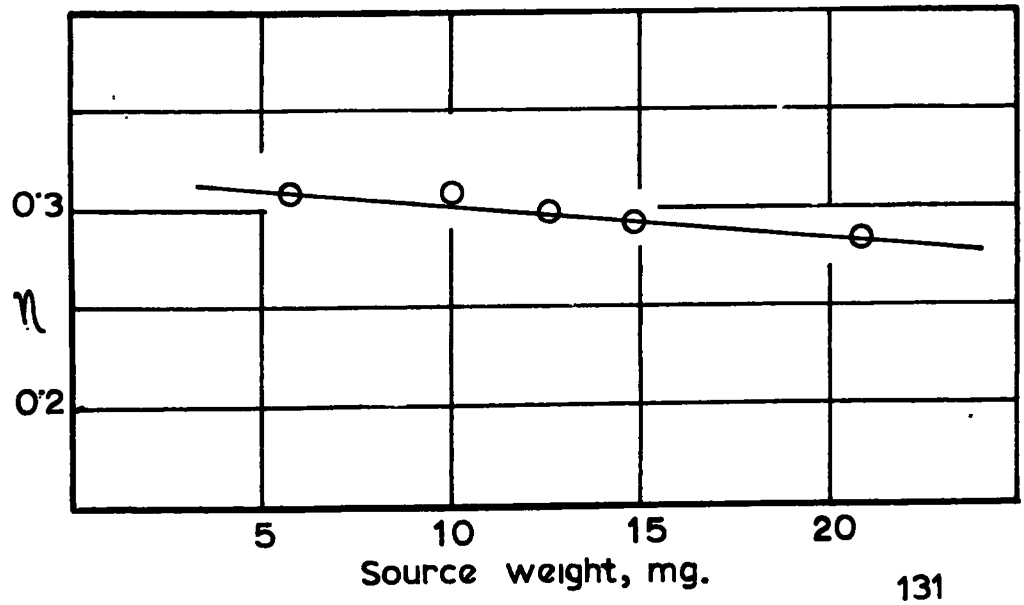

Fig.14. Counting efficiency curve for 8'05d I^{131} as function of source weight.

contribution from long-lived contamination could be allowed for.

Calibration of the Proportional counter for 4.6h. Sb^{129}:
An essentially carrier free solution of Sb^{129} with high specific activity was obtained from a sample of pile-irradiated uranium by the method described above, reduced for working with approximately 1 mg. of added carrier. The final step of precipitating antimony was omitted. After appropriate dilution measured amounts of the active solution were dried on 4π -films for absolute disintegration measurement. The absolute activity of Sb^{129} in the 4-π sources was calculated. The correction for the daughter Te^{129} which is formed directly in 64% of the Sb^{129} disintegrations was calculated from the decay constant.

If $Sb^{129} = 1$, $Te^{129} = 2$, then, when they have reached transient equilibrium,

$$\frac{A_1}{A_2} = \frac{\lambda_2 - \lambda_1}{\lambda_2} \quad \frac{100}{64} = \frac{(0.9367 - 0.2510)}{.64 \times 0.009367} = 1.142$$

Assuming equal detection of Sb^{129} and Te^{129} in the 4π counter,

$$A = A_1 + A_2 = A_1 \left(1 + \frac{1}{1.142}\right) = 1.874\ A_1$$

TABLE X

Results for 4.6h Sb^{129}.

Run No.	Wt. of ppt. mg.	Chem. Yield %	A^o obs.	A^o	η_{Sb}	S x 10^3	Relative Yield
12	10.10	32.97	3,000	9,099	.628	724	.306
13	9.16	29.90	1,175	3,930	.630	633	.287
14	8.51	27.78	2,700	9,719	.632	1,285	.335
15	5.88	19.19	6,201	6,201	.633	1,318	.333

Relative yield of 4.6h Sb^{129} = .315 ± .011

Therefore, $A_1 = A/1.874$.

The activity due to Sb^{129} of each of the solid sources was obtained by resolution of the appropriate decay curve and the efficiency of the proportional counter for counting these sources calculated. The calibration curve of the counter for this nuclide is given in Fig. 13.

Results of the measurements of the yield of 4.6h. Sb^{129} relative to 17.0h. Zr^{97} are given in Table X.

(d) Iodine.

The relative fission yield for mass number 131 was based on 8.05 I^{131}. The decay chain for this mass is:-

$$\begin{tikzcd}
 & & \mathrm{30hTe}^{131} \arrow[d] \arrow[dr] & & \mathrm{12dXe}^{131} \\
\mathrm{3.4mSn}^{131} \arrow[r] & \mathrm{23mSb}^{131} \arrow[ur, "15\%"] \arrow[dr, "85\%"'] & & \mathrm{8.05dI}^{131} \arrow[ur, "0.8\%"] \arrow[dr, "99.2\%"'] & \\
 & & \mathrm{24mTe}^{131} \arrow[ur] & & \mathrm{Xe}^{131}\ \text{(stable)}
\end{tikzcd}$$

The separation method of iodine from other fission products is based on that described by Meinke.[100] The procedure starts with a redox cycle to ensure complete exchange between the fission product iodine and the added carrier. In brief, the method consists of several partitions between carbontetrachloride and aqueous phases of various compositions interspersed with appropriate selective oxidation or reduction steps. The full description of the procedure is given in the appendix.

TABLE XI

Results for 8.05d I^{131}

Run No.	Wt. of ppt.mg.	Chem. Yield %	A^o obs.	A^o	η_I	$S_I \times 10^3$	Relative yield
19	10.51	43.56	250	574	.300	1,968	1,227
20	16.57	68.68	210	306	.289	1,441	1.271
21	19.95	82.69	220	266	.282	1,557	1.181
22	19.75	81.86	155	189	.282	896	1.303

Yield of 8.05d I^{131} relative to 66h Mo^{99} = 1.245 ± .026.

Relative yield of 8.05d I^{131} = .842 ± .045

In order to allow sufficient time for the decay of long-lived precursors of I^{131}, iodine separations were not begun for some 200 hours after the end of the irradiation. The decay of the iodine samples were followed for about five weeks, after which their activities became too low for reliable measurement.

The calibration of the proportional counter for I^{131} was done in the usual way. Radiochemically pure I^{131} was obtained from Radiochemical Centre, Amersham, U.K. The calibration curve is given in Fig. 14.

The results for the relative yield measurements are shown in Table XI.

(e) Praseodymium:

For the determination of the relative fission-yield of mass no. 145, 5.96 h. Pr^{145} was isolated from the Th-fission products. The decay chain of the mass number 145 is:-

$$3.0\text{m } Ce^{145} \longrightarrow 5.96\text{h. } Pr^{145} \longrightarrow Nd^{145} \text{ (stable)}$$

The procedure for the isolation and purification of Pr can readily be divided into two parts; separation and purification of the rare earths as a group from other fission products and ion-exchange separation of Pr from the purified rare-earth fraction.

The conventional method of separating fission-product rare-earths in the form of fluorides cannot be used in the case of thorium because of the insolubility of thorium fluoride. It was therefore found convenient to remove the bulk of thorium from the fission products before isolating the rare-earths. For prior removal of the bulk of thorium, separations based on precipitation,[101] extraction of Th by salicylic acid[102] as well as tri-n-butyl-phosphate (TBP)[103] were investigated. Two extractions of thorium from 6M nitric acid into 20% TBP solution in petroleum ether (boiling point 100-120°C) followed by an iodate precipitation of Th in conc. nitric acid was found to be quite satisfactory and was incorporated into the procedure adapted.

After the removal of Th the solution is made alkaline and rare-earths are precipitated as hydroxides. The rare earths are then purified from other fission products by routine radiochemical operations, as for example, in the method of Nervik.[104] These include, in order, a zirconium phosphate scavenging precipitation, two precipitations of rare-earth fluorides, a barium sulphate scavenging precipitation, precipitation of rare-earths hydroxides, passage of the rare-earth ~~s~~ through a

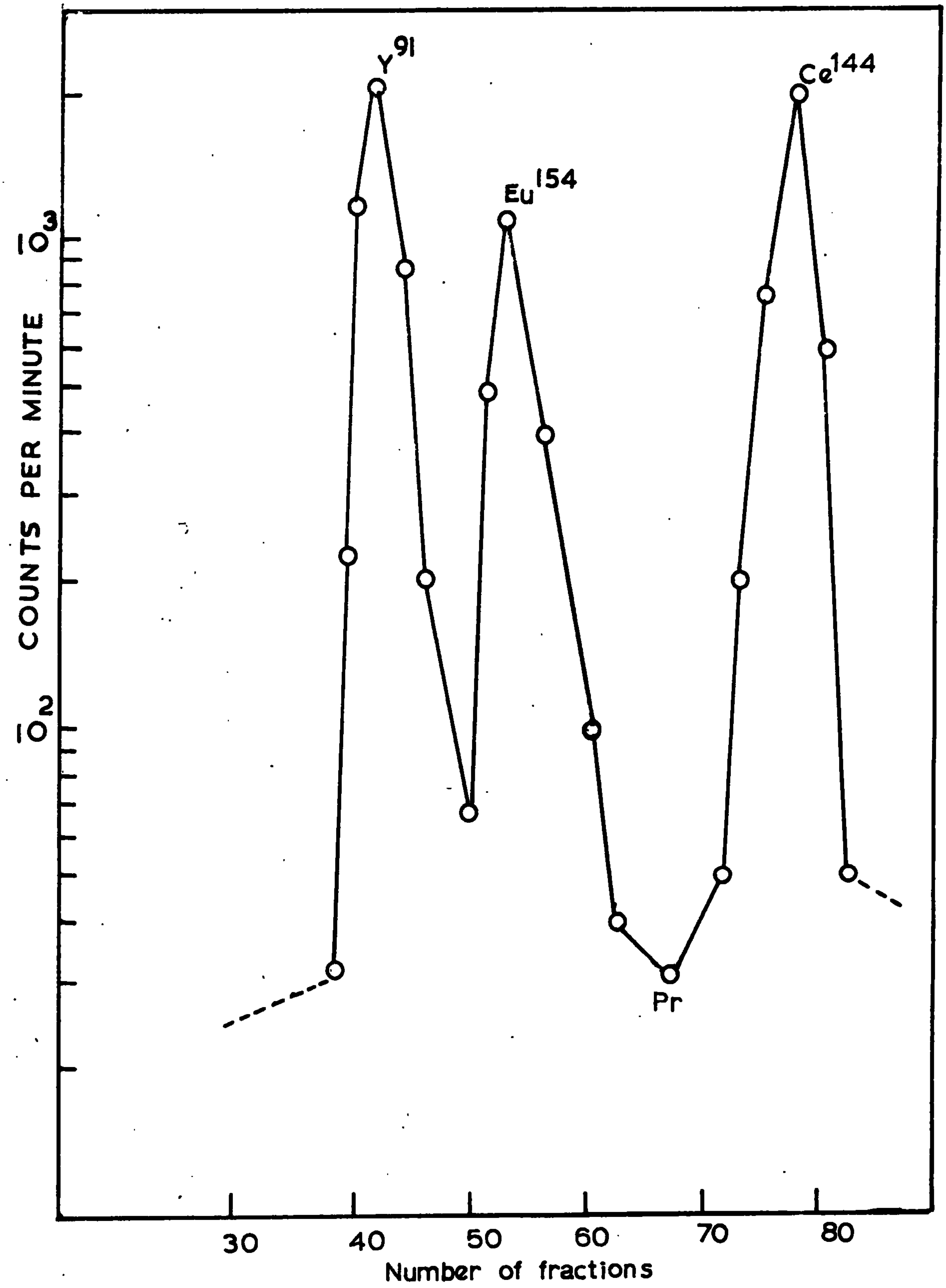

Fig.15. Elution curve of rare earth tracer activities plus 10 mg Pr carrier (no tracer); initial p^H 3·2; p^H changed continuously at ≈ 0.1 p^H unit per hour.

small column in concentrated hydrochloric acid and reprecipitation of rare-earth hydroxides. After each precipitation of rare-earth fluorides or hydroxides, the precipitate is washed with dilute hydrofluoric acid or ammonium hydroxide. From the radiochemically purified rare-earth hydroxides as obtained above Ce is extracted into methyl isobutyl ketone(hexone) in the Ce^{IV} state and Pr is separated from the rest of the mixed rare-earth activities by a gradient elution method.

The general procedure of the method is that a mixture of rare-earths is first adsorbed on the top portion of a long narrow column of cation-exchange resin and individual members are then selectively eluted by passing a solution containing a suitable complexing agent through the column and collecting appropriate portions of the eluant for a particular element. The degree of separation for a particular system depends on various factors, such as, temperature, cross-linking of the resin used, size of the resin particles, dimensions of the column, concentration of the eluting agent and its pH, flow-rate of the eluant through the column and the amount of carrier used for different rare earths. Though many procedures with optimum conditions for such separations have been reported, for the separation of a particular rare-earth carrier from a mixture of other rare-earth activities, other conditions could undoubtedly be found which would give better results. Comparing a number of different procedures previously recommended, a method reported by Nervik[105] with suitable modifications has been used in the present work.

A full description of the apparatus, chemicals and experimental procedures are given in the appendix. Only the experimental conditions are given below:-

Resin: Zeo-Karb--225, 100-200 mesh, 4-5% cross-linked,

Column: 60 cm x 7 mm internal diameter,

Temperature: 90 ± 3°C

Eluant: 1 M ammonium lactate,

pH of the solutions; Upper solution 7.0
Lower solution 3.2

Flow rate: about 4 drops per minute, 30 drops in each fraction,

Appx. time of separation: 8 hours.

In trial runs, 10 mg. of inactive Pr with tracer activities of Y, Eu and Ce was used to demonstrate the efficiency of separation under the conditions described above. It has been shown by Nervik that the use of carrier for a particular element widens its peak in this sort of

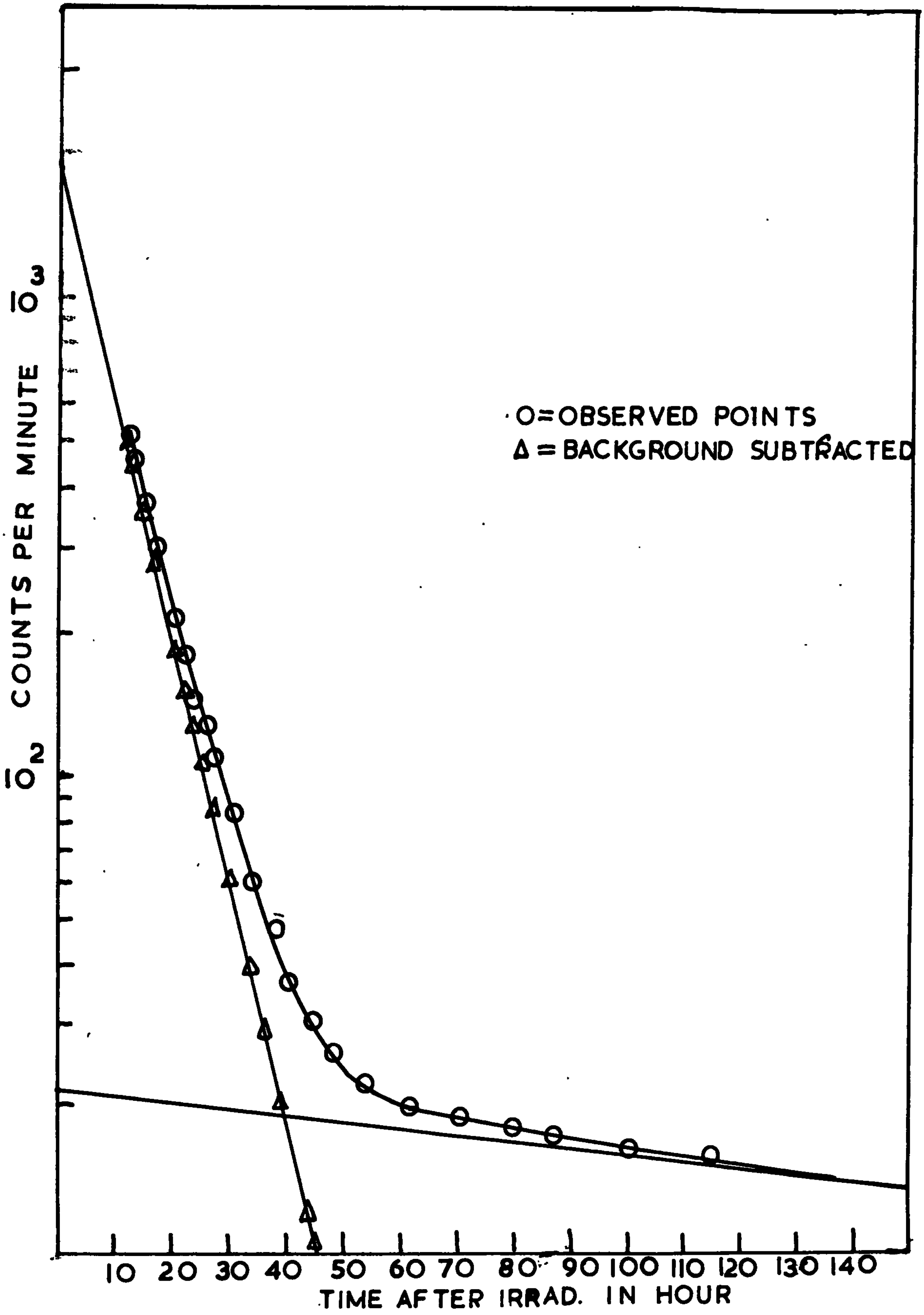

FIG.16. DECAY CURVE FOR 5·96HR Pr^{145}

separation. It is also evident from Fig. 15 that the Pr peak was found to spread over 6 to 7 fractions. To avoid any possible cross contamination, middle fractions were taken for counting and chemical yield determination. Prior separation of fission-product Ce by solvent extraction from purified rare-earth activities before they were put on the column improves the degree of separation on the column. The decay curve in Fig. 16 shows that Pr activities thus separated were essentially free from any other contamination and decayed with a half-life of 5.96 hours. The precursor of 13.7 days Pr^{143} (33 hr. Ce^{143}) is long lived and its separation from the purified rare-earth group should eliminate most of the contamination of Pr^{145} by Pr^{143}. Other isotopes of Pr produced during fission (24.4m Pr^{146}, 12m Pr^{147}, 1.95m Pr^{148}) are too short lived to be seen in the isolated Pr^{145},the separation in all taking about 10 hours. Any possibility of 6.13'hr. actinium contamination is ruled out from the fact that the counting of other fractions in an actual run showed a peak (Fig. 17), after Pr. This peak is due to La and Ac cannot be eluted before La in the present conditions.

During actual runs Pr fractions were located in the collecting tubes by adding 1 ml of saturated ammonium

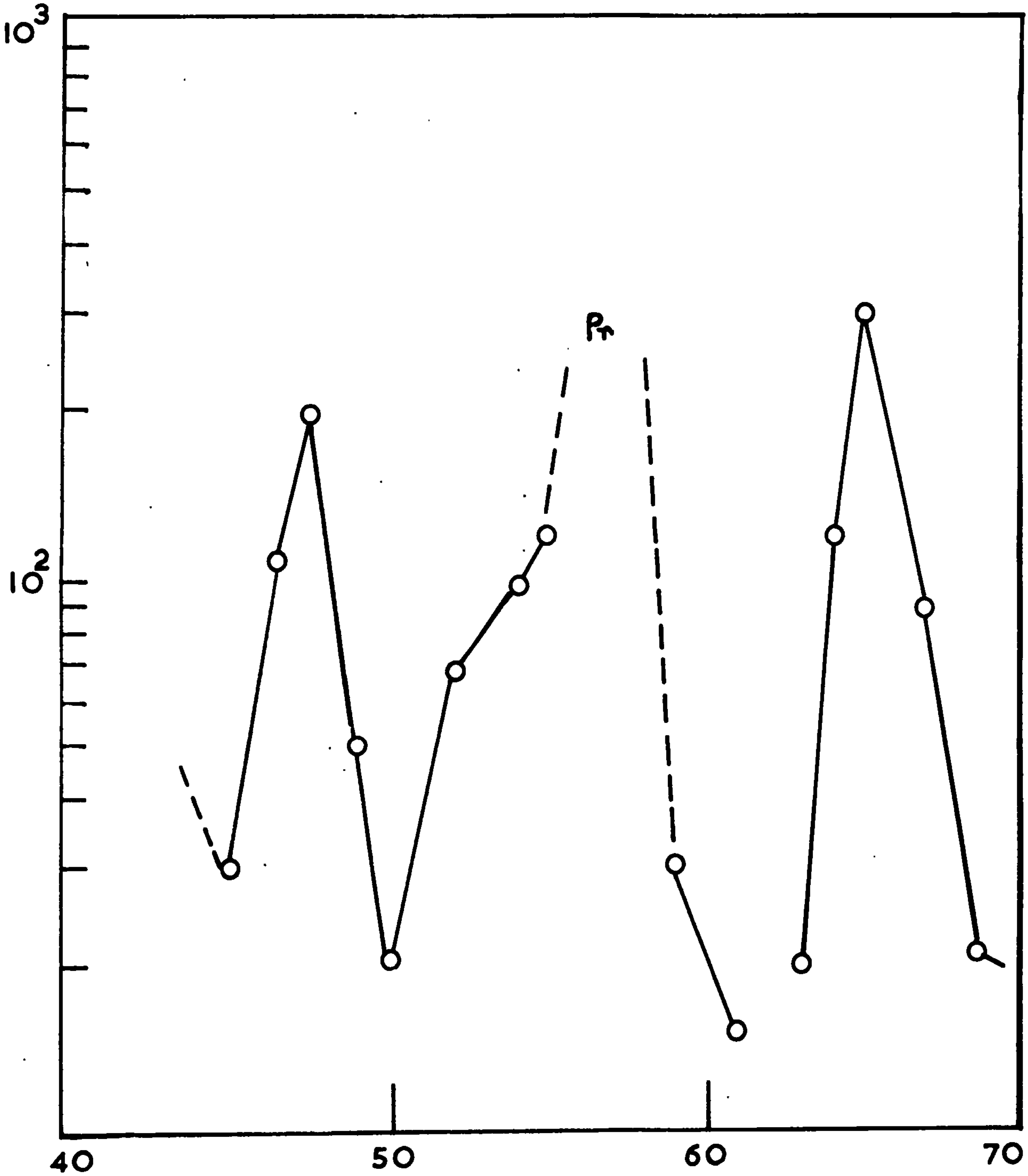

FIG.17. ELUTION CURVE OF FISSION-PRODUCT RARE-EARTHS

oxalate solution which forms a bluish Praseodymium-oxalate precipitate. For yield determinations and counting 3 or 4 middle fractions were added together and a source was prepared in the usual way. After following the decay of the source, its Pr content was determined by a back titration method with EDTA and Zn using Eriochrome Black T as an indicator as described earlier (see page 48)

Calibration of the proportional counter for Pr^{145}:

Due to the lengthy and complicated procedure required for the separation of Pr^{145} from fission products and the shortness of its half-life it was not possible to calibrate the counter directly for Pr^{145}. Instead the counter was calibrated for Pr^{145} using Y^{91}. It has got a long half-life (58 days) and can be easily obtained in the radiochemically pure form from The Radioisotope Centre, Amersham, U.K. Both Pr^{145} and Y^{91} have similar decay schemes with comparable β-energies. (Pr^{145}, β = 1.70 Mev; Y^{91}, β = 1.45 Mev) and similar environment i.e. oxalate precipitates. It has been demonstrated by Bayhurst and Prestwood,[96] that for mean energies above 0.5 Mev. the change of counting efficiency with mean energy in a proportional counter is negligible.

A solution of carrier free Y^{91} was obtained from the Radiochemical Centre, Amersham and after appropriate

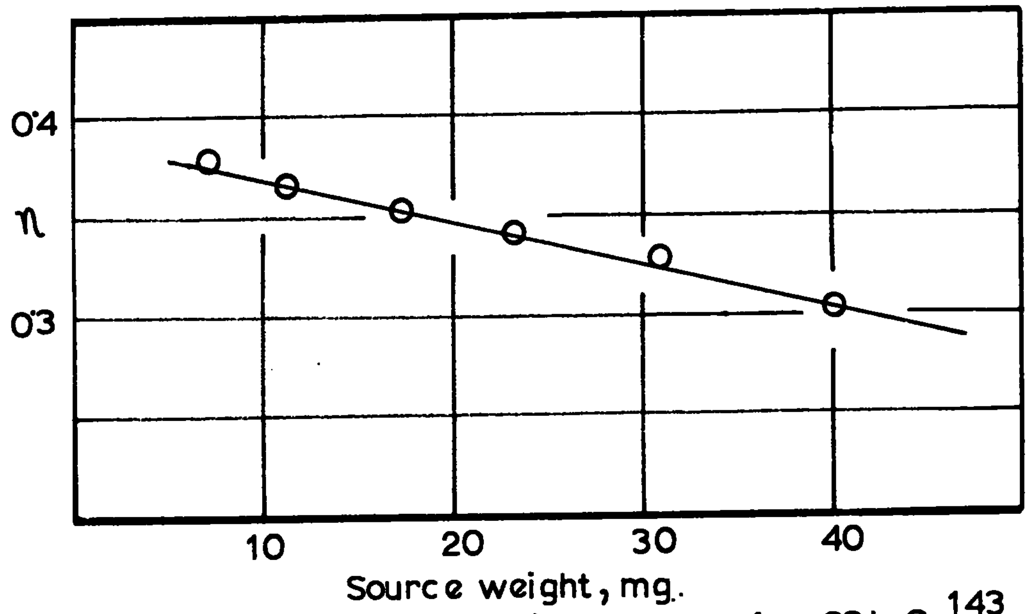

Fig. 20. Counting efficiency curve for 33h Ce^{143} as function of source weight

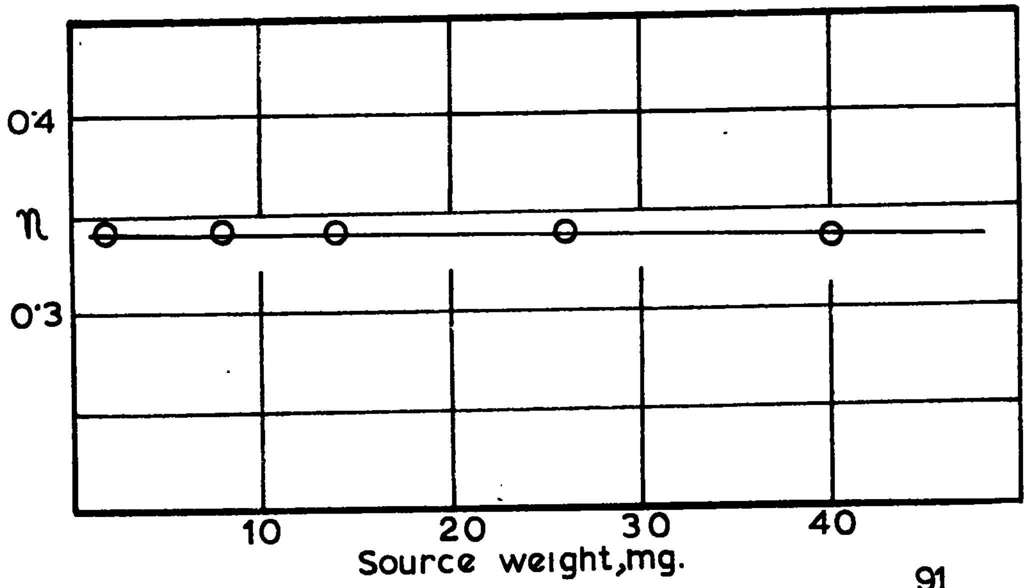

Fig.18. Counting efficiency curve for 59d Y^{91} as function of source weight

TABLE XII

Results for 5.9h Pr^{145}

Run No.	Wt. of ppt.mg.	Chem. Yield %	A^{o}_{obs}	A^{o}	η_{Pr}	S_{Pr} x 10^3	Relative Yield
1	13.79	55.48	3,100	5,588	.345	2,187	.799
2	10.80	43.45	1,900	4,373	.345	1,351	.845
3	7.52	30.25	625	2,070	.347	650	.835
4	8.03	32.31	675	2,089	.346	1,240	.808

Relative yield of 5.9h Pr^{145} = .821 ± .011.

dilution its absolute activity was determined by 4π counting of aliquot parts. A weighed quantity of the active solution was then added to a measured amount of yttrium carrier solution and the yttrium was precipitated as oxalate. A set of sources of different weights was prepared from the precipitate for end-window proportional counting. The efficiency of the counter for counting different sources i.e. $\frac{\text{counts per minute}}{\text{disintegration per minute}}$, was determined and the calibration curve is given in Fig. 18.

The results of the relative yield measurements for Pr^{145} are given in Table XII.

3. 3-Mev. Neutron Fission of Thorium

(a) Bromine

The relative fission yields of mass numbers 83 and 84 were based on 2.4h Br^{83} and 32m Br^{84} respectively. The decay chain of these mass numbers and the description of the experimental procedures have already been discussed on page 63. The full radiochemical procedures for the isolation and purification of these nuclides are given in the appendix. In calculating the relative yields for these mass numbers the values for A^o_{Zr}, S_{Zr} and η_{Zr} were taken from Table VI, while the values for η_{Br} were taken from

TABLE XIII

Results for 2.4 h Br^{83}

Run No.	Wt. of ppt. mg.	Chem. Yield %	A^{o}_{obs}	A^{o}	η_{Br}	S x 10^{3}	Relative yield
33	16.46	69.35	295	424	.342	113	.405
34	19.76	83.26	1,500	1,801	.339	391	.404
37	13.60	57.30	645	1,125	.343	340	.389

Relative yield of 2.4 h Br^{83} = .399 ± .004.

TABLE XIV

Results for 32 m Br^{84}

Run No.	Wt. of ppt. mg.	Chem. Yield %	A^o_{obs}	A^o	η_{Br}	S x 10^3	Relative Yield
30	22.20	93.54	6,350	6,787	.340	130	.626
35	19.52	82.25	3,300	4,012	.342	166	.580
36	14.58	61.43	2,907	3,907	.344	153	.608

Relative Yield of 32m Br^{84} = .604 ± .013

TABLE XV

Results for 66h Mo^{99}

Run No.	Wt. of ppt. mg.	Chem. Yield %	$A^o{}_{obs}$	A^o	η_{Mo}	S x 10^3	Relative Yield
32	23.70	60.96	52	85.3	.375	378	.590
33	30.55	78.57	21	26.7	.360	132	.562
34	10.01	25.75	35	135.9	.412	475	.566
37	15.91	40.92	30	73.3	.390	386	.531

Relative yield of 66h Mo^{99} = .562 ± .016.

Fig. 10 (for Br^{83}) and from Fig. 11 (for Br^{84}). The results for the relative yield measurements for Br^{83} are given in Table XIII and those for Br^{84} in Table XIV.

(b) Molybdenum

The relative yield of mass number 99 was determined by isolating and measuring 66h Mo^{99} produced during the 3-Men. neutron induced fission of thorium. The decay of this mass chain and the experimental procedures relating to the separation and calibration of the counter for this nuclide have already been discussed in full on page 67. For the calculation of the relative yield values for A^{o}_{Zr}, S_{Zr} and η_{Zr} were taken from Table VI and those for η_{Mo} from Fig. 12. The results for the measurements are given in Table XV.

(c) Antimony

To determine the relative yield of mass number 129 in the 3-Mev. neutron induced fission of thorium, 4.6h Sb^{129} was radiochemically separated, purfied and determined from the fission products. The decay chain of this mass number and the experimental procedures relating to the separation and measurement of Sb^{129} have been described on page 70 while the detailed radiochemical procedure is given in the appendix.

TABLE XVI

Results for 4.6h Sb^{129}

Run No.	Wt. of ppt. mg	Chem. Yield %	A^{o}_{obs}	A^{o}	η_{Sb}	S x 10^3	Relative Yield
23	8.75	28.56	68	238	.631	781	.050
24	10.22	33.36	72	216	.628	691	.028
38	10.72	34.99	38	109	.625	361	.032

Relative yield of 4.6h Sb^{129} = .030 ± .001.

The results for the relative yield measurements are given in Table XVI. In calculating the relative yield values of A^{o}_{Zr}, S_{Zr} and η_{Zr} were taken from Table VI and the values of η_{Sb} from Fig. 15.

(d) Tellurium.

The relative fission yield for mass number 132 was determined by the radiochemical separation and determination of 77 hours Te^{132}. The decay chain for this mass number is:-

$$2.2\text{m } Sn^{132} \longrightarrow 2.1\text{m } Sb^{132} \longrightarrow 77\text{h } Te^{132} \longrightarrow 2.30\text{h } I^{132} \longrightarrow xe^{132} \text{ (stable)}$$

Chemical procedures for the separation of tellurium from irradiated samples were not started until about half-an-hour after the end of irradiation in order to allow sufficient time for the decay of its precursors. The separation chemistry started with a redox cycle as described by Hoering[106] in order to ensure complete isotopic exchange between the fission product tellurium and the added carrier. Gross separation of tellurium was performed by precipitating it in the elemental form using stannous chloride as suggested by Hagebo, Kejelberg and Pappas.[99] Further radiochemical purification was done by repeated precipitation and scavenging with ferric hydroxide. In the final step tellurium was precipitated with hydrazine and sulphur dioxide for source preparation and counting. The full radiochemical procedures are given in the appendix. Sources prepared by this method containing fission-product tellurium decayed with the 77h half-life of Te^{132} after the initial growing in of I^{132}.

The efficiency of the end-window proportional counter was determined by Bayhurst's method as described earlier and the calibration curves of the counter efficiency for Te^{132} and I^{132} against source weights are given in Fig. 19.

From the observed counting rate due to Te^{132} — I^{132} in transient equilibrium, disintegration rate due to Te^{132} was calculated as follows:

Let A, N and ϵ denote counting rate, disintegration rate and counter efficiency respectively, then using the subscripts 1 and 2 for Te^{132} and I^{132} respectively, we have,

$$\frac{N_1}{N_2} = \frac{\lambda_2 - \lambda_1}{\lambda_2}$$

$$A_1 = N_1 \epsilon_1 \quad \text{and} \quad A_2 = N_2 \epsilon_2$$

Now, $A = A_1 + A_2$

$$= N_1 \epsilon_1 + N_2 \epsilon_2$$

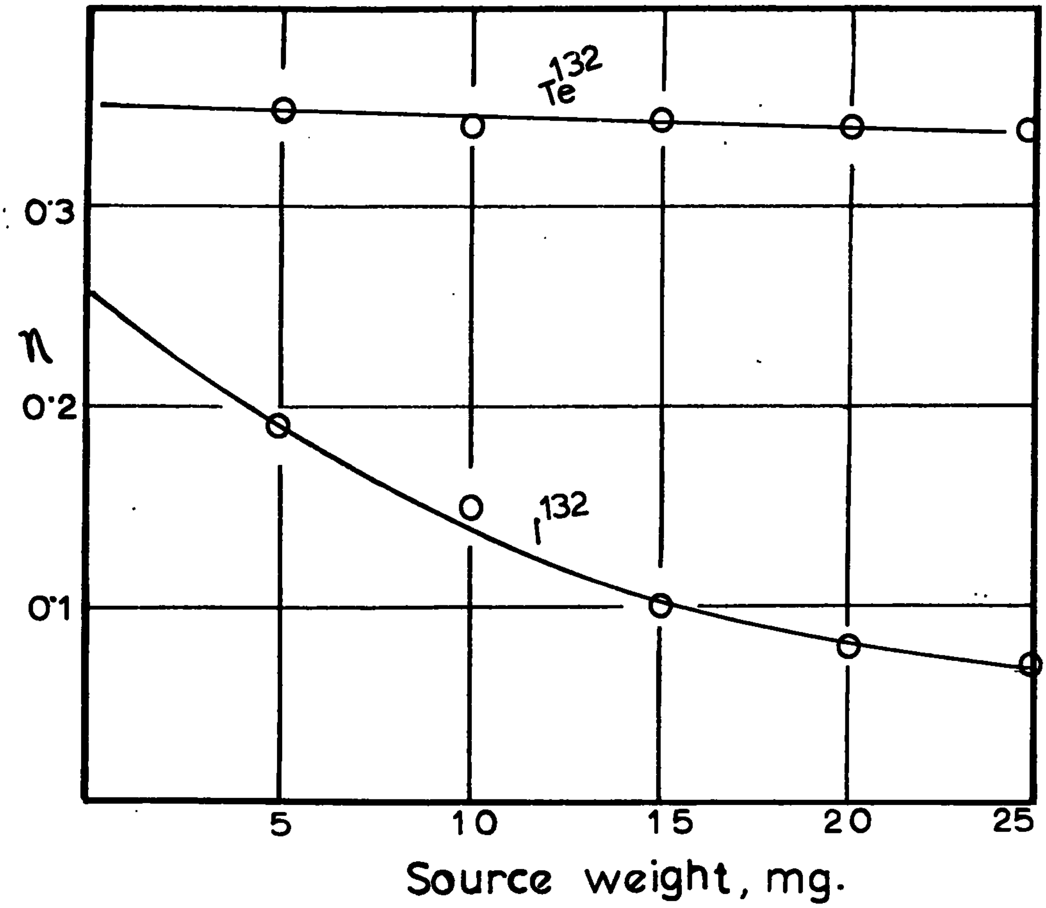

Fig. 19. Counting efficiency curves for 77h Te^{132} and 2·3h I^{132} as function of source weight.

TABLE XVII

Results for 77h Te^{132}

Run No.	Wt. of ppt.mg.	Chem. Yield %	A^o_{obs}	A^o	ϵ_f	S x 10^3	Relative Yield
25	1.873	18.97	62	327	1.721	1,091	.520
26	6.28	63.74	260	408	1.894	965	.638
27	6.06	61.50	185	301	1.880	1,599	.729

Relative Yield of 77h Te^{132} = .629 ± .060.

$$= N_1 \epsilon_1 + N_1 \frac{\lambda_2}{\lambda_2 - \lambda_1} \epsilon_2$$

$$= N_1 \left(\epsilon_1 + \frac{0.00502}{0.00502 - 0.00015} \epsilon_2 \right)$$

$$= N_1 (\epsilon_1 + 1.0308 \epsilon_2)$$

Or $$N_1 = \frac{A}{\epsilon_1 + 1.0308 \epsilon_2}$$

$$= A . e_f$$

The 'efficiency factor' $e_f = \frac{1}{\epsilon_1 + 1.0308 \epsilon_2}$, was calculated for a particular source weight reading the values of ϵ_1 and ϵ_2 from Fig. 19.

The results of the relative yield measurements of this nuclide are given in Table XVII The relative yield was calculated by applying the relative yield equation as deduced on page 25 and the values for S_{Zr} A^{0}_{Zr} and η_{Zr} were taken from Table XVI..

(e) Cerium

The relative fission yield of mass number 143 in the 3-Mev neutron fission of thorium was determined by the radiochemical purification and determination of 33h Ce^{143}. The decay chain for the mass number being

$$1s\,Xe^{143} \longrightarrow (\text{short Cs}) \longrightarrow 13s\,Ba^{143} \longrightarrow 18m\,La^{143} \longrightarrow 33h\,Ce^{143} \longrightarrow$$

$$13.7d\ Pr^{143} \longrightarrow Nd^{143} (\text{stable})$$

To allow decay of the 18m La^{143} precursor of Ce^{143} the separation of the fission product cerium from irradiated thorium was not began until about two hours after the end of an irradiation. Cerium and praseodymium we re always separated from the same irradiated sample. This was done because it was found convenient to separate cerium and praseodymium (together with other rare-earth fission products) as a group during the initial steps of the separation procedure. After the gross separation and purification of fission product rare-earths as a group, as mentioned earlier (see page 73) cerium was oxidised to $Ce^{IV}$and extracted into hexone by the method described by Glendenin and Steinberg.[107] A detailed description of the procedure is given in the appendix. The cerium was finally precipitated as cerous oxalate for source preparation and counting. After following the decay of the sources for about three hundred hours, their cerium contents were determined by a back-titration method with EDTA and Zinc, using Eriochrome Black T as an indicator. (see page 48). Sources of fission product cerium decayed with a half-life of 33 hours with a long tail due to the growing-in of 13.7d Pr^{143}. The decay curves could always be resolved without difficulty, however.

TABLE XVIII

Results for 33h Ce^{143}

Run No.	Wt. of ppt. mg.	Chem. Yield %	A^o_{obs}	A^o	η_{Ce}	S x 10^3	Relative yield
28	9.98	40.00	365	913	.370	1,420	1.284
29	3.94	15.79	84	531	.385	1,200	1.211
31	10.35	41.48	475	1,145	.370	2,593	1.269

Relative yield of 33h Ce^{143} = 1.254 ± .021

Calibration of the Proportional Counter for 33h Ce^{143}

A virtually carrier-free solution of cerium activity was separated from pile-irradiated uranium by the method of Glendenin and Steinberg reduced for working with 1 mg of added carrier and omitting the final precipitation step. The disintegration rate of the solution was determined by 4π counting of aliquot parts. Solid sources containing known amounts of cerium activity were prepared and counted long enough to enable their decay curves to be resolved. A calibration curve was drawn for the efficiency of the proportional counter for detecting Ce^{143} in sources of different weights of cerium oxalate. The calibration curve is given in Fig. 20. The results of the yield measurement are given in Table XVIII.

(f) Praseodymium

The relative fission yield of mass number 145 was based on 5.96h Pr^{145}. The decay chain of this mass number has been given on page 73. The experimental procedures for the separation of praseodymium from fission products of thorium and for the calibration of the proportional counter were the same as those described in connection with the relative yield measurement of Pr^{145} from the 14-Mev.

TABLE XIX

Results for 5.96h Pr^{145}

Run No.	Wt. of ppt.mg.	Chem. Yield %	$A^{o}_{obs.}$	A^{o}	η_2	S x 10^3	Relative Yield
28	7.56	30.42	1,075	3,534	.343	1,294	1.063
29	4.11	16.54	310	1,874	.344	1,116	.930
31	5.37	21.61	945	4,373	.344	2,431	1.005

Relative yield of 5.96h Pr^{145} = .999 ± .038

neutron induced fission of thorium.

The relative fission yield was calculated by applying the relative yield equation as deduced on page 25. A^{o}_{Zr}, S_{Zr} and η_{Zr} values were taken from Table VI and the values for η_{Pr} were obtained from Fig. 18. The results of the relative yield measurements are given in Table XIX.

CHAPTER IV

TREATMENT OF THE DATA, RESULTS AND DISCUSSION

1. General Treatment of the Results:

The method used in calculating the yield of a particular nuclide relative to one of the fission products (in the present work 17h Zr^{97}) has already been discussed in chapter II. Because of the longer 'cooling' time required to allow for the decay of precursers of 8.05d I^{131}, it was found convenient to determine its fission yield relative to 66h Mo^{99}. The yield of I^{131} relative to Mo^{99} was multiplied by the yield of Mo^{99} relative to Zr^{97} to obtain the yield of I^{131} relative to Zr^{97}. The results of the relative yield measurements are given in Table XXI. In each case at least three measurements were made and each datum in column 2 of Table XXI is the mean of such measurements The error shown there is simply the standard error of the mean of the replicate experiments. It was estimated that the relative errors were good to ± 5% except for Te^{132} where the higher error (about 10%) was probably partly due to uncertainty in chemical composition and partly due to low counting rates. However, for calculating the v values, drawing the mass yield curves and determining the maxima of the peaks, only the mean values were used.

2. Correction for the Measured Yields to Total Chain Yields:

It has been mentioned in chapter II that in measuring radiochemically the relative fission yield of any nuclide which is one or two β-isobars away from the stable end of the decay chain, one determines the cumulative yield of the decay chain in question down to and including the nuclide actually determined. To obtain the total chain yield, therefore, an appropriate and necessary correction should be applied. For low and moderately energetic particles inducing fission in heavy elements, the most plausible and widely used procedure by means of which the measured yields are adjusted to total chain yield is the 'equal charge displacement' hypothesis as proposed by Glendenin et al.[113] This postulates that the most probable mode of charge division leads to equal chain length for the complementary fragments i.e.

$$Z_A - Z_p = Z_{A^*} - Z_{p^*} \qquad \text{..........................} \quad \text{(II)}$$

where Z_p is the most probable charge and Z_A is the most stable charge for a chain of isobars. The masses A and A* are related to the mass number A_f of the fissioning nucleus and v, the mean number of secondary neutrons emitted by that particular fragment pair, by the following equation:

$$A + A^* = A_f - v \qquad \text{......................} \quad \text{(III)}$$

Again, the conservation of charge for neutron induced fission requires that:

$$Z_P + Z_{P^*} = Z_f \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (IV)$$

where Z_f is the charge of the fissioning nucleus. From equations (II) and (IV), it follows by the elimination of Z_{P^*} that:

$$Z_P = Z_A - \tfrac{1}{2}\,(Z_A + Z_{A^*} - Z_f) \ldots\ldots\ldots\ldots\ldots\ldots \quad (V)$$

It also follows from equation (III) that:

$$A^* = A_f - A - v \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (VI)$$

The independent yield of the fission products of a given A when plotted against their Z values follow a Gaussian distribution; the Z at the peak of the curve is referred to as Z_P. Wahl et al[114] have shown that in general a single Gaussian distribution curve fits the independent yields fairly well for most of the chains produced by nuclei undergoing fission at low and moderate energies. Alexander and Coryell[115] have measured the independent fission yields of a number of products in the fission of thorium by fast neutrons and have found the results to be consistent with the equal charge displacement hypothesis. In the present work, therefore, this hypothesis of equal charge displacement was used for correcting the measured cumulative yields to total chain yields.

For calculating the Z_P values in the present investigation, values of Z_A and Z_{A*} were calculated as suggested by Coryell.[116] To obtain the A* value using equation (VI), it is necessary to know the values of v, the number of secondary neutrons emitted by that particular pair during fission. It is now well established that there is a strong variation of neutron yield with fragment mass and it is desirable that in calculating A* values, appropriate v values should be used. Unfortunately, no such data are available for Th^{232}. In deed, one of the purposes of the present work was to determine the number of secondary neutrons for a few fragment pairs in the fast neutron induced fission of Th^{232}. However, the contribution of the variation of the number of neutrons in calculating Z_P and hence the total chain yield is so small that the use of a constant $\bar{v}$ value will not make much significant difference in the total chain yield values.

After calculating Z_P, using $\bar{V}$ values of 2.4 and 4.4 respectively for 3- and 14-Mev neutron fission of Th^{232},[48] $Z-Z_P$ values of the nuclides measured were obtained and the independent yield of the successor(s) of the mass chain concerned were read off from the conventional charge

TABLE XX.

Calculated values of $Z-Z_P$ and independent yields of the successors.

A	Z_A	A^*	Z_{A^*}	$Z_A + Z_{A^*}$	Z	Z_P	$Z-Z_P$	I.Y. of the successors.
For 14-Mev. neutron fission of Th^{232}, $\bar{v} = 4.4$								
83	36.1	145.6	60.8	96.9	35	32.7	2.3	$< 10^{-5}$
84	36.5	144.6	60.5	97.0	35	33.0	2.0	$< 10^{-5} x5$
97	42.5	131.6	54.5	97.0	40	39.0	1.0	$= 10^{-2}$
99	43.3	129.6	53.8	97.1	42	39.8	2.2	$< 10^{-5}$
129	53.6	99.6	43.5	97.1	51	50.1	0.9	$\simeq 10^{-2} x1.5$
131	54.3	97.6	42.7	97.0	53	50.8	2.2	$< 10^{-5}$
145	60.6	83.6	36.4	97.0	59	57.1	2.9	$< 10^{-5}$
For 3-Mev. neutron fission of Th^{232}, $\bar{v} = 2.4$								
83	36.1	147.6	61.5	97.6	35	32.3	2.7	$< 10^{-5}$
84	36.5	146.6	61.2	97.7	35	32.7	2.3	$< 10^{-5}$
97	42.5	133.6	55.2	97.7	40	38.7	1.3	$\simeq 10^{-3} x3$
99	43.3	121.6	54.5	97.8	42	39.4	2.6	$< 10^{-5}$
129	53.6	101.6	44.3	97.9	51	49.7	1.3	$= 10^{-3} x3$
132	54.6	98.6	43.1	97.7	52	50.8	1.2	$= 10^{-3} x3.5$
143	59.9	87.6	38.4*	98.1	58	55.9	2.2	$< 10^{-5}$
145	60.6	85.6	37.1	97.7	59	56.8	2.2	$< 10^{-5}$

* Average of two shell values.

TABLE XXI

Correction of measured yields to total chain yields:

Mass No.	Measured yield	% Chain measured	Total Chain Yield	**Energy of the neutron**
83	0.583± .023	100	0.583± .023	**14-Mev**
84	0.831± .013	100	0.831± .013	
97	1.000	99	1.010	
99	0.677± .023	100	0.677± .023	
129	0.315± .011	98.5	0.320± .011	
131	0.842± .045	100	0.842± .045	
145	0.821± .011	100	0.821± .021	
83	0.399± .004	100	0.399± .004	**3-Mev**
84	0.604± .013	100	0.604± .013	
97	1.000	99.7	1.003	
99	0.562± .016	100	0.562± .016	
129	0.030± .001	99.7	0.030± .001	
132	0.629± .060	99.65	0.631± .060	
143	1.254± .021	100	1.254± .021	
145	0.999± .038	100	0.999± .038	

distribution plot of Wahl et al.[114] This particular charge distribution curve is based on the independent fission yield measurement of the majority of the isobars of six chains and it is thought to be the best charge distribution curve so far published. The results of the calculation of $Z-Z_P$ values are given in Table XI and the values of the total chain yield as obtained after applying necessary correction are given in Table XII.

Some refinements of the equal charge displacement hypothesis of Glendenin was made by Pappas[117] taking into account the effect of the neutron and proton shells on stability, in order to explain some experimental results, especially fine structure in the mass yield curves. According to the Glendenin-Pappas equal charge displacement hypothesis, Z_P of a particular nuclide is expressed by the relation:

$$Z_P = Z_{A+n} + \frac{1}{2} (Z_{f-A-n} + Z_{A-n} - Z_f)$$

To use the above relation in calculating Z_P and $Z - Z_P$ values, it is essential to know the exact number of secondary neutrons emitted in association with the production of complementary fragment masses. Because of the non-availability of such information on the neutron fission of Th^{232} it was found impracticable to use this method in the present investigation.

Determination of the Number of Secondary Neutrons in the Fast Neutron Fission of Th^{232}:

Having corrected the measured relative yields to total chain yields, the number of secondary neutrons emitted by a particular fragment pair was determined. The determination was made by adding the masses of the complementary fragments and subtracting the sum from the mass of the compound nucleus. Thus, if v be the number of secondary neutrons, and A_L and A_H, the masses of the heavy and light fragments respectively, then

$$v = A_f - A_L - A_H$$

where A_f is the mass of the fissioning nucleus (233 for Th^{232}).

The relation used for the calculation of the mass of the complementary fragment from measured relative yields of the near complementary fragments was derived in the following way:

Let Y_c be the interpolated relative yield of mass corresponding to C, which is the complementary ~~of~~ mass of C' whose relative yield has been determined experimentally. Also let Y_a and Y_b ~~be~~ are the relative yields of masses A and B which are nearly complementary to C'. From Fig. 22 mass at C = OC

$$= OB + BC$$

$$= OB + \frac{Y_c - Y_b}{Y_a - Y_b} \times BA \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(VII)}$$

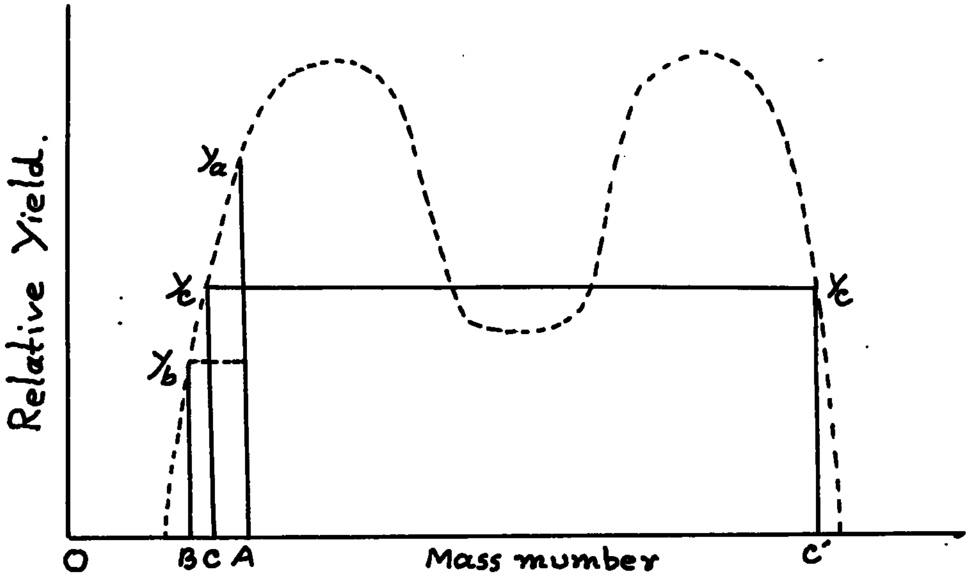

Fig. 22.

In practise, the sign connecting the two terms in equation (VII) will, of course, depend on the position of C' on the mass yield curve.

It should be pointed out here that the above relation, or in other words, the present method of calculation of v is only valid under the following conditions: (i) the measured relative yield Y_i is a sensitive function of mass A_i, (ii) the relative mass yield curve is itself monotonic in the region considered, and (iii) the difference between A and B is small. The relative yield measurements reported here fulfill all the above mentioned conditions.

For the precise drawing of a mass yield curve (absolute or relative) one requires a large number of experimental points. Alternatively, mirror points of

TABLE XXII

Calculation of v values from measured relative yields.

E_n	Fragment mass	Relative Yield	Masses of the near complementary fragments	Relative yield	Mass of the complementary fragments	Sun of the complementary fragments	No. of neutrons
	C'	Y_c	A B	Y_a Y_b		A_L+A_H	
14-Mev	99	.677 (2.479)	131 129	.842 (3.084) .320 (1.172)	130.37	229.37	3.63
14-Mev	131	.842 (3.084)	97 99	1.010 (3.699) .677 (2.479)	98.01	229.01	3.99
14-Mev	145	.821	84 83	.831 (3.043) .583 (2.135)	83.96	228.96	4.04
3-Mev	99	.562 (3.113)	132 129	.631 (3.501) .030 (.166)	131.67	230.37	2.33

TABLE XXII (continued)

E_n	Fragment mass	Relative yield	Masses of the near complementary fragments	Relative yield	Mass of the complementary fragments	Sun of the complementary fragments.	No. of neutrons
3-Mev	132	.631 (3.501)	97 99	1.003 (5.575) .562 (3.113)	98.70	230.70	2.30
3-Mev	84	.604 (3.357)	145 147	.999 (5.510) .510 (4.731)(a)	146.62	230.62	2.38

(a) Extrapolated value.

the experimental points could advantageously be used as supplements. However, to obtain the mirror points a pre-determined value of v is necessary. Sufficient points were not available from the present work for an accurate mass yield curve to be drawn and the use of the mirror points was excluded because ~~of~~ the objective is to determine v values. The advantage of the method followed here is that it requires neither the precise drawing of the mass yield curve nor the absolute fission yield values. However, the absolute fission yields, obtained as discussed in the later section, corresponding to the relative yields used in the calculation, are given in parenthesis for the sake of comparison. The limitations of the method are that it cannot distinguish between the pre-fission neutron emission, the neutron emission that accompanies fission and the delayed neutron, nor is it possible to determine the individual contributions of the light and heavy fragments to v.

The values for v obtained for both the 3- and 14-Mev neutron fission of Th^{232} are given in Table XXII. The values obtained for mass number 145 in the 14-Mev neutron fission and for mass number 84 in the 3-Mev neutron fission of Th^{232} agree within experimental error with the recent published values.[48] It may be pointed out however, that all the existing values for $\bar{v}$ for Th^{232} are the computed average of the number of secondary fission neutrons and are not specific to any particular fragment pair. Moreover, it has been observed[22] that the fragments in the vicinity of any magic number have the tendency to emit lesser numbers of neutrons than the average during fission. Fragment masses in the present investigation (except Br^{84} and Pr^{145}) are close to mass number 132 (mass 99 is a complementary fragment of this mass). The rather lower than the average values of the number of secondary neutrons for masses 99, 131 and 132 found here might be associated with the magic numbers $Z = 50$ and $N = 82$. Such correlations have been strengthened by Terrell[22] who showed that a very similar effect applies to all fissioning species with $Z \geq 92$. Consequently, the v values obtained here were used for drawing the mass yield curves and it was found to give a nice fit.

4. The Mass-yield Curves for the Fission of Th^{232} with Fast Neutrons:

In order to draw the absolute fission yield curves and hence to obtain the absolute fission yield of a particular fission fragment mass-chain, the measured relative yields together with their mirror points were

TABLE XXIII

Absolute mass-yield for the 3- and 14-Mev neutron Fission of Th^{232}.

Mass Number.	Fission Yield, %	
	3-Mev	14-Mev
83	2.218 ± .022	2.135 ± .084
84	3.357 ± .072	3.043 ± .047
97	5.575	3.699
99	3.113 ± .088	2.479 ± .084
129	0.166 ± .005	1.172 ± .040
131		3.084 ± .164
132	3.501 ± .333	
143	6.979 ± .116	
145	5.510 ± .211	3.007 ± .040

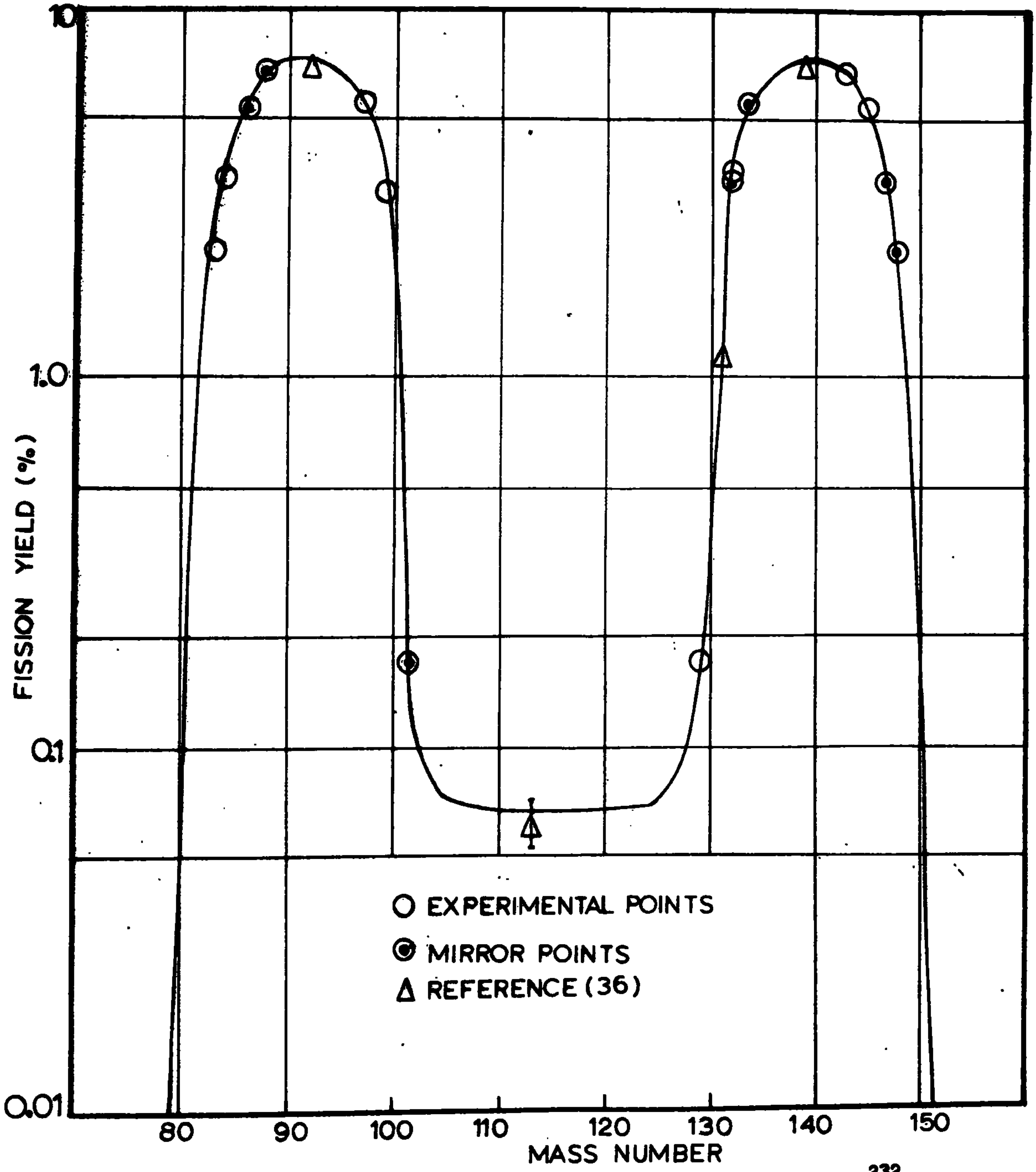

Fig.23. Mass-yield curve for 3-Mev. neutron fission of Th^{232}

plotted as a fission yield curve. The mirror points were obtained from the equation (VI) using v values as determined in the previous section. Where such a v value was not determined, published $\bar{v}$ values (2.4 and 4.4 respectively for 3- and 14-Mev neutron fission) were used. The relative fission yield curves thus obtained were normalized by imposing the condition that the sum of all the fission products should be 200%, assuming that cases of triple fission may be neglected. The absolute yield of individual mass chains thus obtained is given in Table XXIII. Absolute mass distribution curves were then drawn through the experimental points, their mirror points and points supplemented from other measurements, especially in the trough and peak region. Such absolute fission yield curves are given in Fig. 23 (3-Mev fission) and in Fig. 24 (14-Mev. fission).

A comparison of the curves shows the general effect of the increase in the relative amount of symmetric fission with an increase in the excitation energy by the bombarding particle. The peak to valley ratio of about 5 for 14-Mev. neutron fission has increased to about 110 for 3-Mev. neutron fission. A possible explanation of the lack of symmetric fission at lower excitation energies is given by Newson[118]

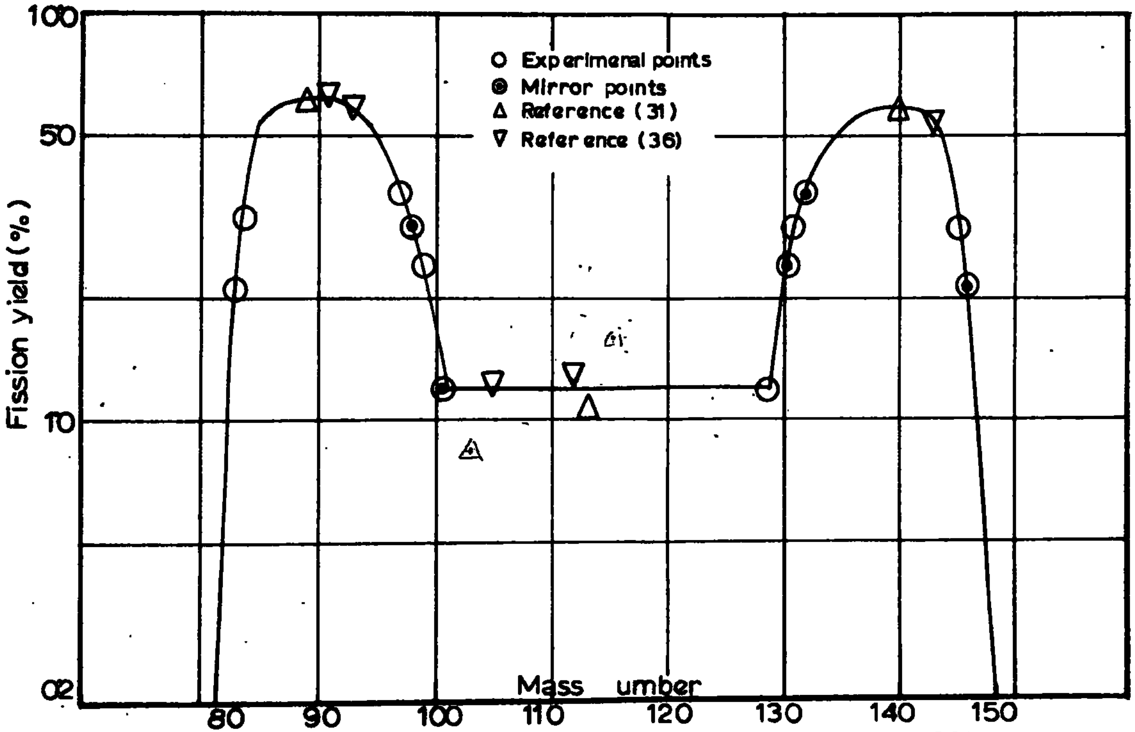

Fig. 24. Mass yield Curve for 14-Mev Neutron Fission of Th^{232}

who considers mass number 132 ($_{50}Sn^{132}_{82}$) a doubly magic nuclide as the core of the heavy mass peak. At low bombarding energy sufficient excitation is not available to disrupt this core as a result of which asymmetric fission predominates. This may also help to explain the fact that in the fission of various heavy nuclides, the heavy peak remains relatively constant, while the light peak shifts as the mass of the fissioning nucleus changes. An alternative explanation of this effect has recently been given by Faisser et al[119] based on the cluster model of nuclear fission.

This general effect of symmetric fission becoming more probable as the energy of the bombarding particle is increased also suggests two separate and distinct modes of fission -- symmetric and asymmetric. It has been observed by Unik et al[33] that α-particle induced fission of Bi^{209} gives a typically single-humped mass yield curve. Fission of U^{238} induced by alpha particles gives a two humped mass yield distribution, with the valley between the two peaks becoming shallower with increasing excitation energy. Helium ion induced fission of Ra^{226} gives a three humped yield distribution. From the mass distribution of the neutron induced fission of Th^{232} at different incident particle energies, indication of the presence

TABLE XXIV

Values of Interpolated masses corresponding to identical and peak maxima.

Energy of bombarding neutron	Absolute yield %	Light peak masses		Centroid (Peak maximum)	Heavy peak masses		Centroid (Peak maximum)
		Outer wing	Inner wing		Inner wing	Outer wing	
14-Mev	3.007 (Pr^{145})	83.96	98.04	91.00	130.93	145.00	137.96
3-Mev	3.357 (Br^{84})	84.00	98.70	91.35	131.94	146.62	139.28

of a third peak in the region of symmetric fission at higher energies, is inconclusive. It appears from the foregoing observations that between bismuth and thorium a transformation from symmetric to asymmetric fission is taking place. It would be of interest to investigate this transformation further as a function of atomic number, mass and excitation energy of the compound nucleus. Characterisation of the very broad valley in the high energy fission mass yield curve of thorium may throw more light on the symmetric and asymmetric mode of fission.

After drawing the absolute fission yield curves for the 3- and 14-Mev. neutron fission of Th^{232}, the centroid or maximum of the peak was determined by drawing a horizontal line through masses of identical yield. The maximum of a peak was taken to be the mean of the masses at identical yield on either wings of the peaks. The results of such determinations are given in Table XXIV. It will be observed from these results that on changing the energy of the bombarding particle from 14- to 3-Mev. the relative change of the light peak is 0.35 mass units while that for the heavy peak is 1.32 mass units. The same effect has also been observed with U^{235} and U^{238}.[44]

The effect of greater relative shift of the heavy peak with lower excitation energy can be explained, at least qualitatively, in the following way: By applying Swaitecki's asymmetry formula, it has been shown by Talat-Erben et al[120] that for some heavy nuclides a neutron added to the fissile nucleus goes preferentially (90%) into the heavy fragment. For Th^{232} in changing the energy of the bombarding neutron from 14- to 3-Mev; the emission of the number of secondary neutrons drops from about 4 to about 2. Or in other words, the mass of the compound nucleus undergoing fission during 3-Mev neutron excitation is greater by about two mass units than the mass of the compound nucleus undergoing fission during 14-Mev. neutron excitation. The difference in the relative shift of peak positions with excitation energy, is therefore, probably due to such a difference of the mass of the compound thorium nuclei undergoing fission at different excitation energies. As a corollary, the above explanation suggests that at higher energies the emission of secondary neutrons is a pre-fission phenomenon rather than a post-fission one.

APPENDIX

1. Initial purification of Thorium

Step 1. To a solution of about 3 gm. of thorium nitrate in 15 ml of water 10 mg. of each of barium and lead carrier were added. The solution was warmed and 0.5 ml. of 5N sulphuric acid added dropwise with stirring, to precipitate barium and lead sulphates. The solution was cooled and filtered through a Whatman No. 42 filter paper.

Step 2. Step 1 was repeated.

Step 3. 10 mg. of bismuth carrier were added to the filtrate from step 2. Bismuth sulphide was precipitated by passing hydrogen sulphide through the solution. The precipitate was removed by filtration and discarded.

Step 4. Step 3 was repeated.

Step 5. The filtrate from step 4 was made alkaline with concentrated ammonia and digested with ammonium carbonate which converted thorium into a soluble carbonate complex. 10 mg. of lanthanum carrier were added to precipitate lanthanum carbonate and the solution was stirred. The precipitate was removed by filtration and discarded.

Step 6. Step 5 was repeated.

Step 7. The filtrate from step 6 was neutralized with concentrated nitric acid and heated to boil off carbon dioxide. Thorium was then precipitated as hydroxide by ammonia, centrifuged and taken into a suitable container for irradiation.

Because of the rapid reappearance of some of the daughter activities it was found desirable that their removal be carried out immediately before irradiation. The reappearance of these activities also prevented drying the hydroxide precipitate before irradiation.

2. ZIRCONIUM

Preparation and standardisation of carrier solution:

A carrier solution containing 5 mg. of zirconium per ml in 1 M nitric acid was prepared and standardised gravemetrically, precipitating and weighing as zirconium tetramandelate, by the method described by Belcher, Sykes and Tatlow.[108]

Radiochemical Procedure:

Step 1. Irradiated thorium nitrate or hydroxide was dissolved in 3 M hydrochloric acid and 2 ml. of zirconium carrier together with carriers for other elements to be separated. After taking steps to ensure isotopic exchange between the added carriers the fission products, 10 ml. of saturated mandelic acid solution were added and the solution was digested for about 20 minutes to precipitate zirconium tetramandelate. The precipitate was centrifuged down and the supernate was reserved for the separation of other elements.

Step 2. The precipitate was transferred into a lusteroid centrifuge tube and dissolved in 60% hydrofluoric acid. 1 ml. of lanthanum nitrate solution was added and the solution stirred well with a polythene rod. On centrifuging, the supernate was transferred to a second lusteroid tube and the precipitate discarded.

Step 3. Step 2 was repeated.

Step 4. The supernate from step 3 was taken into a third lusteroid tube and 2 ml of barium nitrate solution (containing 5 mg./ ml) were added to precipitate barium zirconylfluoride and the solution was stirred thoroughly. The precipitate was centrifuged down and the supernate discarded.

Step 5. The precipitate was dissolved in 2 ml of saturated boric acid and 1 ml of concentrated nitric acid. Zirconium was precipitated by adding 2 ml of barium nitrate solution and 1 ml of hydrofluoric acid. The precipitate was centrifuged down and the supernate discarded.

Step 6. Step 5 was repeated.

Step 7. The precipitate from step 6 was dissolved in 5 ml of water, 2 ml of saturated boric acid solution and 3 ml of concentrated hydrochloric acid. The solution was made alkaline with 6 M sodium hydroxide to precipitate zirconium hydroxide. The precipitate was centrifuged down and the supernate discarded.

Step 8. The precipitate was dissolved in 2 ml of concentrated hydrochloric acid and transferred to a glass centrifuge tube with further rinses of water to make the final volume about 8 ml. 10 ml of saturated mandelic acid solution were added and the solution was digested in a water bath for about 20 minutes to precipitate zirconium tetramandelate.

Step 9. The precipitate was filtered through a tared glass-fibre disc fitted in a demountable filter-stick, washed with 10 ml of a 5% mandelic acid - 2% hydrochloric acid mixture, three 5 ml portions of ethanol and finally with three 5 ml portions of ether. The solid source obtained as above was dried under vacuum desiccation to a constant weight for chemical yield determination and mounted for counting.

3. BROMINE:

Preparation and standardisation of carrier solution: A carrier solution containing 5 mg. of bromine per ml as bromide was prepared by dissolving about 2 gm. of analytical grade potassium bromide in 250 ml of water. The solution was standardised gravimetrically by precipitating and weighing the silver as silver bromide by the method of Glendenin and Metcalf.[109]

(i) The Radiochemical Procedure For 2.4 h Br^{83}

Step 1. The irradiated thorium nitrate was dissolved in 10 ml of 5 M nitric acid and 2 ml of each of bromine and zirconium carrier were added to the solution. The solution was warmed and the bromide oxidized to bromine with Ce^{IV}.

Step 2. The solution was transferred to a separatory funnel and the bromine extracted into carbon tetrachloride. The aqueous phase was reserved for the separation of zirconium.

Step 3. Bromine from the carbon tetrachloride phase was back-extracted into aqueous sodium thiosulphite as bromide and the carbon tetrachloride phase discarded.

Step 4. The aqueous phase was acidified with nitric acid and a few milligrams of iodide carrier were added to it. The iodide was oxidized to iodine with sodium nitrite. Iodine was then extracted into carbon tetrachloride and the organic phase discarded.

Step 5. Step 4 was repeated.

Step 6. The bromide in the aqueous phase from step 5 was oxidized to bromine with potassium permanganate and extracted into carbon tetrachloride; the aqueous phase being discarded.

Step 7. The bromine from the organic phase was back-extracted into aqueous sodium bisulphite. The solution was heated to boil off sulphur dioxide, a few drops of dilute nitric acid were added to it and the bromide was precipitated by the addition of 2 ml of 0.1 M silver nitrate with constant stirring. After digesting for a few minutes, the precipitate was collected on a weighed glass-fibre disc, washed, dried and weighed in the usual way for chemical yield determination and counting.

(ii) The Procedure for 32 m Br^{84}

Step 1. The irradiated sample of thorium nitrate was placed in a 100 ml distillation flask containing 2 ml each of bromine and zirconium carrier in 25 ml of 3M nitric acid.

Step 2. The flask was warmed to accelerate the dissolution of thorium nitrate, and the bromide carrier was oxidized to bromine with Ce^{IV} and the evolved gas swept out by nitrogen into a solution containing freshly prepared ferrous sulphate and a little iodide carrier in a separatory funnel. The residue in the distillation flask was reserved for the separation of zirconium.

Step 3. The iodide was oxidized to iodine with excess sodium nitrite and extracted into carbon tetrachloride; the organic phase was discarded.

Step 4. Step 3 was repeated after further addition of some iodide carrier.

Step 5. To the aqueous phase containing bromide

2 ml of 0.1 M silver nitrate solution were added to precipitate silver bromide. After digesting the suspension for a few minutes, the precipitate was collected on a tared glass-fibre disc. The precipitate was washed, dried, weighed and mounted in the usual way for counting and chemical yield determination.

In trial separations for both the methods in the presence of I^{131} tracer, the final silver bromide precipitate showed a decontamination factor of about 2×10^3 from this isotope.

4. MOLYBDENUM:

Preparation and standardisation of carrier solution:

A carrier solution containing 5.0 mg of Mo per ml. was prepared by dissolving about 2.3 gm. of $(NH_4)_6Mo_7O_{24}.4H_2O$ in 250 ml. of water. The solution was standardized gravimetrically by precipitating and weighing as $PbMoO_4$ by the method described by Weiser.[110]

Radiochemical Procedure

Step 1: To the solution of irradiated thorium nitrate in approximately 1M nitric acid 2 ml. of Mo carrier together with carriers for other elements to be separated was added. After adding 5 ml of a 2% solution of -benzoin oxime in ethanol, the mixture was stirred well and set aside for about five minutes to allow the precipitate to coagulate.

The precipitate was centrifuged down and washed with 50 ml of water. The supernate was set aside for the separation of other elements as required.

Step 2. The precipitate was dissolved in 3 ml. of fuming nitric acid, diluted to 25 ml. with water and partially neutralized with concentrated ammonia. After cooling in an ice bath for a few minutes, Mo was precipitated with 5 ml. of the oxime reagent, stirred well and centrifuged, The supernate was discarded and the precipitate was washed once with water.

Step 3. Step 2 was repeated.

Step 4. The precipitate from step 3 was dissolved in 3 ml. of fuming nitric acid and transferred to a hundred ml conical flask together with the washing from the centrifuge tube with about 3 ml of perchloric acid. The solution was cautiously boiled almost to dryness to destroy the organic reagent and then cooled.

Step 5. The molybdenum residue was dissolved in 4 ml of water and one ml of concentrated ammonia. The solution was transferred to a centrifuge tube and acidified with 6 M nitric acid. 1 ml of ferric iron carrier was added and the hydroxide precipitated by making the solution ammoniacal with concentrated ammonia. The mixture was centrifuged and the supernate transferred to another clean tube.

Step 6. The supernate from step 5 was made acidic (red to thymol blue) by dilute nitric acid. 1 ml of lead nitrate solution (100 mg. Pb^{2+}/ml) was added to the solution and heated to boiling. If no precipitate appeared, dilute ammonium hydroxide was added drop-wise until the precipitate just appeared. The mixture was then boiled for a few minutes, and filtered while hot through a weighed fibre-glass disc. The precipitate was washed, in turn, with hot water, alcohol and ether, dried under vacuum desiccation, weighed for chemical yield determination and mounted for counting.

5. ANTIMONY

Preparation and standardisation of carrier solution:
A carrier solution containing 5 mg of antimony per ml as Sb^{111} was prepared by dissolving an appropriate quantity of antimony trichloride in water containing sufficient hydrochloric acid to prevent any hydrolysis of antimony. The solution was standardised gravimetrically by precipitating and weighing as antimony n-propyl gallate by the method described by Wilson and Lewis.[111]

Radiochemical procedure:

Step 1. The irradiated thorium sample was dissolved in 5 ml of concentrated hydrochloric acid and 2 ml of antimony carrier plus carriers for other elements to be separated were added to the solution. To ensure complete isotopic exchange Sb^{111} was oxidised to Sb^{V} with bromine and the excess bromine was expelled by boiling the solution.

Step 2. The solution was diluted, warmed and saturated with hydrogen sulphide gas until the precipitation was complete. The precipitate was centrifuged down and washed with water while the supernate was reserved for the separation of other elements as required.

Step 3. The precipitate was dissolved in 5 ml of concentrated hydrochloric acid and the solution was boiled down to about 1 ml, cooled and diluted to 10 ml with concentrated hydrochloric acid.

Step 4. The solution was tranferred to a separatory funnel containing 10 ml of di-isopropyl ether previously equilibrated with an equal volume of benzene and a little bromine. The funnel was shaken for about ten seconds, the aqueous phase discarded and the organic phase washed with 10 ml of 9 M hydrochloric acid.

Step 5. The organic phase was transferred to another separatory funnel containing 10 ml of 7 M ammonium thiocyanate solution, 0.5 M in hydrochloric acid and containing a little hydrazine. The funnel was shaken for about a minute, the organic phase discarded and the aqueous phase washed with 10 ml of di-isopropyl ether containing a little ammonium thiocyanate solution.

Step 6. The aqueous phase was transferred to a centrifuge tube and a few drops of tellurium carrier solution were added to it. Elemental tellurium was precipitated and boiling the solution in the presence of hydrazine. The precipitate was centrifuged down and discarded.

Step 7. Antimony was precipitated from the supernate with n-propyl gallate in the usual way; the precipitate was washed three times with 5 ml portions of 0.5 M hydrochloric acid, three times with 5 ml portions of ethanol and finally with ether, dried, weighed for chemical yield determination and mounted for counting.

6. IODINE

Preparation and standardization of Carrier solution: A carrier solution containing 5 mg of iodine per ml as iodide was prepared by dissolving about 1.8 gm. of reagent grade potassium iodide in 250 ml of water. The solution was standardized gravimetrically by precipitating and weighing the silver as AgI by a method described by Glendenin and Metcalf.[109]

Radiochemical Procedure:

Step 1. The irradiated sample of thorium nitrate was dissolved in 10 ml of dilute hydrochloric acid and 2 ml of iodine carrier together with carrier solutions for other elements to be separated were added to it. The solution was made alkaline with ammonia and sufficient saturated sodium carbonate solution added to dissolve thorium as the basic carbonate.

Step 2. 2 ml of 2.5% sodium hypochlorite solution were added to oxidise I' to IO_4' and heated. The solution was made acidic with concentrated nitric acid and transferred to a 250 ml separatory funnel. 3 ml of 1 M hydroxylamine hydrochloride solution were added to reduce IO_4' to I_2. The iodine was extracted into 10 ml of carbon tetrachloride and the aqueous phase retained for the separation of other elements.

Step 3. The carbon tetrachloride phase was shaken with 10 ml of water containing a few drops of sodium thiosulphate until both the phases were colourless. The carbon tetrachloride phase was discarded.

Step 4. To the aqueous phase 1 ml of 6 M nitric acid and a few drops of 1 M sodium nitrite solution were added to oxidise I' to I_2. The iodine was extracted into carbon tetrachloride and the aqueous phase discarded.

Step 5. Step 3 was repeated.

Step 6. After adding 1 ml of 6M nitric acid to the aqueous phase it was heated to boiling before the iodine was precipitated by the addition of 2 ml of 0.1 M silver nitrate solution. After digesting the precipitate for a few minutes it was transferred to a weighed glass-fibre disc by means of filter-stick, washed three times with 5 ml of water, three times with 5 ml of ethanol and finally three times with 5 ml of ether. The precipitate was dried in the usual way, weighed for chemical yield determination and mounted for counting.

7. Standardisation and preparation of carrier solution:

A carrier solution containing 5 mg. of tellurium per ml was prepared by dissolving the appropriate quantity of telluric acid in water. The solution was standardised gravimetrically by precipitating elementary tellurium with hydrazine and sulphur dioxide.[112]

Radiochemical procedure

Step 1. Irradiated sample of thorium nitrate was dissolved in dilute nitric acid and carrier solution (2 ml) for each of tellurium, zirconium and other elements to be separated were added to the solution. To facilitate complete isotopic exchange between the fission product tellurium and the added carrier tellurium was oxidised by potassium permanganate solution. The excess permanganate was removed by adding hydrogen peroxide. Tellurium was then precipitated in the cold by adding with vigorous stirring about 0.5 ml of stannous chloride solution (containing 50 mg of Sn^{++} per ml). After about a minute the precipitate was centrifuged down and the supernate reserved for the separation of other elements.

<u>Step 2.</u> The metallic tellurium precipitate was washed with hot water and dissolved in nitric acid. The solution was heated to dryness. The residue was dissolved in hot dilute hydrochloric acid and tellurium was precipitated by hydrazine and sulphur dioxide. The precipitate was centrifuged down and the supernate discarded.

<u>Step 3.</u> The tellurium was dissolved in concentrated nitric acid and evaporated down with hydrochloric acid as in step 2. The residue was dissolved in hot dilute hydrochloric acid. The solution was made alkaline and scavanged twice with precipitation of ferric hydroxide; the ferric hydroxide being discarded on each occasion. The solution was made 3 M in hydrochloric acid and tellurium was precipitated with hydrazine and sulphur dioxide. The precipitate was centrifuged down and the supernate discarded.

<u>Step 4.</u> The tellurium from step 3 was redissolved and precipitated as in step 2. The precipitate was transferred to a weighed glass-fibre disc through a filter-

stick, washed with alcohol and ether and dried under vacuum for chemical yield determination and counting.

8. CERIUM

Preparation and standardisation of carrier solution: A carrier solution containing 5 mg. of cerium^{III} per ml was prepared by dissolving 5 g. of analytical-grade ammonium nitratocerate in water, reducing with hydroxylamine hydrochloride and diluting to 250 ml with water and a little nitric acid. It was standardised by titration at a pH between 5.8 and 6.2 with EDTA using Xylenol Orange as indicator. (see page 35).

Radiochemical procedure

Step 1 to 11. were the same as those for the initial separation of fission-product rare-earths given in detail in the procedure for praseodymium on page except that a redox cycle was introduced for the complete exchange between the active fission product Ce and the added carrier. The following procedure commences with the precipitate of the rare-earth hydroxides from step 11.

Step 12. The rare-earth hydroxides were dissolved in 5 ml of 10 M nitric acid and approximately 2 ml of 2 M sodium bromate solution were added to oxidise Ce^{III} to Ce^{IV}. The solution remains a slight amber in colour showing the oxidation of cerium.

Step 13. The Ce^{IV} was extracted into a volume of methyl iso-butyl ketone(hexone) equal to ten times the volume of the aqueous phase. The hexone was previously equilibrated with an equal volume of 10 M nitric acid containing about 4 ml of 2 M sodium bromate. The aqueous phase was separated, made alkaline with ammonium hydroxide and reserved for the separation of praseodymium. The organic phase was washed with 10 ml of nitric acid - sodium bromate solution and the washing discarded.

Step 14. The cerium was back-extracted into 10 ml of 10% hydrogen peroxide and the hexone phase discarded. The solution was transferred to a centrifuge tube and made alkaline with ammonium hydroxide to precipitate cerium hydroxide. The precipitate was centrifuged down and the supernate discarded.

Step 15. The hydroxide precipitate was dissolved in 1 ml of concentrated hydrochloric acid, diluted to 15 ml and 10 ml of saturated ammonium oxalate solution were added to the hot solution with constant stirring to precipitate cerium oxalate. The precipitate was filtered on to a glass-fibre disc, washed with water, alcohol and ether; dried in a vacuum desiccator and mounted for counting.

9. PRASEODYMIUM

Carrier. A carrier solution of Pr containing 5 mg. of the element per ml. was prepared by weighing out an appropriate quantity of trioxide and dissolving it in the minimum of hydrochloric acid. It was standardised by titration with EDTA using Xylenol Orange as indicator at pH 6. (see page 35).

<u>Resin</u>; Zeo-Karb--225, 100-200 mesh, 4-5% cross-linked, was used after grading. The grading of the resin was done on the difference of their settling time in distilled water. Commercial resin was introduced in the form of slurry in water at the top of a long tube held in a vertical position and filled with distilled water. Portions of the resin which settled down between 1--1.5 cm/ min. were collected and subjected to the following chemical treatment before putting into the column.

Putting the graded resin into a column of a size which allow adequate stock of resin to be processed, it was washed with 6 M ammonium thiocyanate until the red ferric thiocyanate colour was no longer visible. It was then washed twice, in turn, with distilled water and 6M hydrochloric acid. Finally the resin was washed with sufficient distilled water to free it from chloride and converted into the ammonium form with 1 M ammonium lactate solution of pH 3.2 and stored in distilled water until loaded into the column.

<u>Eluant</u>: The eluting solution was a mixture of 1M ammonium lactate solutions of pH 3.2 and 7.0. They were

prepared from 88% lactic acid of AR-grade. Before using the acid for the preparation of solutions, it was refluxed for about 7 hours in 0.1 M hydrochloric acid to ensure the hydrolysis of any anhydride present in the acid. The pH's of the solution were adjusted with concentrated ammonium hydroxide and measured on a pH meter. The solution was also made about 0.001M in phenol to prevent any deterioration of the lactate on long storing.

Apparatus: The Gradient-Elution equipment shown in Fig. is similar to that described by Nervik.[105] The ion-exchange bed had a dimension of 60 cm x 7 mm (internal diameter). The column was surrounded by a 7 cm. glass tube serving as reservoir for water for uniformly heating the column. An electrothermal heating tape was wound round the outer jacket tube. The temperature controlled by means of a "simmerstat" within ± 3°C. Since the operating temperature of the column was about 90°C, a small water cooled condenser was fitted into the reservoir at the top to minimise loss of water due to evaporation.

The eluting agent system consisted of two 500 ml. flasks fitted one above the other. The lower flask contained the solution of lower pH and the upper one that having the higher pH. The flow rate of the solution from the upper to the lower flask was controlled by means of a stopcock. For applying a positive pressure both the flasks were connected to a nitrogen cylinder by PVC tubing. To attain the required flow rate of eluant, the pressure of nitrogen from the cylinder was controlled with a pressure regulator. In order to ensure continuous and complete mixing of solutions in the lower flask, a small magnetic stirring device was kept in operation during elution. The eluting solution was pre-heated by passing through a glass tube of 2 mm. i.d. fitted inside the reservoir as shown in the figure.

The fraction collector consisted of a turn-table carrying 50 polythene test-tubes, arranged so that each tube collected a pre-selected number of drops of the eluant before the next tube was moved into position by an automatic device.

Procedure: The irradiated thorium hydroxide was dissolved in 15 ml. of 6 M hydrochloric acid and 10 mg. each of Zr, Pr and Ce carriers were added. Half an hour after the irradiation, Zr was precipitated by adding 15 ml. of saturated mandelic acid solution and digesting for about half an hour. The precipitate was centrifuged down and set aside for the isolation of Zr.

Step 2. The supernate from step 1 was made alkaline with concentrated ammonium hydroxide to precipitate Th, Pr and Ce as hydroxides. The precipitate was centrifuged down and the supernate discarded.

<u>Step 3</u>. The hydroxides were dissolved in nitric acid and Th was extracted twice in 20% TBP solution 6 M Kerosene, using 50 ml. of TBP solution each time.

<u>Step 4</u>. The aqueous phase was made alkaline, centrifuged and the supernate discarded. The precipitate was dissolved in 10 ml. of concentrated nitric acid and the last traces of Th was precipitated with 2 M iodic acid solution. After centrifuging the supernate was used for rare-earth separation and the precipitate was discarded.

<u>Step 5</u>. The supernate was made alkaline with sodium hydroxide solution, centrifuged and the remaining supernate discarded.

<u>Step 6</u>. The precipitate was dissolved in 20 ml. of 3 M hydrochloric acid and 6 drops of Zr carrier (containing 5 mg./ml.) added. After adding 5 drops of concentrated phosphoric acid, the solution was digested for a few minutes and centrifuged.

<u>Step 7</u>. The supernate from step 6 was taken in a nitrocellulose (lusteroid) centrifuge tube and 2ml of 1.5 M chromate and 0.5 ml concentrated hydrofluoric acid were added. After digestion for about 5 minutes in a hot bath, the precipitate was centrifuged down and washed once with 20 ml. of 0.1 M hydrofluoric acid.

<u>Step 8</u>. Step 7 was repeated.

Step 9. The rare-earth fluorides were dissolved in 3 ml. of saturated boric acid solution and 2 ml. concentrated nitric acid. To ensure complete dissolution the solution was heated and stirred well. After adding 5 drops of Ba carrier and 1 ml. of 6 M sulphuric acid, the solution was diluted to 20 ml. and digested for 5 minutes in a hot bath. The barium sulphate precipitate was centrifuged down and discarded.

Step 10. The supernate was made alkaline with concentrated ammonium hydroxide and digested for a few minutes. The rare-earth hydroxides were centrifuged down and washed once with dilute ammonia.

Step 11. The precipitate was dissolved in 4 ml. of concentrated hydrochloric acid. The solution was passed through an anion-exchange column (6 mm i.d. x 10 cm.) containing De-Acedite FF, previously equilibrated with concentrated hydrochloric acid. The tube was rinsed with 3 ml. of concentrated hydrochloric acid and the wash solution was passed through the column. The column was finally washed with 2 ml of concentrated hydrochloric acid. All of the eluant and wash solution was collected.

Step 12. The eluate including the rinse and wash solution of step 11 was made alkaline with concentrated ammonium hydroxide. The rare-earth hydroxides were centrifuged down and washed once with dilute ammonia.

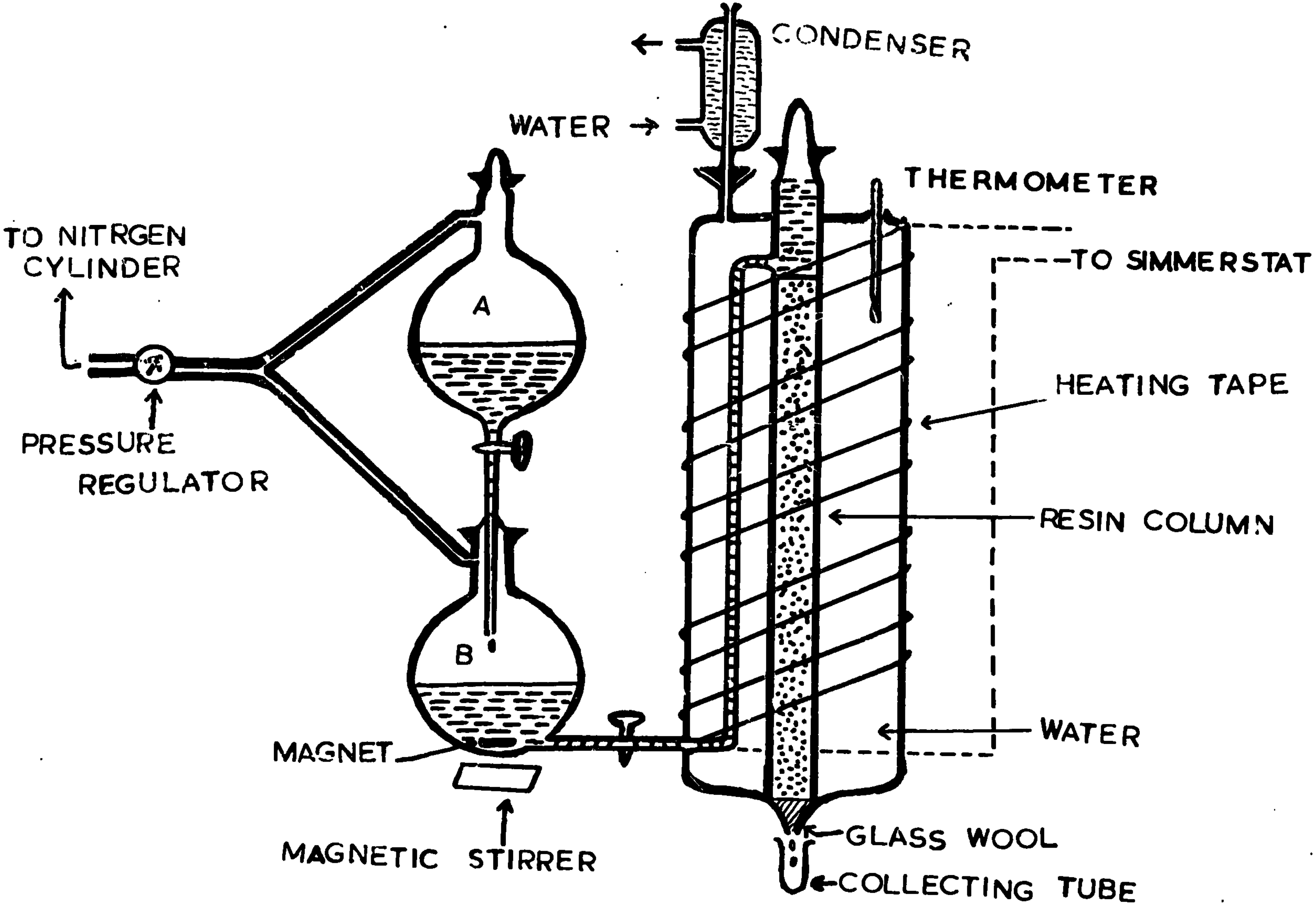

FIG.21 .SCHEMATIC DIAGRAM OF ION EXCHANGE COLUMN

The precipitate was dissolved in 10 ml. of 10 M nitric acid and a few drops of sodium borate solution were added to oxidise Ce^{III} to Ce^{IV}. Ce was then extracted into 'hexone' previously equilibrated with nitric acid-sodium borate solution.

Step 13. The aqueous phase was made alkaline with ammonium hydroxide, the precipitate centrifuged down and washed with dilute ammonia.

Step 14. The precipitate was dissolved in a few drops of concentrated hydrochloric acid and the solution diluted to about 20 ml. About 1 ml. of the resin of the same batch that was to be used for cation separation was added to the solution and digested for about ten minutes. The resin was then centrifuged down and ready to be put into the column.

Step 15. For the separation of Pr from other rare-earth activities: The apparatus described earlier, was assembled as shown in Fig. 21 . The temperature of the water reservoir was raised to 90°C and the column filled with the processed resin in the form of a slurry in boiling water to prevent the formation of air bubbles inside the column. About 100 ml. of 1 M lactic acid solution of pH 3.2 and pre-heated to about 90°C by passing through the inlet tube fitted inside the reservoir, were passed through the column at a rate of 4 drops per minute. Just before starting the separation, the volume of lactic acid solutions in each of the flasks was 60 ml. Rare-earth activities adsorbed on the resin was transferred on the column while hot and elution started. By regulating the pressure from the nitrogen cylinder and controlling the pinch-cock at the outlet of the lower flask, the rate of flow of the eluant was adjusted to about 4 drops per minute. When the column has run for half an hour, the pinch-cock between the two flasks was opened and so adjusted to allow 8 drops of solution to run into the lower flask per minute and the magnetic stirrer was started. 30 drops of eluant were collected in each fraction. The Pr break-through occurred about seven hours after the elution was started and it was located in the collecting tubes by adding saturated ammonium oxalate solution. When all the Pr had been eluted, the precipitate in the 3 to 4 middle fractions was collected together for source preparation, counting and chemical yield determination.

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