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"Radiochemical studies of the fission of thorium by 14 mev neutrons"

John Edward Whitley

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"RADIOCHEMICAL STUDIES OF THE FISSION OF

THORIUM BY 14 MeV NEUTRONS"

THESIS

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by

JOHN EDWARD WHITLEY, B.Sc. (Dunelm).

MEMORANDUM

The work described in this Thesis was carried out in the Londonderry Laboratory for Radiochemistry, University of Durham, between September 1958 and September 1961, under the supervision of Dr. S.J. Lyle, Lecturer in Radiochemistry.

This thesis contains the results of 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 relevant 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.

John E. Whitley

ABSTRACT

The relative yields of 14 mass chains* in the fission of thorium by 14 MeV neutrons have been measured radio-chemically. Fission-product sources were counted with an end-window β-proportional counter which was absolutely calibrated for as many of the nuclides measured as was practicable.

The measured relative yields were corrected to total chain yields on application of the equal charge displacement hypothesis, and a mass-yield curve produced with two narrow peaks and a broad trough. Peak maxima occur at mass numbers 91 and 137.4, with a peak width at half-height of 12.5 mass units. The occurrence of a subsidiary maximum in the centre of the trough is considered, although insufficient evidence is available to delineate this completely.

The relative yields were converted to absolute yields on imposition of the condition that the sum of the yields of all the fission-products must be 200%. The value obtained for the absolute yield of mass number 91 is 6.48 ± 0.33%.

*Mass Numbers: 83, 84, 91, 93, 97, 99, 105, 111, 112, 113, 129, 132, 139, 143.

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CHAPTER   I

INTRODUCTION

(a)   General

Man has sometimes been quick to recognise the technical applications of new scientific observations; not uncommonly before he understands the natural laws governing these observations.   Such has been the case with nuclear fission as a source of nuclear energy.   While applications of the fission process are now extensive, there is as yet no unified theory of the process itself.   Applications already include generation of electrical power, propulsion of ships, and the provision of an intense neutron source of value for both fundamental scientific and technological investigations.   Nuclear fission is also a convenient source of many radioactive isotopes which have numerous applications in research and industry.

After the discovery of the neutron, Fermi[1] suggested that "transuranium" elements might be produced on bombardment of uranium with neutrons followed by β-decay of the uranium isotopes produced.   Many experiments were carried out in which the activities produced in irradiated uranium (and thorium) were erroneously identified as transuranium elements.   However, in 1939 Hahn and Strassman[2] showed that certain activities induced in uranium could not be separated from barium and lanthanum in fractional crystal-

lizations of barium/radium and lanthanum/actinium and con-
cluded that these activities could only arise from a splitting
of the uranium nucleus. In the subsequent years many fission-
product activities of uranium and thorium were identified.
The analogy of a fissioning nucleus with a liquid drop was
first pointed out by Meitner and Frisch.[3] They also sugges-
ted the name for the process.

From a consideration of nuclear binding energies it was
soon realized that fission would be accompanied by a large
energy release.[3,4] When it was discovered that each neutron-
produced fission was accompanied by the emission of more than
one neutron, the production of a divergent chain reaction was
anticipated. At this stage in the investigations of nuclear
fission World War II had broken out. When the possibility
of using nuclear energy in an "atomic bomb" was realized,
investigations in this field became restricted to government
establishments, and classification of results prevented general
publication. The initial investigations of the fission process
which were carried out before the war were reviewed by Turner[5]
in 1940. The work carried out under the "Manhattan Project"
during the war, which culminated in the production of the
first atomic bomb, was eventually declassified, and published
in a comprehensive series of volumes, the "National Nuclear
Energy Series". Of particular relevance to the current

investigation are those volumes edited by Coryell and Sugarman[6] - "Radiochemical Studies: The Fission Products."

In recent years many aspects of the fission process have been investigated in an attempt to obtain a more complete understanding of this complicated process. As will be seen, the models so far suggested for a fissioning nucleus are not capable of explaining all the observed experimental facts. It is only by accumulation of more experimental details and an assessment of all the facts that a comprehensive model might be obtained.

Soon after the discovery of fission Bohr and Wheeler[7] applied the liquid drop model to the fissioning nucleus, and were able to predict several fission parameters which were later experimentally verified (e.g. the threshold for fission of certain nuclides). However, the liquid drop model could not in any way explain the predominance of asymmetric fission, which is a feature common to many of the fissile nuclides investigated. Some success has been achieved in this direction by application of the shell model of the nucleus, in which the asymmetry is explained by the preferential formation of nuclides in the region of closed shells.[8,9] The source of small irregularities in the mass-yield curves, which are termed "fine-structure" is still a source of controversy. Recent studies of fission of elements lighter than

uranium have been comprehensively summarised by Hyde.[10]
The varying contributions from symmetric and asymmetric modes
in the fission of these elements has not been satisfactorily
explained. [10, 14]

(b) Nuclear Fission

The term fission is normally used for processes in which
a heavy nucleus divides into two principal fragments of com-
parable mass. A few fissions have been observed to occur with
the production of three fragments, but in these cases the
third fragment is a light particle (e.g. an α-particle or a
tritium nucleus). The first studies of the phenomenon were
of fission induced by neutron capture, but it is now known to
be a more general process which may follow nuclear excitation
of heavy elements by other methods. Nuclear reactors depend
on neutron-induced fission which therefore occupies a position
of particular significance.

Although a number of neutrons may be released at the
instant of fission, the main fragments retain approximately
the same neutron/proton ratio as the fissioning nucleus.
Since this ratio is normally too high for stability, each
primary fission product decays to a stable isobar by the
emission of a series of β-particles. "Chains" of isobaric
fission products have been tabulated,[11] and examples of
such chains are given in Fig. 1. The wide number of fission

Fig. 1   Examples of Fission Product Decay Chain

$$33s.\ ^{99}Zr \longrightarrow 2.4m\ ^{99}Nb \longrightarrow 66h\ ^{99}Mo \underset{0.13 \searrow 2.1\times10^{5}y.\ ^{99}Tc}{\overset{0.87 \nearrow 6.0h\ ^{99m}Tc}{}} \qquad Stable\ ^{99}Ru.$$

$$45s.\ ^{115}Pd \underset{0.72 \searrow 21m\ ^{115}Ag}{\overset{0.28 \nearrow 205\ ^{115m}Ag}{}} \quad 0.09 \quad 43d.\ ^{115m}Cd \quad 4.51h.\ ^{115m}In \longleftarrow 0.05 \quad Stable\ ^{115}Sn$$

$$0.91 \rightarrow 53h.\ ^{115}Cd \qquad 6\times10^{14}y\ ^{115}In$$

$$2.2m.\ ^{132}Sn \longrightarrow 2.1m.\ ^{132}Sb \longrightarrow 77h.\ ^{132}Te \longrightarrow 2.3h.\ ^{132}I \longrightarrow Stable\ ^{132}Xe.$$
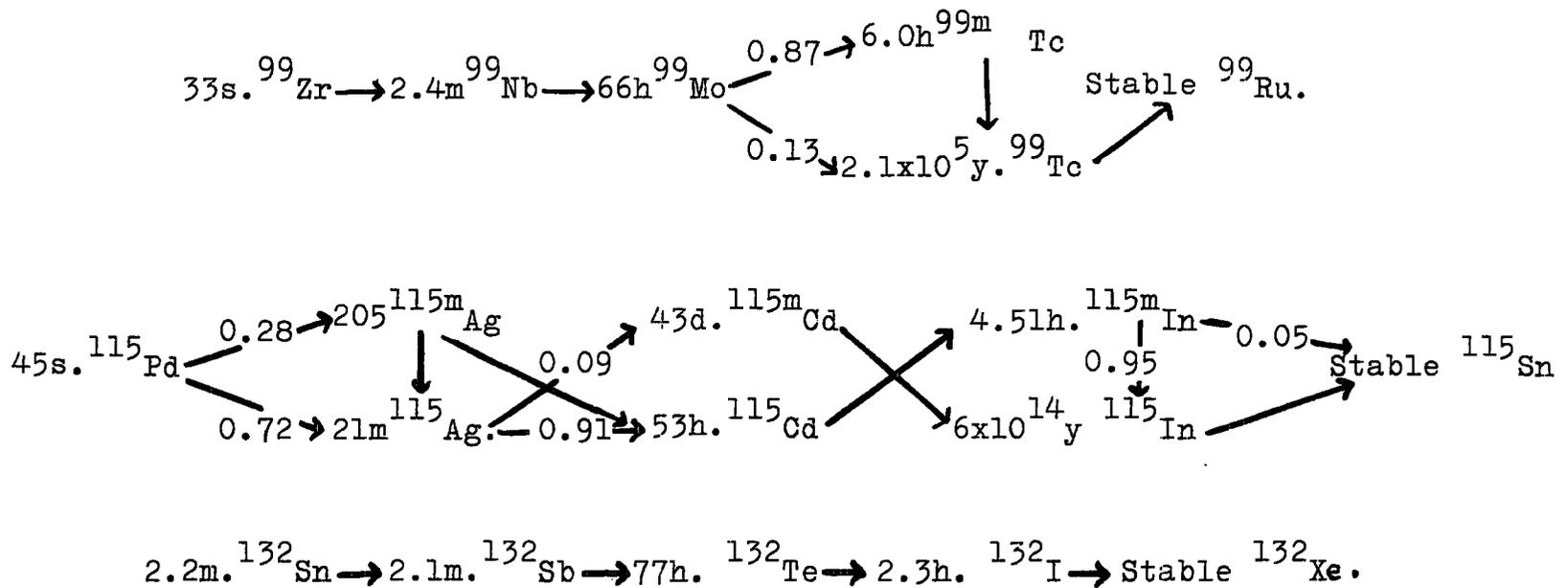
product chains known is indicative of the variety of modes of fission which can occur.

The position of a primary fission fragment in a decay chain is dependent on the nuclear charge distribution at the instant of fission. The fraction of fissions in which a given isobar is produced as an initial fragment is known as the independent yield of that isobar. Because of the rapid decay of many of these initial fragments independent yields are often difficult to measure experimentally. However for a limited number of chains measurements are possible in those cases where a given isobar is preceded by a much longer-lived or stable isobar and its yield in a short irradition can clearly be attributed to its direct production.

Measurements of independent yields have shown that the nuclear charge for any given mass, Z_A, is usually distributed about a most probable charge Z_P. For low and medium energy fission this distribution is best accounted for by the hypothesis of equal charge displacement, as first suggested by Glendenin and Coryell,[12] which may be written as

$$(Z_A - Z_P)_{\text{light fragment}} = (Z_A - Z_P)_{\text{heavy fragment}}.$$

For high energy fission, results are best fitted by an unchanged charge distribution, i.e.

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

From these hypotheses it is possible to estimate that fraction

of the <u>total yield</u> for a given mass number which is represented
by the measured yield of an isobar removed from the end of the
mass chain.

If the absolute fission yield of one nuclide can be measu-
red, others may be found by measuring relative yields. A
direct determination of the absolute yield of a given nuclide
requires knowledge of (1) the total number of fission events
in the sample considered, and (2) the total number of nuclei
of that species which had resulted from the measured number of
fissions.

The number of fissions occuring in a given sample of
irradiated material may be determined by counting the number
of fissions in a small sample of material in a fission chamber
irradiated simultaneously with the bulk of material under
investigation. Alternatively where sufficient knowledge of
cross-sections is available the number of fissions may be
estimated from the yield of some other reaction.

Absolute fission yields may also be determined by normal-
ization of relative yields, i.e. by imposing the condition
that the sum of all the yields should be 200%, since each
fission results in the formation of two main fragments. This
is the method which is frequently used to fix the absolute
scale for yields on the mass-yield curves which are drawn.

Measurements of the yields of fission product nuclides
may be performed by mass-spectrometric or radiochemical methods.

If the fission products to be considered are stable or sufficiently long-lived they can be determined mass-spectrometrically. Where suitable radioactive species occur, their yields may be measured radiometrically. Considerable accuracy has been claimed for mass-spectrometric measurements, but such determinations are only possible where sufficient atoms are produced for mass-spectrometer sources. Because of this restriction, measurements of this type have been restricted to yields from pile-neutron fission, where the fissions have been induced by neutrons of varying energies.

Greater insight into the mechanism of the act of fission might be gained by studies of fission induced by mono-energetic particles. However, where such particles are available, the number of fissions which can be made to occur is too low to produce sufficient atoms for mass-spectrometric studies, and fission yields can only be measured by radiochemical techniques. Because of the difficulties of determining absolute disintegration rates, the accuracy of this method is seldom considered better than 10%.

(c) Fission Product Mass Distribution

The predominance of asymmetric fission is a common feature of fission of the heavier elements. The original radiochemical investigations of Hahn and Strassman[2] showed that the products of neutron-induced fission of uranium were comple-

mentary light and heavy fragments rather than fragments of comparative mass. The mass-yield curve for thermal neutron fission of ^{235}U,[11] which has been obtained by mass-spectrometric and radiochemical measurements, consists of two peaks with a deep trough between them, indicative of predominantly asymmetric fission. As the energy of the fissioning nucleus is raised, the occurrence of symmetrical fission and highly asymmetrical fission increases, resulting in the raising of the valley of the mass-yield curve and a splaying of the sides of the peaks. At very high energies symmetrical fission predominates, and the mass-yield curve takes the form of a single broad hump. These features are common to the highly fissile elements which have been investigated[11] (thorium, uranium, plutonium).

Fission product mass distributions have been inferred from kinetic energy measurements of fission fragments in ionization chambers.[13] Whilst this method confirms asymmetric fission, with the maximum yields at mass numbers comparable with those obtained radiochemically, the peak/trough ratio is different to that obtained by radiochemical methods. This discrepancy might be explained by the total fragment kinetic energies depending upon the mass ratio. It has been implied from fission fragment range measurements that the kinetic energy available in symmetrical fission is lower than that of asymmetric fission.[14]

Owing to its importance in the nuclear energy industry,
fission of uranium is the most thoroughly investigated. In
order to obtain a better understanding of the fission act
it is desirable that fission of as many nuclides as possible
should be investigated, and also the variations of the
phenomenon with different bombarding particles of different
energies. With the advent of high energy accelerating
machines, and their development to very high energies, it
has become possible to study fission induced by particles over
a considerable energy range. Improvements of counting equip-
ment to give reliable measurements at low counting rates has
facilitated study of fission products produced in low yields
e.g. in spontaneous fission. Considerable radiochemical work
has been done, and is currently being carried out to increase
our general knowledge and to elucidate the mechanism of the
fission process.

In recent years it has become possible to synthesise
elements heavier than uranium by nuclear reactions. These
elements are increasingly fissile with increasing atomic
number, and the limit to the heaviest element attainable
appears to be the instability of these elements with respect
to spontaneous fission. The mass-yield curves for fission of
these elements are of the familiar double-humped shape. As
the mass number of the fissioning nucleus is increased, the

position of the peak for high yields of light fission frag-
ments moves to a heavier mass number, whilst the position
of the peak for heavy fragments remains unaltered. The con-
stant position of the heavy peak has been attributed to the
special stability of nuclides in the region of mass number
132 where a nuclear shell is completed (50 protons, 82
neutrons).

The curves of mass yield for fission of bismuth and
lighter elements consist of single symmetrical peaks. In a
recent study of the fission of radium with 11 MeV protons.[16]
a mass-yield curve consisting of three humps was observed.
The transition between the three humps of the mass-yield curve
for radium and the familiar two-humped curves for the asym-
metric fission of the heavier elements might show itself in
the neighbourhood of thorium.

(d) Fission of Thorium

In their discovery of the fission process, Hahn and
Strassman[2] also investigated the effect of neutrons on
thorium as well as uranium, and were able to identify some
thorium fission products. A preliminary study of the fission
products of thorium was made by N.E. Ballou and co-workers,[17]
whilst working for the Manhattan Project. However, owing to
the greater interest in uranium fission at the time, fission

product activities were only tentatively identified, and
suggestions made for separation procedures where the daughters
of thorium might interfere.

A radiochemical study of the fission of ^{232}Th with
pile neutrons of estimated effective energy 2.6 MeV was pub-
lished by Turkevitch and Niday in 1951.[18]   A double-
humped mass-yield curve was produced, as shown in Fig. 2,
with a peak-to-trough ratio of 110. The curve was found to
be very flat in the region of symmetrical fission compared
with the corresponding curves for uranium and plutonium.
The possibility of a subsidiary maximum in the centre of the
trough was suggested, but not confirmed, owing to the large
experimental error in the yield of ^{115}Cd which would define
it. It was also suggested that the curve produced might be
the superimposition of two mass-yield curves:- the double-
humped curve of asymmetric fission, and a curve with a broad
maximum in the region of symmetrical fission.

The work with pile neutrons was followed by an investi-
gation of the fission of thorium by neutrons of 6-11 MeV
from the Li + D reaction.[19] The error of the relative yields
for this investigation was estimated to be 20%, and even
greater for certain nuclides counted. A curve has been
drawn through the measurements published, and is produced
in Fig. 3. Once again, there would appear to be the possi-
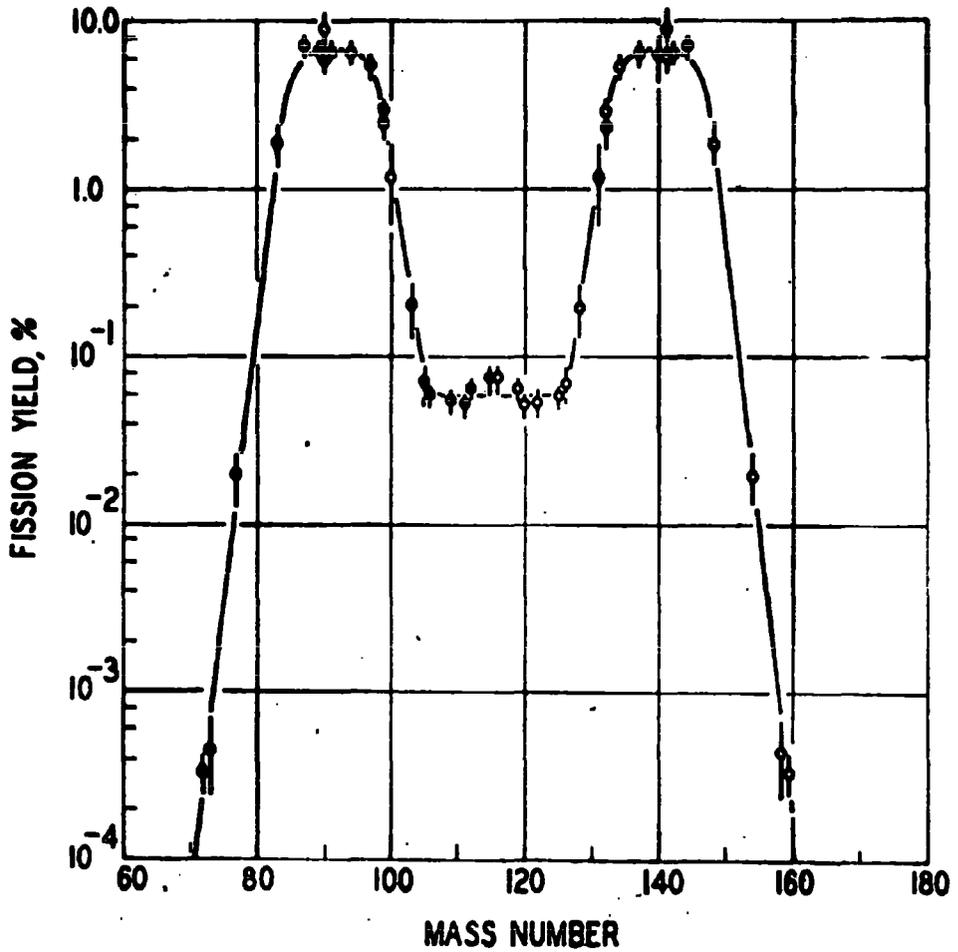
Fig. 2

Mass-yield curve for the fission thorium with
pile neutrons, from the data of Turkevitch
and Niday[18],

FISSION YIELD PERCENT. (y-axis)

MASS NUMBER. (x-axis)

●-EXPERIMENTAL POINTS   ⊙-MIRROR POINTS
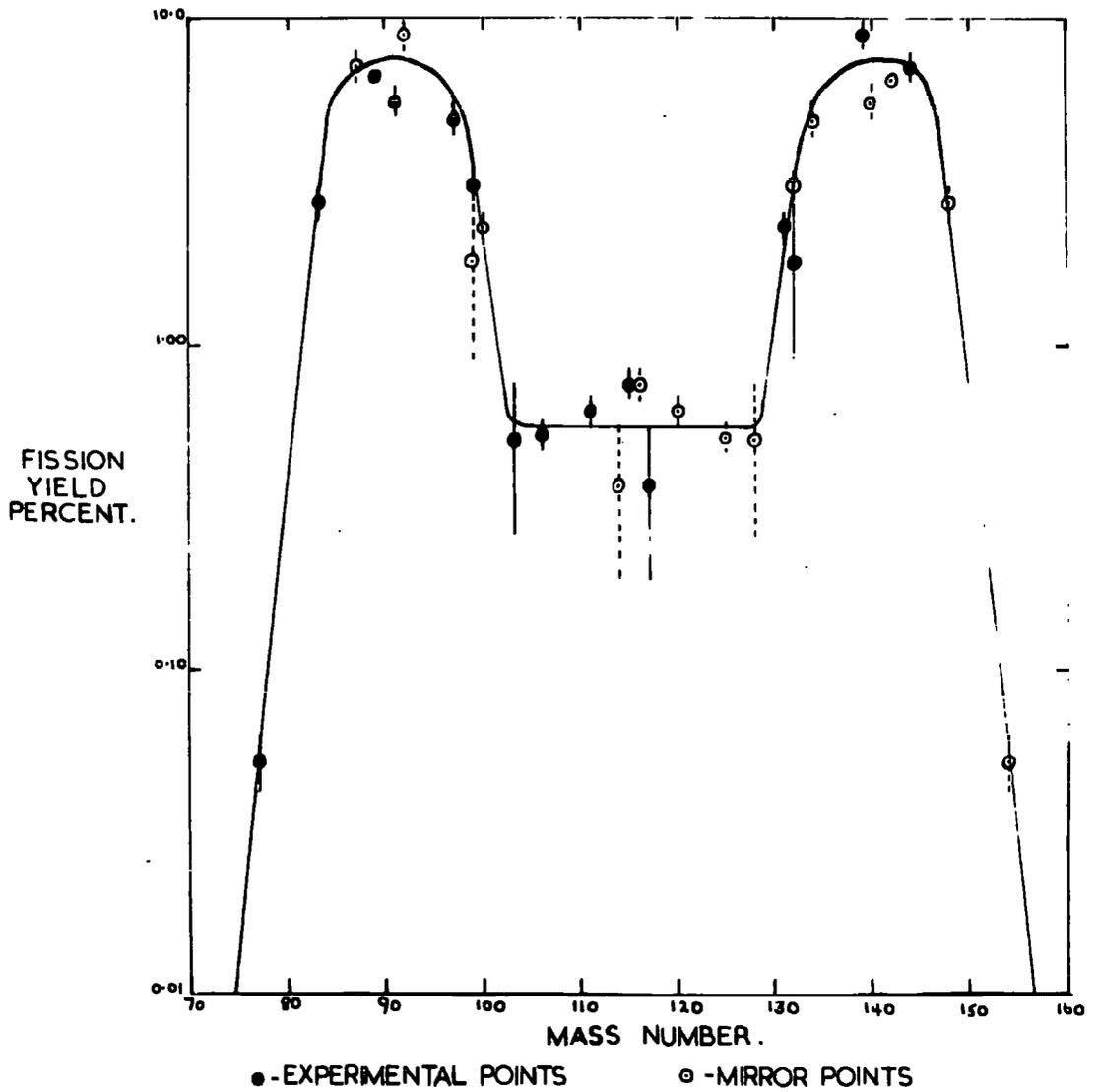
<u>Fig. 3</u>

Mass-yield curve for the fission of thorium with
6-11 MeV neutrons, from Turkevitch, Niday, and
Tomkins[19].

bility of a subsidiary maximum in the centre of the trough.

Mass-yield curves have also been produced for fission of thorium with α-particles,[20] protons,[21] and for photo-fission,[22] of the double humped type. However these curves are not directly comparable with neutron induced fission of thorium, as different compound nuclei are formed in each case. Kennett and Thode[23] have measured the cumulative yields of krypton and xenon isotopes produced in the fast neutron fission of ^{232}Th by the mass-spectrometric technique. Apart from supplementing the data of Turkevitch and Niday, some fine structure was detected in the regions of mass numbers 84 and 132.

The present investigation of fission of thorium (^{232}Th) with 14 MeV neutrons was undertaken as part of a series of investigations of fission of actinide elements being carried out at the Londonderry Laboratory for Radiochemistry in order to determine the mass-yield curve for fission of thorium at this energy. It is only by the accumulation of data such as this that a complete understanding of the pheno-menon of fission will be possible.

CHAPTER II

INVESTIGATIONS OF DETAILED PARTS OF EXPERIMENTAL PROCEDURE
AND DESCRIPTION OF APPARATUS

(a) Outline of Investigations

The extent to which activities present in the material
to be irradiated contaminate the activities of the radio-
chemically separated fission products after irradiation is
dependent on the yields of the latter, and the efficiency of
the radiochemical separations. For the current study such
interferences were expected to result in the contamination
of fission-product barium activities by radium daughters of
thorium: $MsTh_1$ (^{228}Ra) and ThX (^{224}Ra) and a chemical pro-
cedure was devised to reduce these activities in the samples
of thorium before irradiation.

The irradiations were performed using a Cockroft-Walton
accelerator to produce 14 MeV neutrons by the bombardment of
tritium with accelerated deuterons. To make allowance for
the effect of fluctuations of the neutron flux on the yields
of different nuclides the neutron yield was monitored through-
out irradiations by counting proton recoils in an organic
scintillator fixed in the irradiation chamber. The effect of
position of sample and hence of slight variations of neutron
energy, on fission product yields was investigated.

After irradiation the target material was dissolved and
inactive carriers added for the fission products to be separa-
ted. In order to reduce errors due to adsorption of the

radioactive species on glassware the carriers were added to the total solution of irradiated material. In order to obtain the highest possible counting rates the elements to be measured were isolated from the total solution. Thus the choice of elements to be separated from a given irradiated sample was restricted by the compatability of the added carriers and the requirements.pertaining to the chemistry needed for the separation of each element.

After steps to ensure complete isotopic exchange between fission products and added carriers (e.g. digestion, redox cycles) the chosen elements were separated and radiochemically purified, in preparation for counting. Several collected radiochemical procedures for the isolation of fission products have been published[6,24,25]. The methods used in the current investigation were based upon these procedures, with suitable modifications taking account of the chemistry of thorium in the solution and the presence of and need for separating other elements. The effect of thorium and its daughters on the isolated fission products could be investigated by carrying out trial separations from solutions of unirradiated thorium and counting the sources so produced.

In order to relate the results of several irradiations it is necessary to separate a reference element from each irradiation. For the current investigation 17.0 hour ^{97}Zr was chosen as the reference element. The reason for this will

be outlined later. The reliability of this fission-product internal standard was checked by a comparison with an external reference element.

The separated fission products were mounted on fibre-glass filter discs and dried for weighing and counting.

Assay of radioactive fission products was carried out by counting with a gas-flow end-window β-proportional counter. In order to determine the absolute disintegration rates this counter was calibrated against a 4π gas-flow β-proportional counter. Where direct calibration was not possible owing to the half-life of the species counted, or the presence of other isotopes of the element with comparable half-lives, extrapolations were made from the known calibration curves, taking account of the β-energies of the nuclides concerned and the electron densities of the sources. Use of the end-window counter facilitated rapid exchange of sources when several sources were to be counted, and eliminated the tedious production of 4π sources after each irradiation. The proportional counter was also used to detect α-radiation from thorium contamination when the separation procedures were being investigated.

(b) Preparation of Thorium for Irradiation

In all investigations thorium nitrate of 'Analar' quality was used as a starting material. In those cased where trial

separations of added carrier materials had shown the sources prepared to be free of contamination from the radioactive daughters of thorium it was possible to use this thorium nitrate directly for irradiation. For these irradiations, the thorium nitrate was oven-dried and a sample (usually 2 gm.) heat-sealed in a 1.5 cm. square packet of polythene (.003 ins. thick).

In those cases where the daughters of thorium were shown to follow fission products in their separation procedures it was more convenient to remove the daughter activities from the thorium before irradiation than to separate the induced fission-product activities from the thorium daughters which followed them after irradiation. It is simpler to remove ^{228}Ra and ^{224}Ra from a solution of thorium by scavenging precipitations of barium sulphate than to isolate a comparatively small barium activity from a large radium contamination. Other procedures in which the separated elements were found to be contaminated with thorium daughters were (i) the separation of ruthenium in which ^{220}Rn was carried over with ruthenium in a distillation procedure, and (ii) the separation of antimony by solvent extraction where ^{212}Bi was found to follow the antimony.

The thorium series is shown in Fig. 4. It can be seen that it is possible to remove the gross daughter activities by repeatedly scavenging for radium (MsTh$_1$ and ThX), actinium (MsTh$_2$), lead (ThB), and bismuth (ThC). The effect of different scavenging precipitations was measured by observing

Fig. 4   The Thorium Decay Series

^{232}Th
1.39x10^{10}y.

^{228}Th, RdTh
1.90y.
β

↓ α

^{228}Ac, MsTh$_2$
6.13h

↓ α

^{228}Ra, MsTh$_1$
6.7y.
β

^{224}Ra, ThX
3.64d.

↓ α

^{220}Rn, Tn
54.5s.

↓ α

^{216}Po, ThA
0.158s.

^{212}Po, ThC
3.0x10^{-7}s.
β

↓ α

^{212}Bi, ThC
60.5m.

66.3%
↓ α

^{212}Pb, ThB
10.6h.
β

33.7%
↓ α

^{208}Pb, ThD
Stable
β

^{208}Tl, ThC
3.1m.

the decreased activity of the scavenged thorium solutions in a liquid G.-M. counter of the annular type. The recovery of purified thorium was determined by titration with E.D.T.A. as described by Schwarzenbach.[26] The procedure finally adapted, which consisted of scavenging precipitations of barium and lead sulphates, bismuth sulphide, and lanthanum carbonate, is given below.

Removal of thorium daughters and preparation for irradiation

Step 1. A sample of 2 gm. of thorium nitrate was dissolved in 10 ml. of water, and 1 ml. each of carrier solutions for barium and lead (each containing about 10 mg./ml. as nitrate) was 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 Whatman No. 42. filter paper.

Step 2. A second precipitation of barium and lead was carried out by addition of the carrier solutions and sulphuric acid to the filtnate from Step 1. The precipitate was removed by filtration and discarded.

Step 3. 1 ml. of bismuth carrier solution (containing 10 mg. Bi/ml.) was added to the filtrate from Step 2. Bismuth sulphide was precipitated on passing hydrogen sulphide through the solution for one minute. The precipitate was removed by filtration and discarded.

Step 4. The bismuth sulphide scavenging precipitation was repeated.

Step 5. The solution was made alkaline with concentrated ammonia, and digested with addition of powdered ammonium carbonate until the thorium hydroxide which was precipitated redissolved as the double carbonate. 1 ml. of lanthanum carrier solution was added, and the solution stirred as lanthanum carbonate was precipitated. The precipitate was removed by centrifugation and discarded.

Step 6. The scavenging precipitation of lanthanum carbonate was repeated twice more.

Step 7. Basic thorium carbonate was recovered from the solution by precipitation on addition of concentrated nitric acid to adjust the pH to 4. The precipitate was centrifuged and the supernate discarded. The precipitate was then washed with water and centrifuged down to a thick paste, which was transferred to a polythene capsule for irradiation.

With the foregoing procedure it was possible to reduce the activity associated with a sample of thorium by a factor of 150 at the end of the purification, with a recovery of purified thorium of 60%. The reduced yield was attributed to some precipitation of thorium sulphate and incomplete precipitation of the basic carbonate. The activity associated with 1 gm. of thorium at the end of a purification was found

to be less than 100 c.p.m. when measured in the annular G.-M. counter. The observed reappearance of activities in purified thorium is illustrated graphically in Fig. 5.

Owing to the fairly rapid reappearance of some of the daughter activities it was considered desirable that their removal be carried out immediately before an irradiation. The reappearance of activities also prevented drying of the basic carbonate precipitate as this required considerable time.

(c) The Neutron Source

A high flux of essentially monoenergetic neutrons was produced by the reaction:-

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

This reaction has a high broad resonance for deuterons of 100 keV striking a thin tritium target. 14 MeV neutrons are produced.

A deuteron beam of suitable energy was available in the Londonderry Laboratory for Radiochemistry from the Cockroft-Walton type accelerator built by G.R. and E.B.M. Martin.[27]

The tritium targets, as described by Wilson and Evans[28], were obtained from the Atomic Energy Authority. Each target contained about one curie of tritium absorbed in a thin film of zirconium or titanium metal supported on a copper disc (2.5 cms. diameter). For convenience each disc was divided into four segments which were bombarded separately.
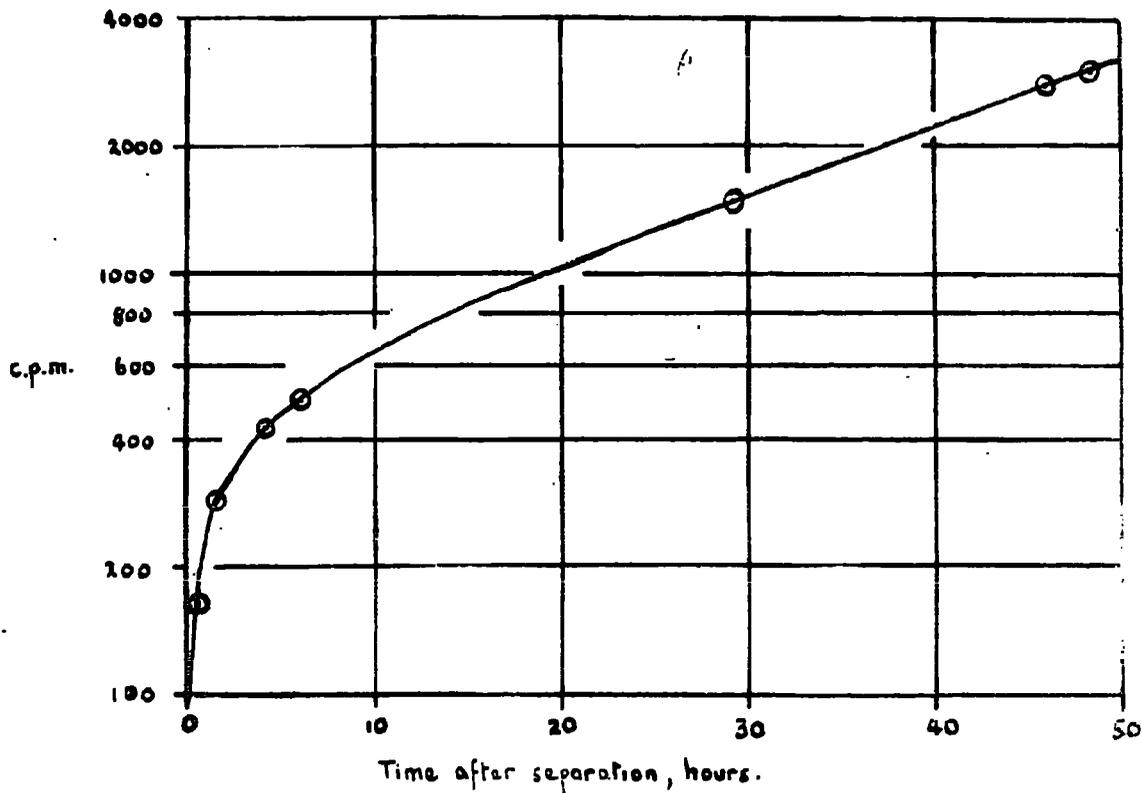
Fig. 5

Growth of daughter activities into 1 gm. of purified
thorium, recorded with annular type liquid G.M. counter.

The target segments were soldered onto a copper disc
(2.0 cms. diameter) which was then mounted in the target block
with Wood's metal. Owing to the considerable dissipation of
heat in the target on bombardment good thermal contact was
essential in its mounting. The target assembly is illustrated
in Fig. 6. It is situated centrally in the target chamber,
well removed from any objects which might increase the flux
of scattered, degraded neutrons in the vicinity of the sample.
The sample to be irradiated was attached to the bottom of the
target block by rubber bands.

Under normal running conditions a deuteron beam current
of the order of 200 μ amps was obtained. This was capable of
producing a neutron flux of about 10^8 neutrons /cm.^{2}/second
at the surface of the target block, with a fresh target.
The life of a given segment was limited to about a thousand
μ amp-hours bombardment. This has been attributed to the
loss of tritium from the heated area of the target and the
deposition of pump oil on the target.[28]

For a given D-T interaction, the energy of the neutron
produced is dependent on its angle of emission relative to
the incoming particle. The neutron energy may be calculated
from kinetic considerations. The neutron energy as a function
of the angle of emission is plotted in Fig. 7. for several
deuteron energies.

D

Molybdenum
Shutter

Water cooling

Tritium target

Sample
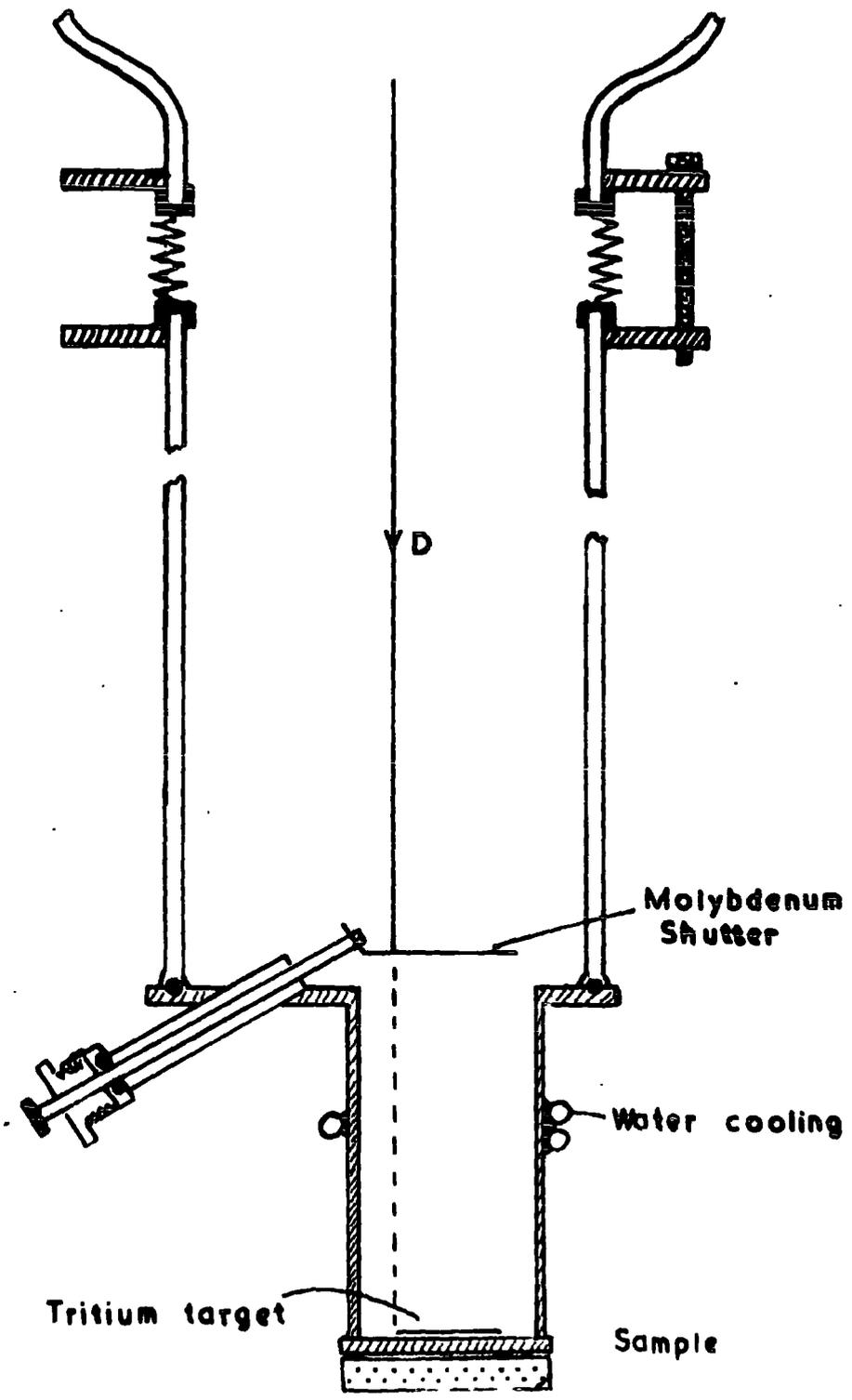
Fig. 6

Target Assembly.
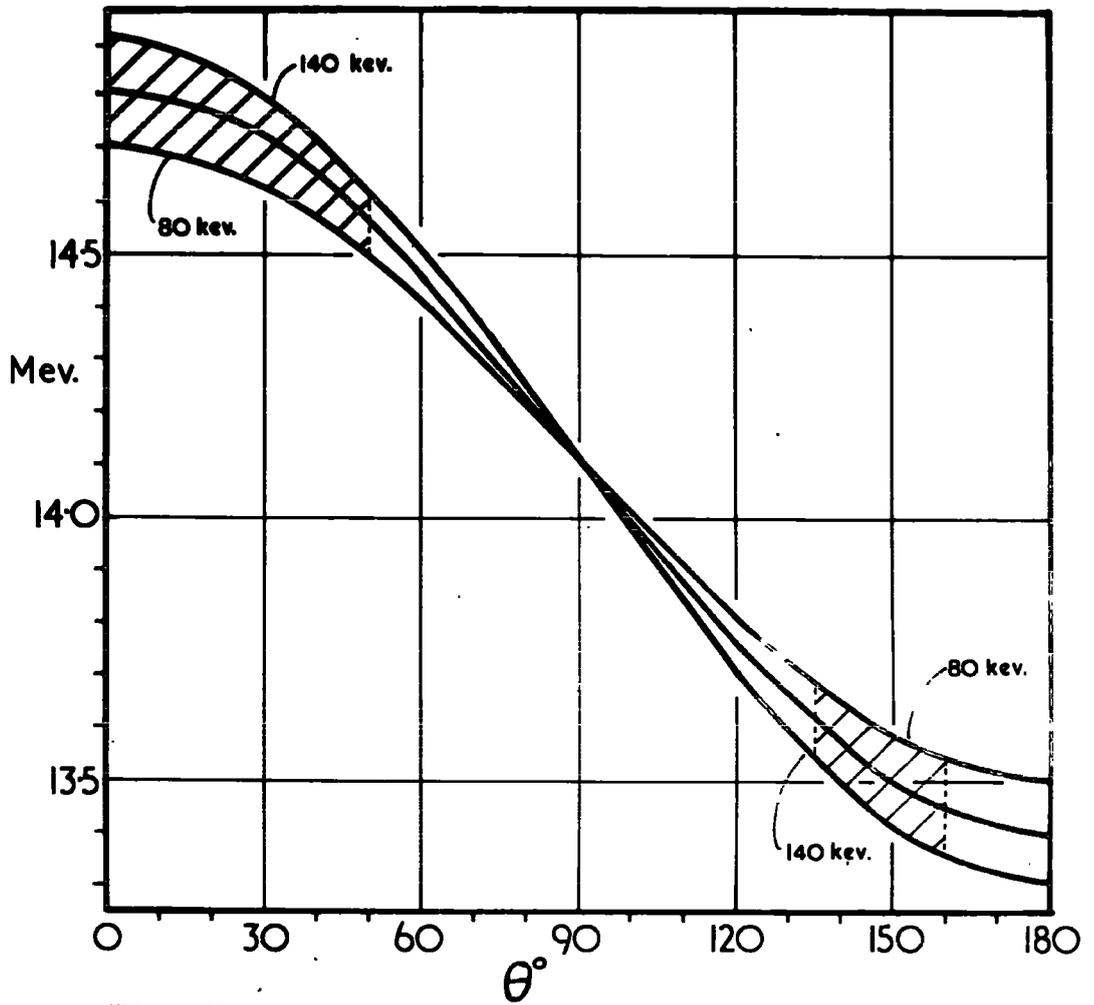
Fig. 7

NEUTRON ENERGY AS A FUNCTION
OF ANGLE OF EMISSION.

In the 14 MeV region the fission cross-section of thorium
is a varying function of neutron energy, and if different
fission mechanisms are involved the relative yield values
may also vary. To obtain sufficient neutron intensity
irradiations were normally carried out very close to the
target of the accelerator, with correspondingly poor defini-
tion of the effective neutron energy. The effect of slight
variations in neutron energy on the shape of the mass-yield
curve was investigated by irradiating pairs of samples placed
respectively in the foreward direction and perpendicular to
the deuteron beam, where the effective neutron energies were
14.8 and 14.1 MeV respectively. From these samples zirconium
and silver were isolated and the ratios of the activities of
^{113}Ag and ^{97}Zr measured. The results, which are treated in
detail in the section on silver activities (page 64) indicated
no significant variation of the relative yields with the
variation of neutron energy indicated.

(d) The Reference Element

This fission-product element must be isolated after each
irradiation in order to correlate the relative yields measured
in each experiment. The element should be easily isolated
from the solutions of irradiated material and its radiochemical
purification easily carried out. It is desirable that the

chosen element be produced in high yield (to ensure sufficiently high counting rates for good statistical accuracy) and the choice of half-life is determined by the length of irradiations and the time available for chemistry and counting.

In their early studies of thorium fission Turkevitch and Niday[18] determined yields relative to 54 day ^{89}Sr. This nuclide was far too long-lived for the current investigations. 82 minute ^{139}Ba has been used as a reference element for studies of uranium fission,[30] but its use here was precluded because of the problem of decontamination from radium isotopes. 67 hour ^{99}Mo has also been used as a reference in studies of uranium fission, and its use was considered for the present work. However, preliminary experiments indicated that the molybdenum activities attainable were rather small. These low counting rates may be attributed to the lower yield of molybdenum in thorium fission as compared with uranium owing to the altering of the position of the lighter mass peak, and to the lower fission cross-section of thorium compared to uranium.

Preliminary experiments indicated that 17 hour ^{97}Zr might prove a suitable reference element, and it was the nuclide finally chosen for this purpose. Produced with a greater yield than molybdenum, its activity was also enhanced by a 67 minute niobium daughter. Its radiochemical purification provided no difficulty and the decay of zirconium sources

showed them to be free of contaminating activities. The
chemical separation procedure is given on page 40, and results
on page 45.

The variability in the determination of the reference
nuclide yield was investigated by comparison with an external
standard. The homogeneous mixture technique, developed in
the Londonderry Laboratory for Radiochemistry for cross-section
measurements[29], was used. Samples of an intimate mixture of
thorium nitrate and pure iron granules were irradiated. After
separation and counting, the fission-product zirconium activity
was compared with the activity of ^{56}Mn produced in the iron
by an (n,p) reaction. The ratio of the activities was found
to be reproducible within about 1%. The details of this work
are included in the section on zirconium (page 43).

(e) Preparation of Solid Sources For The End-window Counter

In the final stage of a radiochemical separation pro-
cedure the fission product activity with its inactive carrier
was precipitated in a suitable gravimetric form for chemical
yield determination and counting.

It has been common practice to mount such precipitates
on filter-paper discs for weighing and counting. Sources
prepared in this manner tend to curl up and their hydrophylic
property necessitated their weighing under very carefully
regulated conditions.

The possibility of using discs of sintered polythene for mounting the precipitates was investigated. An attempt to mount a precipitate of barium oxalate on a sintered polythene disc was unsuccessful, the pore size of the sinter being too large to support the precipitate. Although unsuitable for the mounting of sources, this sintered polythene was used as a support in the filter funnel for the filter discs finally chosen.

The use of glass-fibre filter discs for gravimetric purposes was reported by Ma and Benedetti-Pichler in 1953[31]. Such discs became commercially available at the time of commencing the current investigations (Whatman GF/A, 2.1 cms. diameter). These discs were supported on sintered polythene in a demountable filter chimney (Fig. 8) which limited the area of the precipitate on the discs to a reproducible circle, $\frac{5}{8}$ inches diameter. The discs were placed in the filter chimney and washed by a standard procedure of three washings with 5 ml. of water, two washings with 5 ml. of alcohol, and two washings with 5 ml. of ether. The discs were then placed in a vacuum desiccator which was evacuated for two minutes using a water pump. The vacuum was released, and the desiccator evacuated again for transference to the balance room.

The discs were weighed on a Stanton semi-micro balance

Ball-joint
clip

Polythene
sinter
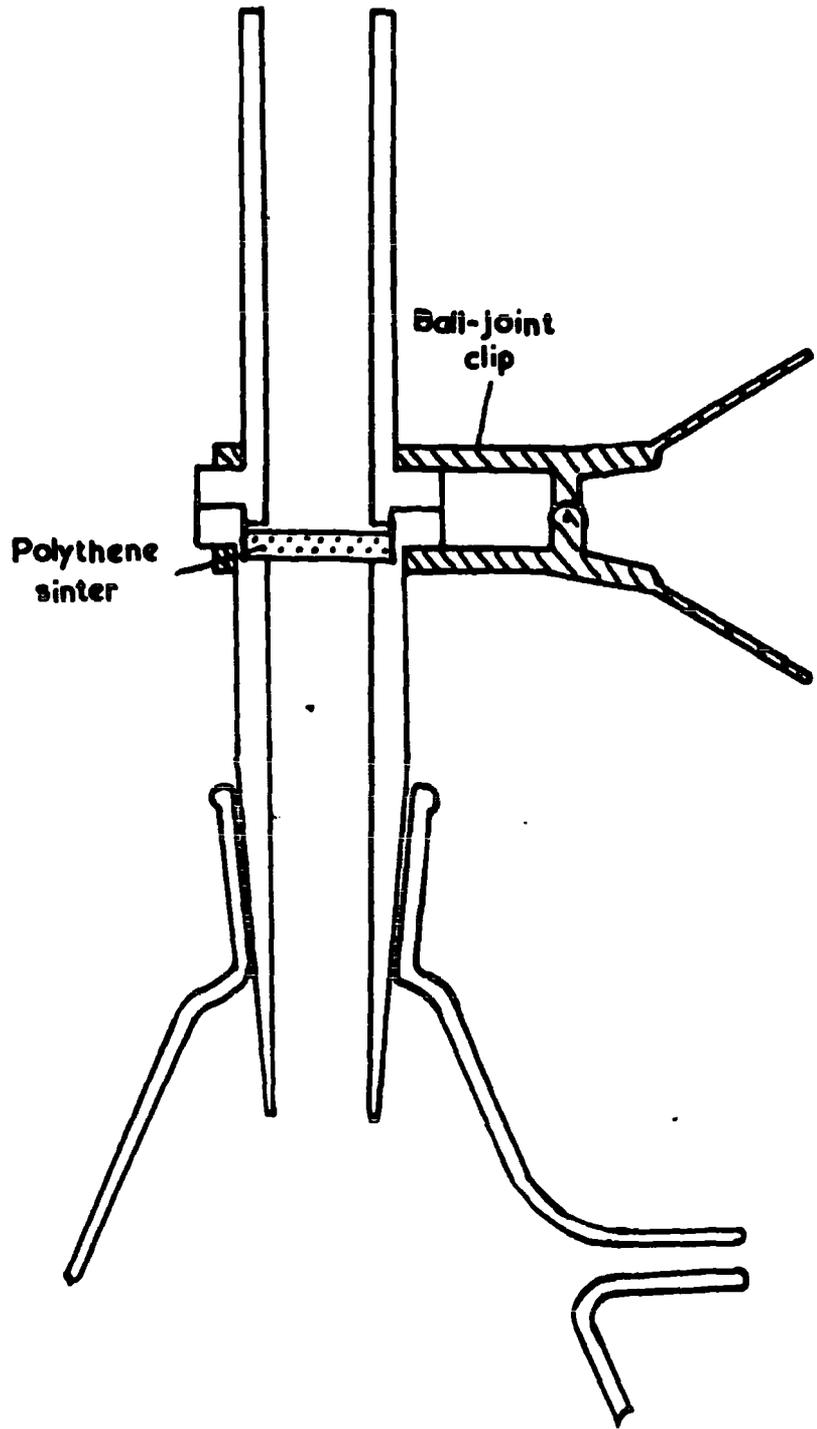
Fig. 8

Demountable filter stick

(Model MC1A) to the nearest 0.01 mg. When treated in the foregoing manner, the weight of the disc was found to be constant, even after standing in room conditions for several days. The weight of the discs was also unaffected by washings with dilute acid solutions from which the precipitates were usually filtered.

The precipitates produced from the radiochemical separations normally weighted 10-20 mgs., depending upon the chemical yields of the procedures. The balance weights were accurately known to $\pm$ 0.05 mg. so that the chemical yields determined by weighing were accurate to within $\pm$ 0.5%.

The sources were mounted in standard aluminium planchets which were stored in dust-proof trays until required for counting.

(f)   The End-window Gas-flow β -proportional Counter

The counter, which was constructed mainly of brass, is shown in Fig. 9. The end window of the counter (2.6 cms. diameter) was a thin VYNS plastic film (80 $g/cm.^2$) prepared in the same way as 4π films (see page 31), but with several layers of film on the support. The film was gold-coated on its interior side in order to conserve a uniform electric field inside the counter.

Gas-flow

Anode loop

VYNS window
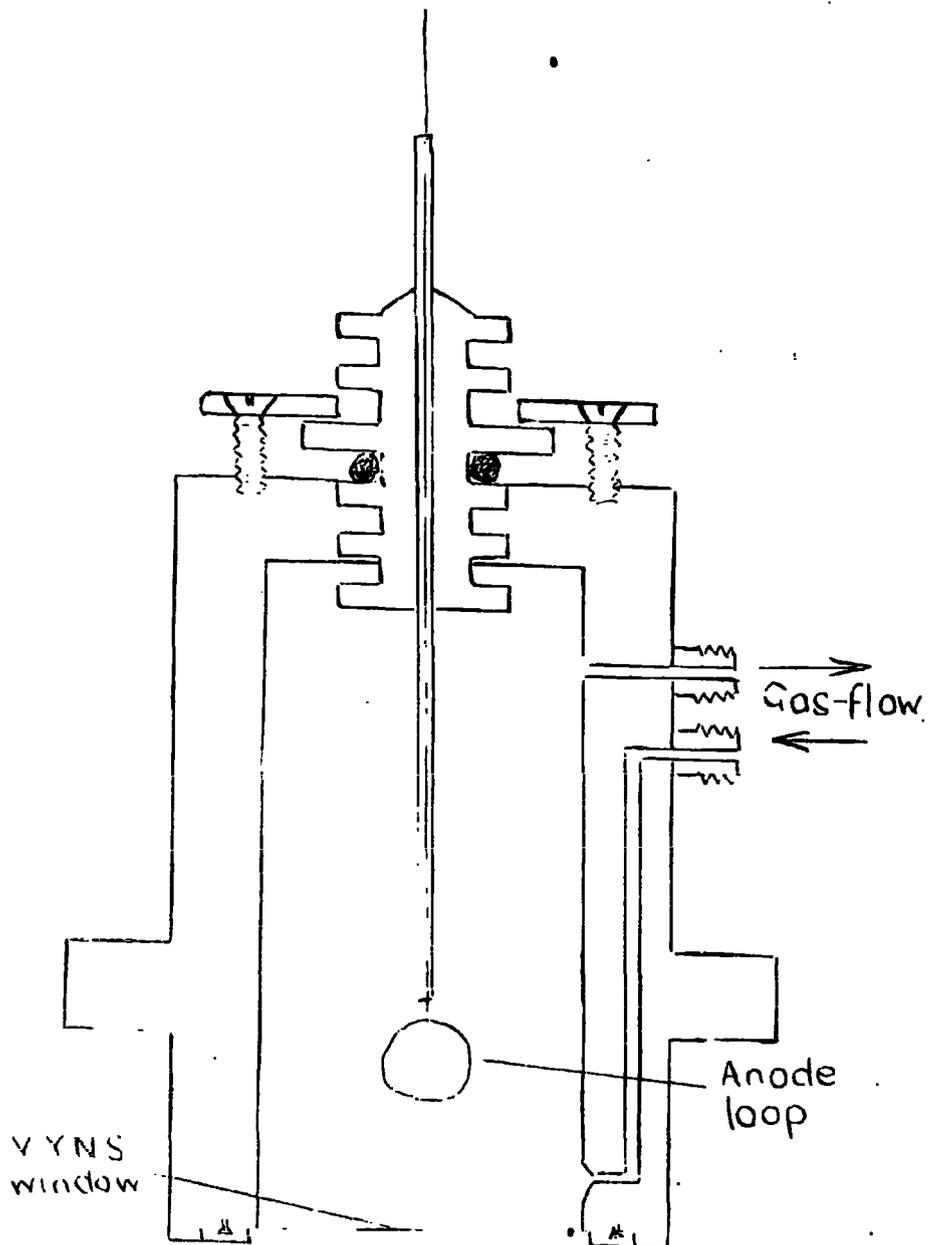
Fig. 9

The end-window β-proportional counter.

The anode was a circular loop ($\frac{3}{8}$ inch. diameter) of constantan (0.001 inch diameter). This was soldered to a nickel tube which was held in the top of the counter by an insulating teflon plug.

The counter filling was a standard mixture of 90% argon and 10% methane, which was purified by passage over heated platinum gauze (to remove oxygen) and "Anhydrone" to remove water vapour.

The gas-flow system and associated electronics for the counter are depicted diagramatically in Fig. 10. The counter was mounted on a perspex stand with milled slots to accurately position the counting trays. This was contained in an aluminium-lined lead castle in order to reduce back-scattering and background effects respectively.

The E.H.T. supply was obtained from a 2kV line in the laboratory, through a 1007 potentiometer unit and a filter unit to eliminate spurious pulses. This was connected to the counter anode through a high resistance (1.5 Megohms).

The pulses produced were amplified by a head amplifier (Type 1008) mounted close to the castle and a main amplifier (Type 1008). The overall amplification obtained was of the order of 10^6.

The amplified pulses were fed into a scaler (Type 1009A) containing a variable discriminator level which was set to
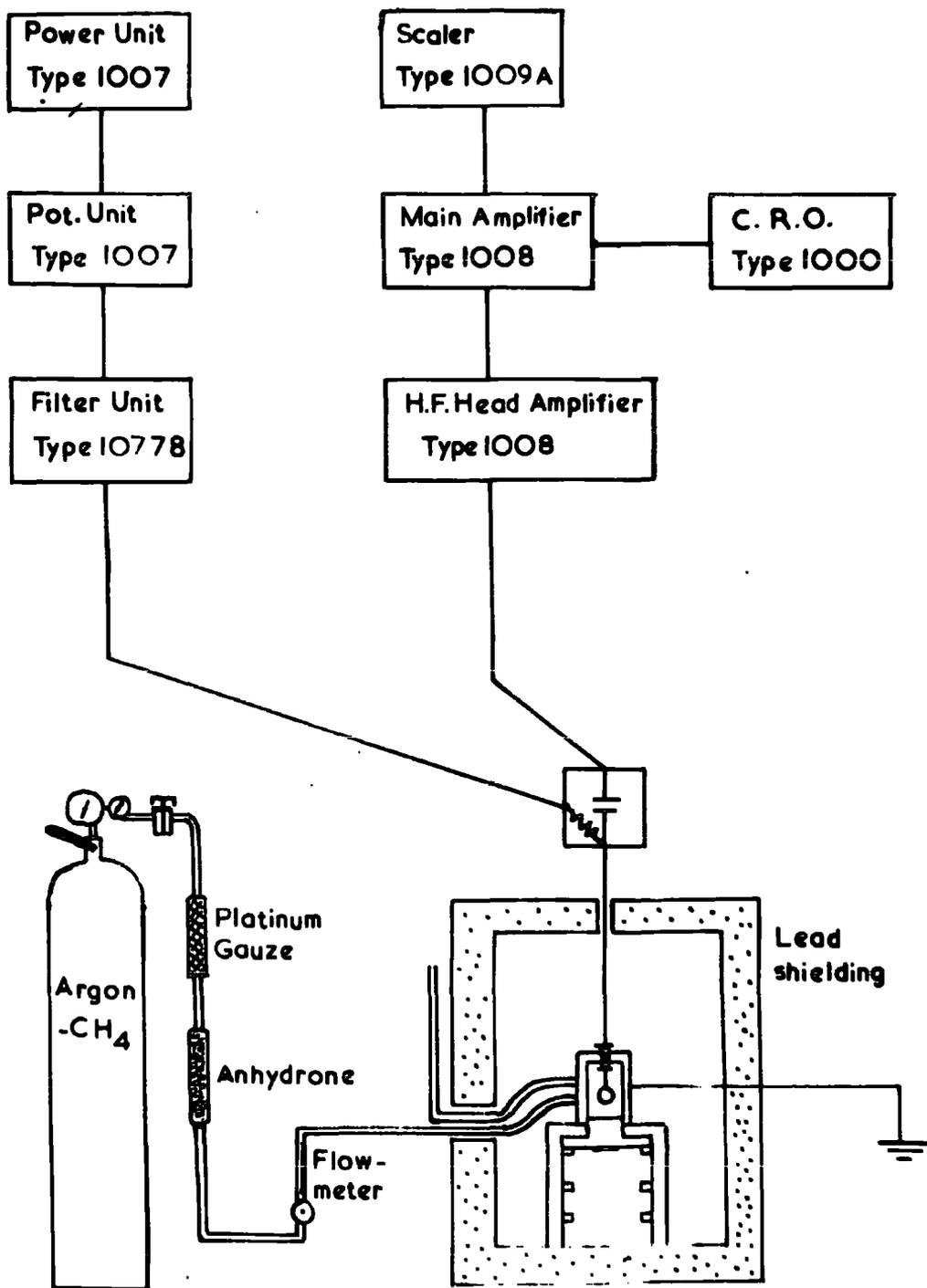
Fig. 10

Gas flow system and electronics for the end-window counter.

exclude valve noise from the amplifier. The pulses were also fed into a cathode ray oscilloscope monitor (Type 1000) for visual observation. This was especially useful in the diagnosis of faults.

The optimum working conditions for the counter are tabulated below. With the settings indicated a plateau of 200 volts was obtained, with a slope of 0.05% per volt for β -counting. For α-counting a similar plateau was obtained, but at a lower working voltage.

Table 1

End-window β -proportional counter No. 54

Amplifier Type 1008

    Differentiation Time = 0.4 μsec.

    Integration Time   = 0.4 μ sec.

    Attenuation   = 10 db.

Scaler Type 1009A

    Paralysis Time   = 50 μ sec.

    Disc. Bias   = 15 volts.

E.H.T.

    For β - counting   = 1.84 kV.

    For α - counting   = 1.15 kV.

Occasional sources of spurious pulses which had to be eliminated were:-

1. Electrical breakdown of counter insulation due to humidity.

2. Faulty connections, sometimes occasioning pick-up.

3. Spurious pulses from the mains which passed the filter unit.

Breakdown of insulation due to humidity was overcome by wiping the teflon part of the counter with methanol, and drying with a hot-air drier. Similar treatment was sometimes also necessary for the connecting unit.

Pick-up from faulty connections was located by isolating different parts of the set-up, and the faulty connections replaced.

Spurious pulses from the mains were often traced to miscellaneous switching circuits in the laboratory (e.g. thermostats, ovens, etc.) to which suppressors were fitted.

The reproducibility of counting measurements was frequently checked by counting a standard source (Ra - DEF.) The standard count was found to vary by $\pm$ 2%, possibly due to the effects of temperature on the electronics associated with the counter.

The accuracy of counting fission-product sources was limited by the time available to count several sources, and the counting rates of the sources. In general more than 10^3 counts were recorded for a measurement, to ensure a standard deviation of not more than 3%.

In order to obtain the absolute disintegration rates for the sources counted in the end-window counter, it was calibrated for sources of varying weights which were prepared from solutions whose absolute activity was determined by 4π counting.

(g) Calibration of The End-window β -proportional Counter

General Procedure

The procedures used for the calibration of the proportional counter can conveniently be divided into two parts: (i) Preparation of solutions of high specific activity and an accurate measurement of that activity, and (ii) Addition of the activity to a measured quantity of carrier solution, and preparation of sources of varying weights from this solution, for counting in the end-window β -proportional counter. From the data obtained curves can be drawn of the efficiency of the end-window counter $\left(\dfrac{\text{observed counting rate}}{\text{absolute disintegration rate}}\right)$ against source weight and used to determine the efficiency of counting fission-product sources.

(i) Preparation of solutions of high specific activity

These solutions were prepared from samples of pile-irradiated uranium or carrier-free solutions obtained from the Radiochemical Centre, Amersham. Where radiochemical separations had to be carried out to isolate the required

activities from solutions of irradiated uranium the procedures used were those reported in the literature or those developed for the current work scaled down for use with 1 mg. added carrier. The activity associated with less than 1 mg. recovered carrier in solution was usually so great that considerable dilution was necessary before preparation of sources for 4π counting. The solid content of the solutions used for absolute counting was thus reduced, and the 4π sources could be made virtually weightless.

(ii) <u>Preparation of solid sources for calibration of the end-window counter.</u>

A measured quantity of the solution of high specific activity (containing about 10^5 d.p.m.) was added to a solution containing 50 mg. inactive carrier. When complete isotopic exchange was secured the activity and carrier were precipitated in a similar manner to that used in the fission-product investigation. Sources of differing weights of precipitate were prepared and weighed and counted in the usual manner.

<u>Absolute Counting</u>

Absolute counting was carried out using 4π gas-flow proportional counters of the type described by Hawkins et al, and illustrated in Fig. 11. Such a counter is essentially two gas-flow proportional counters hinged together so that

Anode
wires

Gas-
flow

VYNS 4π Source support
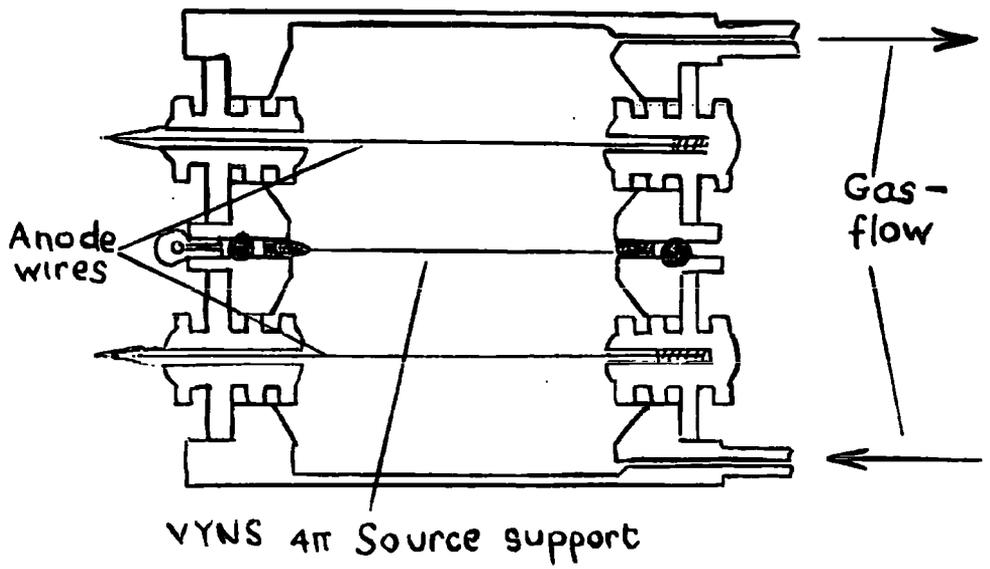
Fig. 11

The 4π counter.

a source can be placed between them. The gas-flow system
and electronics associated with the 4π counter were identical
to those associated with the end-window counter, as described
on page 26 et seq. A slightly higher gas-flow rate was
required (50 cc./min.) and the optimum counting voltage for
a standard RaE source was 1.75 kV.

The source supports consisted of thin VYNS plastic films
(ca 20 μg./cm.^{2}) supported on aluminium rings (internal
diameter 2.6 cm.) which fitted into the 4π counter. The
films were rendered conducting by evaporation of about
5 μg./cm.^{2} of gold onto their lower surface. A few drops of
a dilute solution of insulin were evaporated on the upper
surface of the film to facilitate the even spreading of active
solutions dried thereon. Further details of the preparation
and properties of these 4π sources have been given by Pate
and Yaffe[33], and by Davies[29].

Owing to the limitations of half-lives and complexities
of decay schemes it was not possible to calibrate the end-
window counter for all the nuclides measured in the fission-
product investigations. For those nuclides where calibration
was impracticable the efficiency of the end-window counter
was estimated from measured data for other nuclides, taking
into account the β-spectra and density of sources. The

details of the calibrations and estimation of efficiencies
are included in the following chapter, where all the work on
the nuclides investigated is presented.

CHAPTER III

THE MEASUREMENT OF RELATIVE YIELDS OF THE PRODUCTS OF FISSION
OF THORIUM INDUCED BY 14 MeV NEUTRONS

(a) Introduction

In fission of the heavy elements a wide range of
radioactive nuclides are produced. The number of these
which are suitable for radiometric assay is limited by their
half-lives and absolute fission yields. In the times of
irradiation used for the present work the build-up of long-
lived fission product activities was negligible. The measure-
ment of short-lived activities was limited by the time required
for chemical separations.

The principal aim of the current investigation is to
delineate the mass-yield curve for the fission of thorium
induced by 14 MeV neutrons. Such curves are drawn through
points representing the total chain yields for given mass
numbers. The contribution to the total chain yield of the
yield of a given nuclide is determined by the charge distri-
bution at the instant of fission. This factor will be dis-
cussed and applied to the measured experimental yields in
Chapter IV. Since the total chain yield is totally represen-
ted by nuclides near the end of the chain these isobars have
been measured wherever possible.

The 14 MeV fission cross-section for thorium is com-
paratively low (0.35 barns[34]), limiting the amount of activity

which is induced in a given irradiation. A major portion of the work of identifying fission-product activities and elucidating fission-product decay chains has been performed in investigations of the thermal neutron fission of ^{235}U, for which the cross-section is greater than 500 barns. A recent compilation of decay chains by Katcoff[11] was used as a source of information for the current work. Unfortunately measurements of branching ratios of the more complex decay chains are not complete and so measurements of nuclides in certain of these branched chains were not possible. This imposed a severe restriction on the number of nuclides suitable for investigation in the trough of the mass-yield curve where such complex branched chains predominate. Detailed information of the decay systematics of specific nuclides was obtained from "Nuclear Data Cards".[35]

A list of nuclides for which the yields were measured in the current work is given in Table 2. The remainder of this chapter is devoted to the measurement of the yields of these nuclides. A description of the mathematical treatment of the experimentally measured quantities is first given. The work carried out on the reference element is next described, followed by a description of the work performed on the other fission-product nuclides in order of increasing mass number.

TABLE 2

Nuclides measured in the investigation of fission of ^{232}Th with 14 MeV neutrons.

Mass Number	Nuclide measured.
83	2.4 hour Br.
84	6.0 minute Br.
	31.8 minute Br.
91	9.7 hour Sr.
93	10.3 hour Y
97	17.0 hour Zr.
99	66 hour Mo.
105	4.45 hour Ru.
111	7.6 day Ag.
112	21 hour Pd / 3.2 hour Ag.
113	5.3 hour Ag.
129	4.6 hour Sb.
132	77 hour Te / 2.3 hour I.
139	82.5 minute Ba.
143	33 hour Ce.

For each element investigated the mass-chains involved
are discussed and the chemistry of its separation briefly
described. (The complete radiochemical procedures are pre-
sented in the appendix). The results of measurements for
each nuclide are presented after having discussed the calibra-
tion of the end-window counter for that nuclide. The collec-
ted results and subsequent discussion are given in Chapter IV.

(b) <u>General Method of Treatment of Results</u>

The 14 MeV neutron generator does not produce a steady
neutron flux and the effect of this on the rate of produc-
tion of each fission-product nuclide investigated must be
allowed for, in addition to correcting for radioactive decay
over the duration of the irradiation.

Consider an irradiation of duration T after which a
nuclide 1 is isolated after a time t', as illustrated in
the accompanying diagram.

(i) Suppose that the pre-
cursors of 1 in the decay
chain   1 $\longrightarrow$ 2 (stable)
are short-lived compared
with T and t'. Through-
out the irradiation the nuclide 1 is produced at an irregular
rate $R(t)$. During the short time interval dt the number of
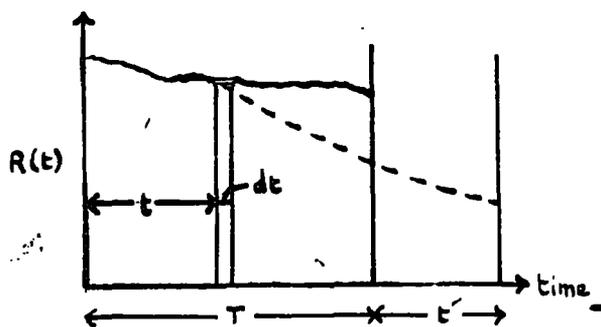
nuclei of 1 which are produced is $dN = R(t)dt$, and these decay exponentially. At the time of isolation (t') the number remaining of those produced in the time dt is:-

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

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

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

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

The rate of production of nuclide 1, $R(t)$ is given by

$$R(t) = B\sigma_f Y_1 \varphi(t),$$

where B is a constant depending on the quantity of fissionable material irradiated.

Y_1 is the fission yield of nuclide 1

$\varphi(t)$ is the neutron flux over the sample.

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

$$R(t) = B \cdot \sigma_f Y_1 \frac{I(t)}{\eta}$$

where η = efficiency of the neutron monitor.

Thus $N_1(t') = \dfrac{B\,\sigma_f Y_1}{\eta}\ e^{-\lambda_1 t'} \displaystyle\int_{t=0}^{t=T} I(t)e^{-\lambda_1(T-t)}\ dt.$

The integral can be replaced by the summation:-

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

provided that the δt intervals taken are very much shorter than the half-lives of the species concerned.

Thus $N_1(t') = \dfrac{B\,\sigma_f Y_1}{\eta}\ e^{-\lambda_1 t'} S_1.$

Similarly, if a reference nuclide r is isolated at a time t'':

$$N_r(t'') = \dfrac{B\,\sigma_f Y_r}{\eta}\ e^{-\lambda_r t''} S_r.$$

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

By extrapolation of their decay curves the activities of the isolated species at the end of the irradiation, A^o, can be determined:- $A^o = N^o\lambda$

so $\dfrac{A_1^o}{A_r^o} = \dfrac{Y_1 S_1 \lambda_1}{Y_r S_r \lambda_r}$

$$\text{and } \frac{Y_1}{Y_r} = \frac{A_1^o \, \tau_1 S_r}{A_r^o \, \tau_r S_1}$$

where τ_1, τ_r are the half-lives of the species concerned.

The above equation was used in calculating the relative yields of the fission products of thorium measured in the current work. The values of S_1 and S_r were calculated from the recordings of the neutron monitor during the irradiations. Values for A^o were obtained by extrapolating the decay curves of the fission-product sources prepared for counting to the time of the end of irradiation and applying corrections for chemical yield and counter efficiency.

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

Consider the decay chain:-

$$(\text{short}) \longrightarrow 1 \xrightarrow{\lambda_1} 2 \xrightarrow{\lambda_2} 3 \ (\text{stable})$$
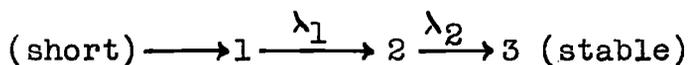
in which λ_1 and λ_2 are comparable, and the species 2 is isolated at a time t' after the irradiation. Using the same nomenclature as above:-

$$N_2(t') = \frac{\lambda_2}{\lambda_2 - \lambda_1} \left[e^{-\lambda_1 t} \int_{t=o}^{t=T} R(t) e^{-\lambda_1(T-t)} dt - \right.$$

$$\left. e^{-\lambda_2 t} \int_{t=o}^{t=T} R(t) e^{-\lambda_2(T-t)} dt \right]$$

also $N_2(t') = \dfrac{B \sigma_f Y_1}{\eta} \dfrac{\lambda_1}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t'} S_1 - e^{-\lambda_2 t'} S_2)$

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

$$N_2^O = \frac{N_2(t')}{e^{-\lambda_1 t'}} = \frac{B \sigma_f Y_1}{\eta} \frac{\lambda_1}{\lambda_1 - \lambda_2} S_2$$

Since $A_2^O = \lambda_2 N_2^O$ the value of the activity of species 2 in equation 1 must be multiplied by the factor $\dfrac{\lambda_1 - \lambda_2}{\lambda_2}$ to allow for the effect of the comparative half-lives of species 1 and 2. This correction was necessary in the case of fission-product barium (see page 74).

(c)   <u>Measurement of Relative Yields</u>

(1)   <u>Zirconium - Reference Element</u>

   <u>Introduction</u>

   The choice of reference element has been discussed
in Chapter II. Of the isotopes of zirconium produced in
fission, only 17.0 hour ^{97}Zr was suitable for counting. The
decay chain for this mass number is:-

$$17 \text{ hr. } {}^{97}\text{Zr} \overset{0.96}{\nearrow} \underset{0.04}{\searrow} \begin{array}{c} 60 \text{ sec. } {}^{97m}\text{Nb} \\ \\ 73 \text{ min. } {}^{97}\text{Nb} \end{array} \rightarrow \text{Stable } {}^{97}\text{Mo.}$$
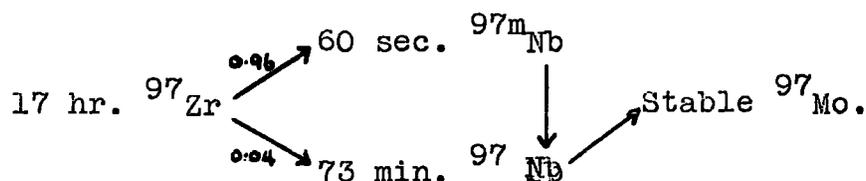
Other radioactive isotopes of zirconium produced are
1.1 x 10^6 year ^{93}Zr, 65 day ^{95}Zr, and 30 sec. ^{99}Zr, none of
which were detected in the sources prepared for the current
work. In the chain of mass number 97, no precursors of the
zirconium have been reported, their half-lives being pre-
sumably too short.

   After each irradiation, the thorium nitrate or basic
carbonate was dissolved in an acid solution containing 10 mg.
of zirconium carrier and carriers for the other elements to
be isolated. After digestion to facilitate complete isotopic
exchange between fission-product species and added carriers,

zirconium was separated at a convenient stage in the
separation of other elements by precipitation with mandelic
acid. It was then purified and prepared for counting by
several precipitations of barium zirconyl fluoride, with a
final precipitate of zirconium tetramandelate, after the
method of Hahn and Skonieczny[36]. The radiochemical procedure,
which is given in detail in the appendix, (page 85), could be
carried out in less than one hour. Blank separations from
samples of unirradiated thorium were shown to produce sources
uncontaminated by the activities of thorium and its daughters.
The fission product sources prepared decayed with a half-life
of 17.0 hours, and their decay was followed for several days
until only the background activity was observed.

Calibration of end-window counter for 17 hour ^{97}Zr.

A solution of zirconium - 97 of high specific activity
was prepared by isolating zirconium from a sample of pile-
irradiated uranium by the foregoing chemical procedure
reduced for working with 1 mg. of added carrier and omitting
the final precipitation. After a hundred-fold dilution,
drops of the solution were weighed onto 4π films for absolute
counting. To prevent losses from the sources by recoil in
the decay of the metastable daughter, ^{97m}Nb, the sources
were covered by a layer of VYNS film similar to the source
support.

A weighed quantity of the active solution was added to a solution containing 50 mg. of zirconium carrier, and zirconium tetramandelate precipitated as in the preparation of fission-product sources. A convenient method of producing a range of sources of different weights for the end-window counter was to slurry the precipitate and to take different volumes of the slurry to prepare the solid sources.

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

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

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

$$\frac{A_1}{A_2} = \frac{\lambda_2 - \lambda_1}{\lambda_2} = \frac{0.5776 - 0.0408}{0.5776} = 0.929$$

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

$$A = A_1 + A_2 = A_1(1.023 + \frac{1}{0.929}) = 2.10A_1$$

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

Thus the ^{97}Zr activity used in the preparation of the solid sources for the end window counter could be calculated, and

the efficiency of the counter for the different weights of sources found. The results of the calibration are shown in Fig. 12. The high efficiency of the counter for this nuclide is due to the contribution to the total counting rate of its daughter ^{97}Nb which was always in transient equilibrium when the solid sources were counted.

Investigation of the reliability of the determination of the reference element.

To check the variability in the measurement of the reference nuclide, its yield in several irradiations was compared with the yield of ^{56}Mn induced in pure iron granules which were irradiated in the form of an intimate mixture with dried thorium nitrate.

Experimental Procedure

An intimate mixture of 2.0 gm. of dried thorium nitrate and approximately 0.5 gm. of pure iron granules was prepared and sealed in a polythene packet for irradiation. The samples were attached to the neutron generator and irradiated for periods of one or two hours, the neutron flux being monitored at ten minute intervals throughout the irradiation.

At the end of the irradiation a primary separation of the iron and thorium nitrate was achieved by removing the iron with an electromagnet. The thorium was dissolved in 5 ml. of conc. HCl containing 10 mg. of zirconium carrier in preparation for
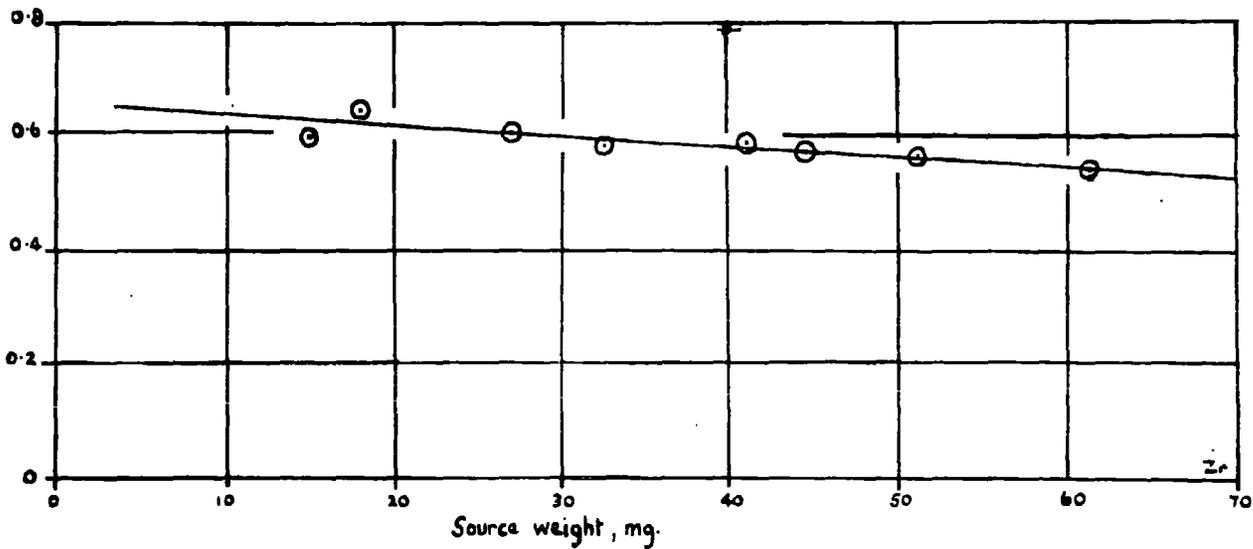
Fig. 12

Efficiency of the end-window counter for counting 17.0 hour ^{97}Zr in sources of different weights of zirconium tetramandelate.

the separation of fission-product zirconium. The iron granules were washed with 5 ml. of water and the washings added to the thorium solution. Zirconium was separated from the solution in the usual way, and counted, to obtain $A^{O}_{corr,Zr}$, the activity of zirconium at the end of the irradiation.

The iron granules were washed with a 5% solution of E.D.T.A. followed by water, then acetone and finally dried and weighed. They were then quantitatively dissolved in a nitric-sulphuric acid solution containing manganese carrier and the solution transferred to an annular G.-M. counter. The decay of ^{56}Mn was followed for several half-lives and a value obtained for the activity induced in the iron at the end of the irradiation.

The yield of zirconium from 2.0 gm. of thorium nitrate was compared with the yield of manganese from 1.0 gm. of iron by the relative yield equation:-

$$\frac{Y_{Zr}}{Y_{Mn}} = \frac{A^{O}_{corr,Zr} \; \tau_{Zr} \; S_{Fe}}{A^{O}_{Fe} \; \tau_{Fe} \; S_{Zr}}$$

Results

The results of the comparative yield measurements are given in Table 3. The standard deviation is less than 2%

TABLE   3

Comparison of yields of fission-product ^{97}Zr

and ^{56}Mn from Fe (n.p)

Run	Wt.Fe gm.	A^Oobs.Mn c.p.m.	c.p.m. gm.Fe	A^Ocorr.Zr c.p.m.	S_{Fe}	S_{Zr}	$\frac{Y_{Zr}}{Y_{Fe}}$
15	0.5069	8.95×10^4	1.77×10^5	8.76×10^3	0.989	1.072	0.318
19	0.5113	7.47×10^4	1.46×10^5	9.39×10^3	3.796	4.997	0.321
20	0.4350	8.38×10^4	1.92×10^5	1.12×10^4	3.339	4.125	0.310

Relative yield of ^{97}Zr from 2.0 gm. of thorium nitrate to ^{56}Mn from 1.0 gm. of iron = 0.316 ± 0.005.

Results of thorium fission-product measurements

The results of the measurements of ^{97}Zr for the relative yield determinations of other thorium fission products are given in Table 4. The efficiency of the end-window counter for the sources counted was obtained from Fig. 12. $A^O_{corr.}$ was obtained by applying corrections for chemical yield and counter efficiency to $A^O_{obs.}$. Values of S_{Zr} were calculated from the recordings of the neutron monitor throughout the irradiations. $A^O_{corr.Zr}$ and S_{Zr} were used in calculating the relative yields of other nuclides isolated from the irradiated material.

TABLE 4

Results for reference element – 17 hour ^{97}Zr.

Run No.	Duration minutes	Source wt., mg.	Yield %	η	A^{o} obs.	A^{o} corr.	S_{Zr} x 10^{5}
1	180	24.2	44.0	0.614	3.44×10^{3}	1.27×10^{4}	3.267
2	180	24.9	45.5	0.611	1.23×10^{3}	4.42×10^{3}	1.141
3	180	42.2	76.8	0.577	1.30×10^{3}	2.92×10^{3}	0.973
4	120	21.4	38.9	0.619	4.06×10^{2}	1.68×10^{3}	3.595
5	180	32.0	58.3	0.598	5.80×10^{3}	1.66×10^{4}	8.353
6	140	38.0	69.2	0.586	3.23×10^{3}	7.90×10^{3}	2.232
7	120	36.6	66.6	0.589	6.33×10^{3}	1.64×10^{4}	0.979
8	120	24.5	44.5	0.612	2.23×10^{3}	8.20×10^{3}	2.634
9	120	21.1	38.3	0.619	1.16×10^{3}	4.87×10^{3}	2.778
10	120	24.5	44.6	0.612	2.68×10^{3}	9.86×10^{3}	4.511
11	120	33.7	61.4	0.595	4.07×10^{2}	1.12×10^{3}	3.393
12	120	37.5	68.2	0.587	3.53×10^{3}	8.74×10^{3}	3.393
13	180	23.8	43.4	0.614	6.14×10^{3}	2.31×10^{4}	9.510
14	180	35.1	64.0	0.582	3.95×10^{2}	1.04×10^{3}	1.146
15	60	29.9	54.5	0.602	2.89×10^{3}	8.76×10^{3}	1.072
16	120	38.5	70.0	0.585	4.12×10^{3}	1.08×10^{4}	6.388
17	120	30.7	55.9	0.600	8.76×10^{2}	2.60×10^{3}	6.052
18	120	34.3	62.4	0.594	5.11×10^{3}	1.39×10^{4}	6.052
19	120	30.2	60.0	0.601	3.38×10^{3}	9.39×10^{3}	4.997
20	120	25.0	49.7	0.611	3.41×10^{3}	1.12×10^{4}	4.125
21	100	27.2	54.0	0.607	1.50×10^{3}	4.62×10^{3}	2.176

Run No.	Duration minutes	Source wt., mg.	Yield %	η	A° obs.	A° corr.	S_{Zr} x 10^5
22	100	16.5	32.9	0.628	3.61×10^2	1.74×10^3	5.831
23	120	27.8	55.3	0.605	2.22×10^3	6.59×10^3	7.248
24	120	32.3	64.3	0.597	1.65×10^3	4.27×10^3	2.762
25	60	35.7	71.0	0.590	3.97×10^3	9.45×10^3	8.292
26	120	41.2	81.9	0.579	4.28×10^3	9.01×10^3	6.737
27	90	42.8	85.0	0.575	3.66×10^3	7.40×10^3	5.456
28	100	24.1	48.2	0.614	2.18×10^2	7.41×10^3	3.162
29	90	36.9	73.6	0.588	1.03×10^3	2.37×10^3	4.435
30	100	28.9	57.6	0.603	1.34×10^3	3.87×10^3	3.755
31	120	31.6	62.8	0.598	9.7×10^3	2.57×10^2	1.376
32	70	30.1	59.9	0.602	9.43×10^2	2.62×10^3	2.953
33	100	7.0	14.0	0.647	4.81×10^2	5.28×10^3	4.493
34	50	33.4	66.4	0.595	2.40×10^3	6.01×10^3	2.386
35	120	27.1	53.9	0.607	6.24×10^3	1.91×10^4	5.456
36	120	33.8	67.2	0.594	5.03×10^3	1.25×10^4	5.985
37	60	30.6	60.8	0.600	1.66×10^3	4.55×10^3	6.010
38	30	37.7	75.2	0.586	1.46×10^3	3.28×10^3	1.955
39	10	31.9	63.4	0.598	7.78×10^3	2.04×10^4	9.560
40	10	29.0	57.6	0.603	4.22×10^2	1.22×10^3	8.910
41	10	11.5	22.9	0.639	4.00×10^2	2.72×10^3	1.560
42	30	22.3	44.3	0.617	1.06×10^2	3.85×10^2	1.834
43	60	17.6	34.9	0.626	3.76×10^2	1.74×10^3	5.371
44	60	40.7	81.0	0.580	1.06×10^3	2.25×10^3	3.981

(2) Bromine

Three isotopes of bromine were detected in the current investigation. The decay chains containing these nuclides are:-

$$69s. \quad 83m. \quad Se \searrow$$
$$\downarrow <0.10 \qquad 2.4h. \quad ^{83}Br \nearrow \quad 114m. \quad 83m. \quad Kr.$$
$$25m. \quad ^{83}Se \nearrow \qquad\qquad\qquad \downarrow$$
$$\qquad\qquad\qquad Stable \quad ^{83}Kr.$$

$$6.0m. \quad ^{84}Br \searrow$$
$$\qquad\qquad\qquad Stable \quad ^{84}Kr.$$
$$3.3m. \quad ^{84}Se \rightarrow 31.8m. \quad ^{84}Br \nearrow$$
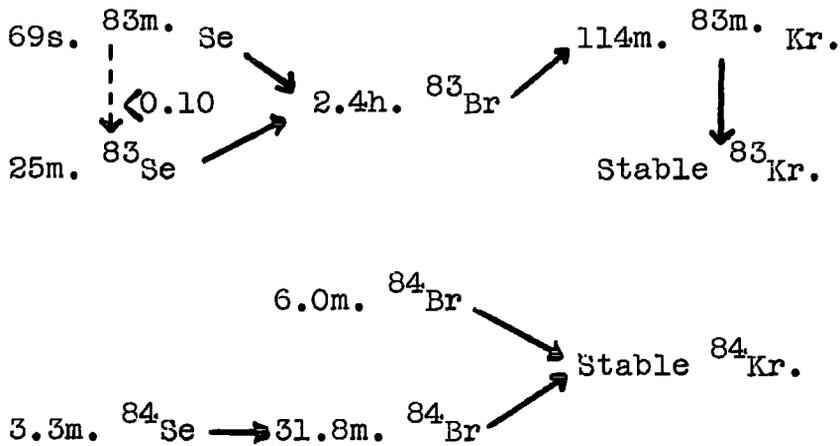
Owing to timing requirements it was not possible to determine the relative yields of all the bromine isotopes in the above decay chains from the same irradiation. The yields of 2.4 hour ^{83}Br and 31.8 minute ^{84}Br were determined after irradiations of an hour or more. The yield of 6.0 minute ^{84}Br was determined after irradiations of a few minutes using new tritium targets to ensure the optimum neutron flux.

The same chemical procedure was used for all the bromine isotopes investigated (see Appendix, page 87). Exchange of fission product bromine and added carrier was achieved by addition of carriers for bromate and bromide to the solution of irradiated material. The bromine was then converted into its elementary form and extracted into carbon tetrachloride.

Its subsequent purification was based on the method of
Glendenin et al.[37] A trace of iodine was added to the carbon
tetrachloride solution of bromine, to act as hold-back carrier
for fission-product iodine when bromine was next extracted into
hydroxylamine solution. The bromine was extracted into carbon
tetrachloride once more, and back-extracted into a dilute
solution of sodium bisulphite. After expelling excess sulphur
dioxide, silver bromide was precipitated for the preparation of
sources for the end-window counter. No iodine activity was
detected in any of the fission-product bromine sources pre-
pared.

The chemical procedure could be carried out, with care, in
twenty minutes. When investigating the short-lived isotope,
a rapid separation could be performed in five or six minutes.

Calibration of the end-window counter for 2.4 hour ^{83}Br

A solution containing 1 mg. of bromine was added to a
solution of pile-irradiated uranium, and fission-product bro-
mine separated by the solvent extraction procedure mentioned
above, omitting the final precipitation of silver bromide.
The activity of ^{83}Br in the solution obtained was determined
by 4π counting of aliquot parts. A weighed quantity of the
active solution was added to inactive bromine carrier, and
silver bromide precipitated for the preparation of sources for
the end-window counter. The efficiency of the counter for

counting ^{83}Br in sources of different weights of silver bromide
was calculated from the observed activities, and the resultant
calibration curve is given in Fig. 13.

It was not possible to calibrate the end-window counter
for 6.0 minute ^{84}Br and 31.8 minute ^{84}Br owing to the short
half-lives of these species. The efficiency of the counter
for detecting these nuclides in sources of silver bromide was
estimated from a knowledge of their decay energies and the
data obtained for similar sources of ^{83}Br.

Results of Relative Yield Measurements

The results of the relative yield measurements of ^{83}Br
and the two ^{84}Br species to ^{97}Zr are given in Table 5. The
values for A_{Zr}^{o} and S_{Zr} are taken from Table 4. The relative
yields were calculated by application of the relative yield
equation (page 38) to the measured activities and calculated
values of S. Further discussion of results is given in
Chapter 4, where corrections are applied for the distribution
of charge at the instant of fission and a normalized yield
curve produced.
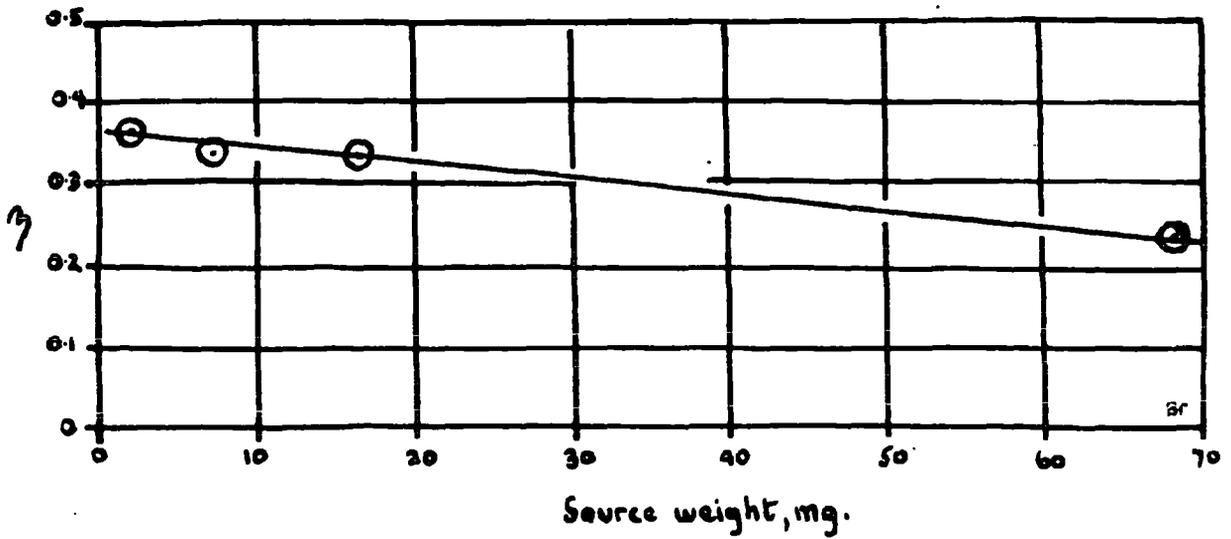
Fig. 13

Efficiency of the end-window counter for counting 2.4 hour ^{83}Br in sources of different weights of silver bromide.

TABLE 5(a)

Results for 2.4 hour ^{83}Br

Run No.	Source wt., mg.	Chemical Yield %	η	$A^o_{obs.}$	$A^o_{corr.}$	S_{Br} x 10^5	A^o_{Zr}	S_{Zr} x 10^5	Relative Yield
7	·3.76	14.8	0.369	2.30×10^3	4.21×10^4	0.721	1.64×10^4	0.979	0.490
32	10.32	40.6	0.346	6.38×10^2	4.53×10^3	2.243	2.62×10^3	2.953	0.321
33	14.46	57.0	0.339	2.08×10^3	1.07×10^4	4.493	5.28×10^3	5.667	0.362
34	12.68	50.0	0.342	3.17×10^3	1.84×10^4	2.138	6.01×10^3	2.386	0.484
37	8.45	33.4	0.349	1.07×10^3	9.16×10^3	5.341	4.55×10^3	6.010	0.320

Relative Yield of 2.4 hour ^{83}Br = 0.395 ± 087

TABLE 5(b)

Results for 31.8 minute ^{84}Br

Run No.	Source wt., mg.	Chemical Yield %	η	$A^o_{obs.}$	$A^o_{corr.}$	S_{Br} x 10^5	A^o_{Zr}	S_{Zr} x 10^5	Relative Yield
32	10.32	40.6	0.347	2.5×10^3	1.77×10^4	1.176	2.62×10^3	2.953	0.502
34	12.68	50.0	0.342	1.08×10^4	6.29×10^4	1.423	6.01×10^3	2.386	0.518
38	12.06	47.5	0.343	6.04×10^2	3.70×10^4	1.439	3.28×10^3	1.955	0.455

Relative yield of 31.8 minute ^{84}Br = 0.492 $\pm$ 0.031

Results for 6.0 minute ^{84}Br

Run No.	Source wt., mg.	Chemical Yield %	η	$A^o_{obs.}$	$A^o_{corr.}$	S_{Br} x 10^5	A^o_{Zr}	S_{Zr} x 10^5	Relative Yield
39	9.07	35.7	0.349	3.90×10^3	3.13×10^4	5.678	2.04×10^4	9.560	0.015
40	6.93	27.3	0.352	1.36×10^3	1.41×10^4	5.055	1.22×10^4	8.910	0.012
41	10.76	42.3	0.347	7.5×10^2	5.1×10^3	0.940	2.72×10^3	1.560	0.018

Relative yield of 6.0 minute ^{84}Br = 0.015 $\pm$ 0.003

(3) <u>Strontium</u>

Of the radioactive isotopes of strontium produced in fission, only 9.7 hour ^{91}Sr was suitable for measurement in the current investigation. The decay chain containing this nuclide is:-

$$10\text{s.}\,^{91}\text{Kr} \longrightarrow 72\text{s.}\,^{91}\text{Rb} \longrightarrow 9.7\text{h.}\,^{91}\text{Sr} \begin{array}{c} \nearrow^{0.6}\; 51\text{m.}\,^{91\text{m.}}\text{Y} \\ \searrow_{0.4}\; 58\text{d.}\,^{91}\text{Y} \end{array} \longrightarrow \text{Stable } ^{91}\text{Zr.}$$
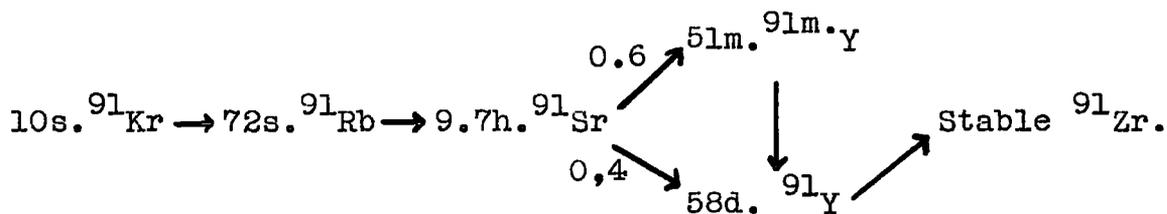
The longer-lived species, 50.5 day ^{89}Sr and 28.0 year ^{90}Sr were not produced in sufficient amount to be detected. The yield of mass number 93 in which 7.9 minute ^{93}Sr precedes 10.3 hour ^{93}Y was determined by radiochemical measurement of the yttrium (see yttrium, page 51).

It was usually convenient to separate strontium and barium together by precipitation of their nitrates from a solution of irradiated thorium in nitric acid. The steps used in the radio-chemical separations of strontium and barium were based on those recommended by Sunderman[38] in his evaluation of the radiochemical separation procedures for these elements. The precipitated nitrates were dissolved and scavenging precipitations of ferric hydroxide made from an alkaline solution. Barium was removed by precipitation of barium chromate from a buffered solution, and strontium oxalate precipitated from

an alkaline solution. (For details see Appendix, page 89).

Trial separations of strontium from samples of thorium which had not been irradiated, showed the strontium sources produced to be free of contamination from thorium daughter activities. The sources prepared of fission-product strontium initially contained some 2.7 hour ^{92}Sr - 3.6 hour ^{92}Y, but after standing overnight decayed with the 9.7 hour half-life of ^{91}Sr.

Calibration of end-window counter for 9.7 hour ^{91}Sr.

A solution of strontium of high specific activity was prepared from pile-irradiated uranium by the chemical procedure outlined above, reduced for working with 1 mg. of added strontium carrier. The absolute activity of the solution was determined by 4π counting, and a weighed quantity of the solution added to 50mg. strontium carrier for preparation of a set of sources of strontium oxalate for the end-window counter in the usual way. Owing to the length of the pile irradiation (1 week) long-lived strontium fission products were present in the sources prepared. These long-lived contributions to the activity were subtracted from the initial portions of the decay curves to obtain the activity due to 9.7 hour ^{91}Sr. In calculating the absolute ^{91}Sr activity from the 4π sources account was taken of 51 minute ^{91m}Y which is produced in 60% of the strontium disintegrations, and decays by internal transition with 5% conversion to 0.55MeV electrons. The

efficiency of the end-window counter for sources of different weights of strontium oxalate is shown in the graph in Fig. 14.

Results of Relative Yield Measurements

The results of the measurements of the yield of 9.7 hour ^{91}Sr relative to 17.0 hour zirconium are given in Table 6.

(4) Yttrium

Of the six radioactive isotopes of yttrium observed in fission products, only 10.3 hour ^{93}Y was suitable for measurements in the current investigation. The decay chain containing this nuclide is:-

$$2.0s.\,^{93}Kr \longrightarrow 5.6s.\,^{93}Rb \longrightarrow 7.9m.\,^{93}Sr \longrightarrow$$

$$10.3h.\,^{93}Y \longrightarrow 1.1 \times 10^6 y.Zr \nearrow 12y.\,^{93m.}Nb.$$

Stable ^{93}Nb.
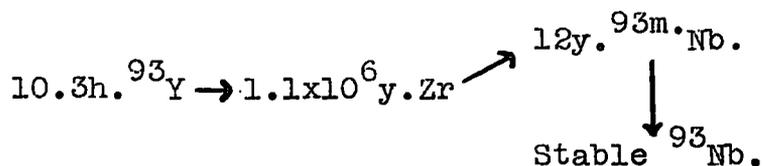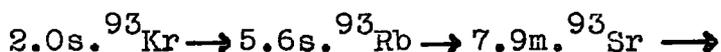
It was usually convenient to separate yttrium and cerium together from a solution of irradiated thorium. Their chemical separation was not commenced until sufficient time had elapsed for the parents of the nuclides to be separated to be almost completely decayed. In the separation of yttrium and cerium,
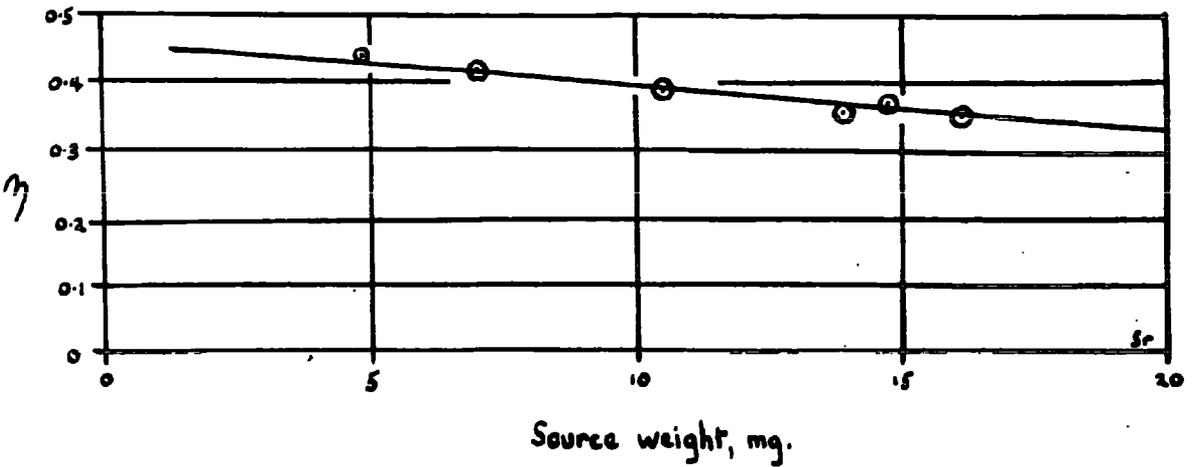
Fig. 14

Efficiency of the end-window counter for counting 9.7 hour ^{91}Sr in sources of different weights of strontium oxalate.

TABLE 6

Relative Yield Measurements of 9.7 hour ^{91}Sr

Run No.	Source wt., mg.	Chemical Yield %	η	$A^o_{obs.}$	$A^o_{corr.}$	$S_{Sr} \times 10^5$	$\hat{A}^o_{Zr}$	$S_{Zr} \times 10^5$	Relative Yield.
4	16.4	69.3	0.361	1.30×10^3	5.19×10^3	3.451	1.68×10^3	3.595	1.83
9	15.5	65.5	0.368	3.31×10^3	1.37×10^3	2.678	4.87×10^3	2.778	1.66
22	13.6	57.4	0.382	1.17×10^3	5.32×10^3	5.673	1.74×10^3	5.831	1.79
28	16.4	69.3	0.361	5.88×10^3	2.34×10^4	3.085	7.41×10^3	3.162	1.85
31	13.3	56.0	0.385	2.10×10^2	9.75×10^2	1.330	3.04×10^2	1.376	1.84
37	10.9	46.0	0.403	2.38×10^3	1.28×10^4	5.915	4.55×10^3	6.010	1.64

Relative yield of 9.7 hour ^{91}Sr = 1.77 $\pm$ 0.09

the time interval was determined by the 18 minute ^{143}La parent of ^{143}Ce, and the solution was left at least 90 minutes before commencing the chemical separation of the elements.

After digestion and a redox procedure to ensure complete exchange between fission products and added carriers, cerium was reduced to its trivalent form and the bulk of the thorium removed from the solution by precipitation of thorium iodate. Cerium and yttrium hydroxides were precipitated on making the solution alkaline. The precipitates were dissolved in nitric acid and cerium (IV) extracted into hexone. Yttrium hydroxide was reprecipitated on making the solution alkaline. The yttrium was then purified and prepared for counting by a method due to Kleinberg[25] in which yttrium was extracted into T.B.P. Further details of the work on cerium are given in the section devoted to that element (page 74).

Trial separations from solutions of thorium which had not been irradiated showed the above procedure to give sources of yttrium oxalate free of contamination from thorium and its daughter activities. Sources of fission-product yttrium decayed with a half-life of 10.3 hours, and their decay was followed until only the background activity was observed.

The stoichiometry of the yttrium oxalate sources prepared for counting has been questioned.[39] A set of sources of yttrium oxalate was prepared, each precipitate being made under slightly different experimental conditions. Analysis of these sources

for yttrium indicated the composition of the sources to be sufficiently reproducible for the current investigation. The results of this investigation are included in this section.

Reproducibility of Yttrium Oxalate Sources

A set of twelve precipitates of yttrium oxalate was prepared, each precipitate being made under slightly different conditions. The precipitates were transferred to sintered glass crucibles, washed, dried, and weighed. The precipitates were then dissolved in acid and their yttrium content determined by titration with E.D.T.A. as described by Schwarzenbach.[40] The results obtained, which are given in Table 7, indicated that although the efficiency of the precipitation of yttrium may vary, the composition of the sources was sufficiently reproducible for the present work.

Calibration of the end-window counter for 10.3 hour ^{93}Y

Yttrium was separated from a solution of pile-irradiated uranium by the method of Kleinberg,[25] reduced for working with 1 mg. of added carrier. In the final step the precipitate of yttrium hydroxide was dissolved in 5 ml. of 5N HCl and quantities of this solution were used for preparation of 4π sources and added to an yttrium carrier solution for preparation of sources for the end-window counter. The measured counting rates of the sources contained a contribution from long-lived yttrium, since the uranium was irradiated for several days. When this

TABLE 7

Sources of yttrium oxalate prepared from equal quantities of a solution of yttrium, under different experimental conditions

Source No.	Experimental Conditions	Source wt. mg.	Wt. of Y. mg.	%Y
1	Standard*	83.1	24.46	29.4
2	Standard*	84.7	24.42	28.8
3	Dried overnight in oven at 120°C.	85.0	24.71	29.1
4	25ml. each of solutions	87.9	25.49	29.0
5	100ml. each of solutions	79.5	23.47	29.5
6	Stood at room temp. 2 hours	83.3	24.71	29.7
7	100ml. oxalate solution added	38.9	11.41	29.4
8	10ml. dil. HCl added	82.6	24.36	29.5
9	Washed with 250ml. each solvent	61.6	17.99	29.2
10	Cooled with running water	80.7	23.97	29.7
11	5 mins. at 100°C, 5 mins. in ice.	78.1	23.22	29.7
12	30 mins. at 100°C.	72.1	21.16	29.3

Average composition = 29.4%Y, which corresponds to the formula
$$Y_2(C_2O_4)_3 \cdot 8 H_2O.$$

*Standard Conditions: 50 ml. of saturated ammonium oxalate were added to 50ml. of the yttrium solution, and the mixture heated in a steam bath for ten minutes, then cooled in an ice bath for ten minutes. The precipitate was then transferred to a sintered glass crucible, and washed with two 50ml. portions of water, two 50ml. portions of alcohol, and two 50 ml. portions of ether, and transferred to a desiccator in preparation for weighing.

long-lived contribution was subtracted from the plotted decay curves the counting rates of the 10.3 hour ^{93}Y were obtained and the end-window counter calibrated for this nuclide. The results of the calibration are shown in Fig. 15.

Results of Relative Yield Measurements.

The results of the measurements of the yield of 10.3 hour ^{93}Y relative to 17.0 hour ^{97}Zr are given in Table 8.

(5) Molybdenum.

The fission yield for the decay chain of mass number 99 was determined by the radiochemical estimation of 66 hour ^{99}Mo. The decay chain for this mass number is:-

$$30s.\ ^{99}Zr \longrightarrow 3m.\ ^{99}Nb \longrightarrow 66h.\ ^{99}Mo \overset{0.87}{\underset{0.13}{\diagdown}} \begin{array}{c} 6.0h.\ ^{99m}Tc \\ \downarrow \\ 2.1\times10^5 y.\ ^{99}Tc \end{array} \longrightarrow Stable\ ^{99}Ru.$$
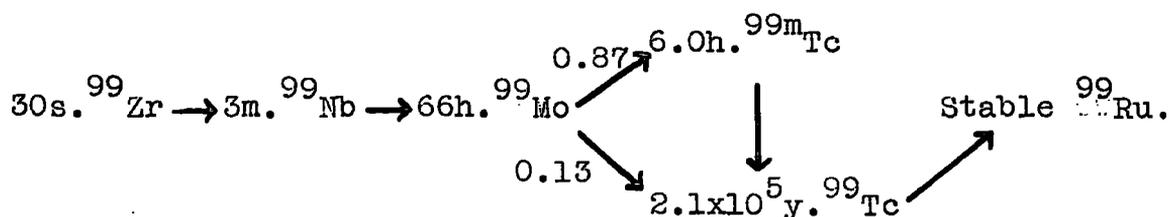
Fission-product molybdenum was separated from solutions of irradiated thorium by a modification of the method of Ballou[41] which consisted of several precipitations of molybdenum with α-benzoin oxime and a final precipitation of molybdenum oxinate for chemical yield determination and counting. Complete details of the chemical procedure are
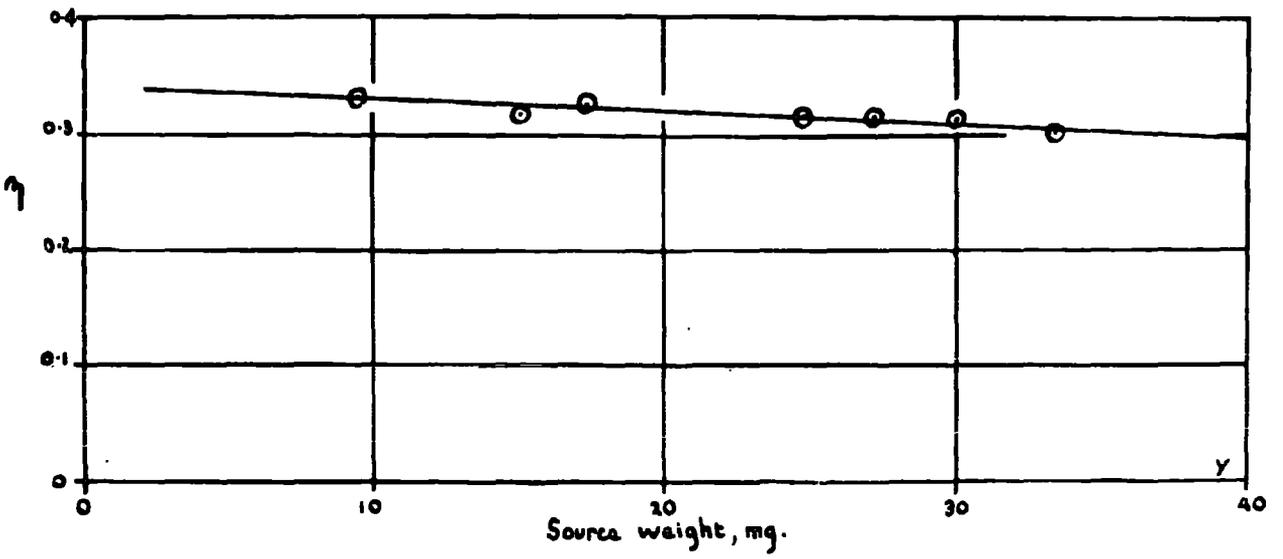
Fig. 15

Efficiency of the end-window counter for counting 10.3 hour ^{93}Y in sources of different weights of yttrium oxalate.

TABLE 8

Relative yield measurements of 10.3 hour ^{93}Y

Run No.	Source wt., mg.	Chemical Yield %	η	$A^o_{obs.}$	$A^o_{corr.}$	S_Y x 10^5	A^o_{Zr}	S_{Zr} x 10^5	Relative Yield.
10	7.29	21.3	0.330	1.88×10^3	2.60×10^4	4.431	9.86×10^3	4.511	1.65
19	10.80	31.7	0.326	2.22×10^3	2.14×10^4	4.834	9.39×10^3	4.997	1.42
20	9.32	27.4	0.328	2.44×10^3	2.71×10^4	4.021	1.12×10^4	4.125	1.50
23	4.86	14.3	0.333	8.29×10^3	1.73×10^4	6.941	6.59×10^3	7.248	1.67
30	10.37	31.5	0.326	1.05×10^3	1.02×10^4	3.643	3.87×10^3	3.735	1.64

Relative yield of 10.3 hour ^{93}Y = 1.58 $\pm$ 0.11

given in the Appendix (page 91). The reproducibility of the final precipitation stage was investigated, and the results of this work is included in this section.

The radiochemical procedure could be carried out in two hours. Fission-product molybdenum sources decayed with the expected half-life of 66 hours after the initial growing-in of the 6.0 hour daughter technetium. The sources prepared were counted for two weeks after an irradiation, by which time the activity observed was comparable with the background.

Reproducibility of Molybdenum Oxinate Sources

A set of eight molybdenum oxinate sources of different weights was prepared by the method used in the fission-product investigation. It was possible that as the precipitates were formed, excess oxine was carried down, and this was investigated by analysing the precipitates for their oxine content.

Each precipitate was digested with 5 ml. of 5N.NaOH, and 0.5 gm of KBr and 10 ml. of 5N.HCl added. 10 ml. of 0.1N $KBrO_3$ was added, then excess solid KI. The iodine liberated was titrated with thiosulphate solution. In this method of determination of oxine, which has been described by Charlot and Bezier[42] the bromine liberated by the $KBrO_3$ brominates the oxine, and the excess bromine is determined by titration of the iodine which it liberates.

The results of the investigation, which are presented in Table 9, indicate that the molybdenum oxinate sources prepared were sufficiently reproducible for the current work.

TABLE 9

Reproducibility of molybdenum oxinate sources

Source No.	Source wt. mg.	BrO_3 used ml.	% oxine*
1	41.87	8.25	69.9
2	40.91	7.74	70.2
3	38.21	7.54	69.9
4	29.12	5.70	70.5
5	19.35	3.85	69.3
6	14.51	2.82	70.7
7	11.46	2.27	69.6
8	8.87	1.74	70.5

*The theoretical percentage of oxine in the sources of molybdenum oxinate, $MoO_2(C_9H_6ON)_2$ is 69.2%.

Calibration of the end-window counter for 66 hour ^{99}Mo

A carrier-free solution of 66 hour ^{99}Mo was obtained from the Radiochemical Centre, Amersham. Approximately 1 mg. of inactive molybdenum was added to the solution to facilitate chemical manipulations. The solution was made alkaline and repeatedly scavenged with ferric hydroxide precipitations. The

solution was made acid and molybdenum ⍺-benzoin oxime pre-
cipitated. The precipitate was centrifuged down and the super-
nate discarded. The precipitate was dissolved in nitric-
perchloric acid and heated to near-dryness to destroy the
organic reagent. The remaining solution was diluted to 5 ml.
for preparation of 4π sources and addition to 50 mg. of inac-
tive molybdenum for preparation of solid sources.

The growth of 6.0 hour ^{99m}Tc was observed in the 4π sources,
and the contribution of ^{99}Mo to the total counting rate at the
time of precipitating molybdenum ⍺-benzoin oxime determined.
The ^{99}Mo added to the solution for the preparation of solid
sources was determined. A set of solid sources was prepared
in the usual way, and counted for several days with the ^{99m}Tc
in transient equilibrium with the ^{99}Mo, and the activities
extrapolated to the time of separation. The efficiency of
the end-window counter for counting the different sources
($\frac{\text{observed counting rate}}{\text{d.p.m. of } ^{99}\text{Mo}}$) was determined, and the calibration
curve is given in Fig. 16.

Results of Relative Yield Measurements

The results of the relative yield determinations of ^{99}Mo,
calculated in the usual way, are given in Table 10.
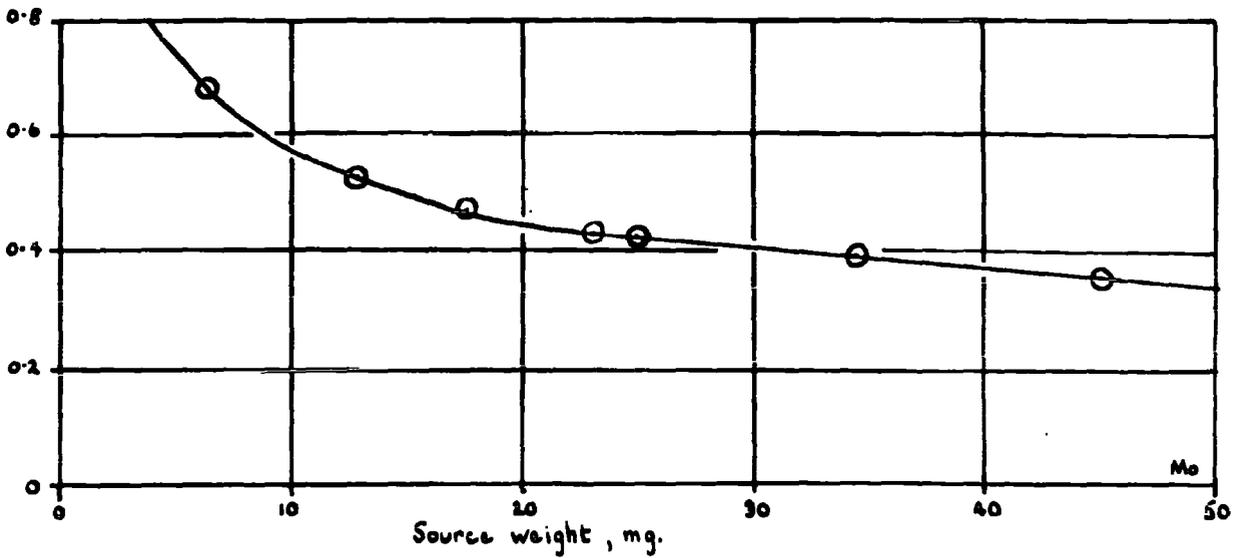
Fig. 16

Efficiency of the end-window counter for counting 66 hour ^{99}Mo
in sources of different weights of molybdenum oxinate.

TABLE 10

Relative Yield Measurements of 66 hour ^{99}Mo

Run No.	Source wt., mg.	Chemical Yield %	γ	$A^o_{obs.}$	$A^o_{corr.}$	$S_{Mo} \times 10^5$	A^o_{Zr}	$S_{Zr} \times 10^5$	Relative Yield
1	17.12	38.0	0.477	2.98×10^2	1.64×10^3	3.322	1.27×10^4	3.267	0.500
3	15.13	33.5	0.498	6.2×10^1	3.75×10^2	1.038	2.92×10^3	0.973	0.476
16	25.58	60.3	0.425	2.93×10^2	1.14×10^3	6.388	1.08×10^4	6.099	0.519
27	17.17	40.5	0.477	1.80×10^2	9.30×10^2	5.636	7.40×10^3	5.456	0.478
32	16.46	38.8	0.484	6.9×10^1	3.68×10^2	3.048	2.62×10^3	2.953	0.536
33	17.93	42.3	0.470	1.41×10^2	7.06×10^2	5.878	5.28×10^3	5.667	0.508

Relative yield of 66 hour ^{99}Mo = 0.503 ± 0.024

(6) <u>Ruthenium</u>

The fission yield for mass number 105 was determined by the radiochemical separation of 4.45 hour ^{105}Ru. The decay chain containing this isotope is:-

$$(2m.\,^{105}Mo) \rightarrow 10m.\,^{105}Tc \rightarrow 4.45h.\,^{105}Ru \nearrow 38s.\,^{105m}Rh \rightarrow 35.3h.\,^{105}Rh \nearrow Stable\ ^{105}Pd$$
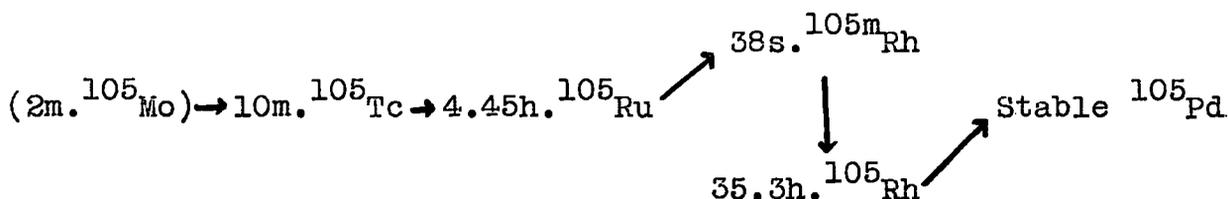
The recently reported method[43] for the determination of fission-product ruthenium in which ruthenium tetroxide is distilled from a mixture of sulphuric acid and sodium bismuthate did not prove fessible for the current work owing to the insolubility of thorium sulphate and the introduction of relatively large quantities of bismuthate into a solution from which other elements had subsequently to be separated. Distillation of ruthenium from a solution of thorium in perchloric acid gave sources which were found to contain some α -activity, attributed to carry-over of thoron in the distillation. The ruthenium, therefore, was first separated from the bulk of the thorium by precipitation of ruthenium sulphide before the distillation step. Ruthenium dioxide was precipitated for counting, as described by Larsen, Ross and Kesser.[43] Complete details of the chemical procedure are given in the appendix (page 95). Sources of fission-product ruthenium contained

4.45 hour ^{105}Ru which decayed to 35.3 hour ^{105}Rh. The con-
tributions from long-lived nuclides to the total counting
rates were subtracted to obtain the decay curves for the
ruthenium.

Calibration of the end-window counter for 4.45 hour ^{105}Ru

^{105}Ru activity was separated from pile-irradiated uranium
by the method of Larsen, Ross and Kesser[43] reduced for working
with 1 mg. added carrier. The final precipitate was dissolved
in HCl to provide a solution of high specific activity for
calibration purposes. The absolute disintegration rate of
^{105}Ru in the solution was determined by preparing 4π sources
from aliquot parts and counting the 35.3 hour ^{105}Rh in these
sources when the ruthenium had decayed. By calculating the
^{105}Ru activity from the measured ^{105}Rh activity, any in-
accuracy introduced by estimations of the 4π counter efficiency
for ^{105}Ru - ^{105m}Rh was avoided.

A weighed quantity of active solution was added to a
solution of ruthenium carrier, and after a redox cycle and
digestion to ensure isotopic exchange, ruthenium dioxide was
precipitated, and a set of sources of different weights pre-
pared and counted in the end-window counter. By comparing
the ruthenium activities measured by the end-window with the
absolute ^{105}Ru content calculated from 4π measurements the
efficiency of the end-window counter for counting this nuclide

was obtained. The calibration curve of counter efficiency against source weight is given in Fig. 17.

Results of Relative Yield Measurements

The results of the relative yield measurements for ^{105}Ru are given in Table 11.

(7) Milking of Silver from Palladium

Direct measurement of fission-product palladium species did not prove to be practicable owing to the complexity of their decay chains and the β-energies of the nuclides involved. However, by milking 3.2 hour ^{112}Ag from 21 hour ^{112}Pd it was possible to determine the yield for mass number 112. The decay chain for this mass number is:-

$$21\text{h.}\,^{112}\text{Pd} \longrightarrow 3.2\text{h.}\,^{112}\text{Ag} \longrightarrow \text{Stable } ^{112}\text{Cd.}$$
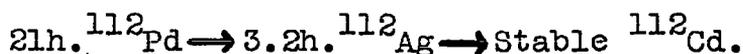
Palladium was separated from solutions of irradiated thorium nitrate by precipitation with dimethylglyoxime and purified by scavenging precipitations of ferric hydroxide and silver halides, as described by Glendenin[44] The time of the last removal of silver was noted. Palladium dimethylglyoxime was precipitated for the determination of the chemical yield of palladium. The precipitate was immediately dissolved in nitric acid and silver carrier added. After a time interval
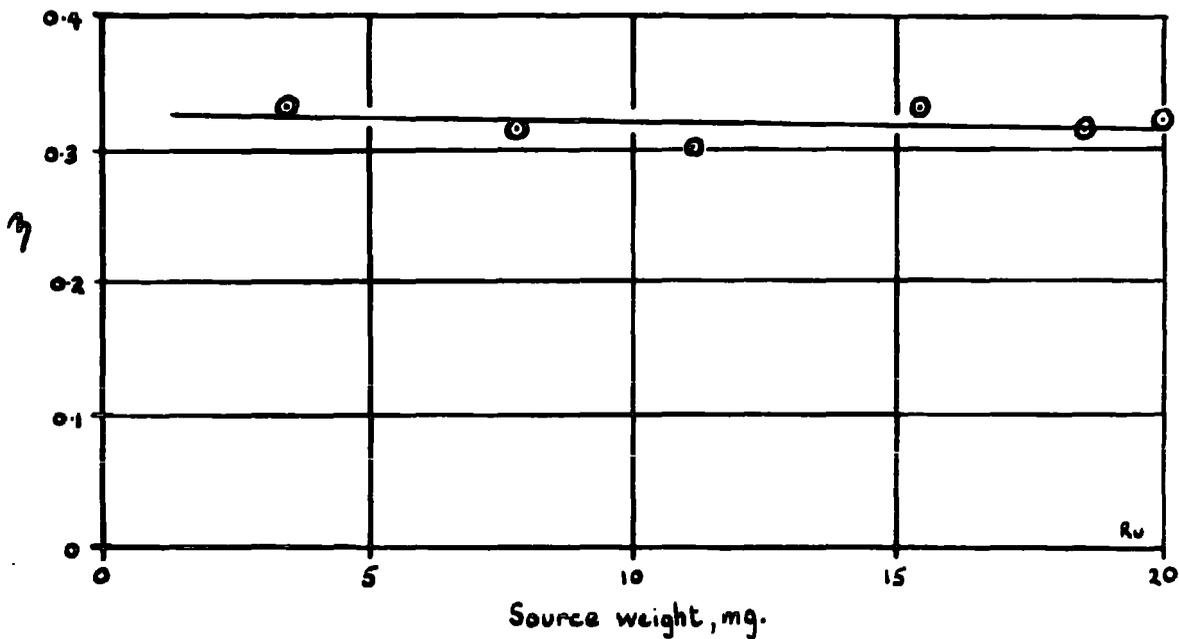
Fig. 17

Efficiency of the end-window counter for counting 4.45
hour ^{105}Ru in sources of different weights of
ruthenium dioxide.

TABLE 11

Relative Yield Measurements of 4.45 hour ^{105}Ru

Run No.	Source wt., mg.	Chemical Yield %	η	$A^{\circ}_{obs.}$	$A^{\circ}_{corr.}$	$S_{Ru} \times 10^5$	A°_{Zr}	$S_{Zr} \times 10^5$	Relative Yield
4	3.05	24.5	0.325	1.34×10^2	1.68×10^3	3.096	1.68×10^3	3.593	0.309
19	13.39	81.4	0.317	2.73×10^3	1.06×10^4	4.335	9.39×10^3	4.997	0.343
20	7.28	44.4	0.321	1.70×10^3	1.19×10^4	3.698	1.12×10^4	4.125	0.310
23	6.34	38.7	0.322	9.9×10^2	7.99×10^3	6.303	6.59×10^3	7.248	0.363

Relative yield of 4.45 hour ^{105}Ru = 0.331 $\pm$ 0.026

of approximately twelve hours, when sufficient silver activity
had grown into the solution, silver chloride was precipitated,
purified by ferric hydroxide scavenges, and reprecipitated for
counting. Precipitation of silver iodate, as in the separation
of fission-product silver, was not found to be practicable
owing to the subsequent interference of HIO_3 with the recovery
of palladium by·re-precipitation with dimethylglyoxime. The
silver milkings were repeated at approximately twelve-hour
intervals until the activity on the silver sources produced
was too low to be of significant value.

Calibration of the end-window counter for 3.4 hour ^{112}Ag

There are several silver isotopes present in a sample of
pile-irradiated uranium and silver decay curves would therefore
have been difficult to resolve. By separating fission-product
palladium from such a sample, and milking silver from the
palladium when it had grown in sufficiently, a solution was
obtained which contained only 3.4 hour ^{112}Ag. The chemical
procedures used. were similar to those employed in the thorium
investigation, reduced for working with less than 1 mg. of
added carrier. Exact timing of the separation was not neces-
sary as calibration only required the comparison of the
counting rates of the solid sources with the absolute dis-
integration rate at a set time. The calibration curve pro-
duced for sources of silver chloride is given in Fig. 18.
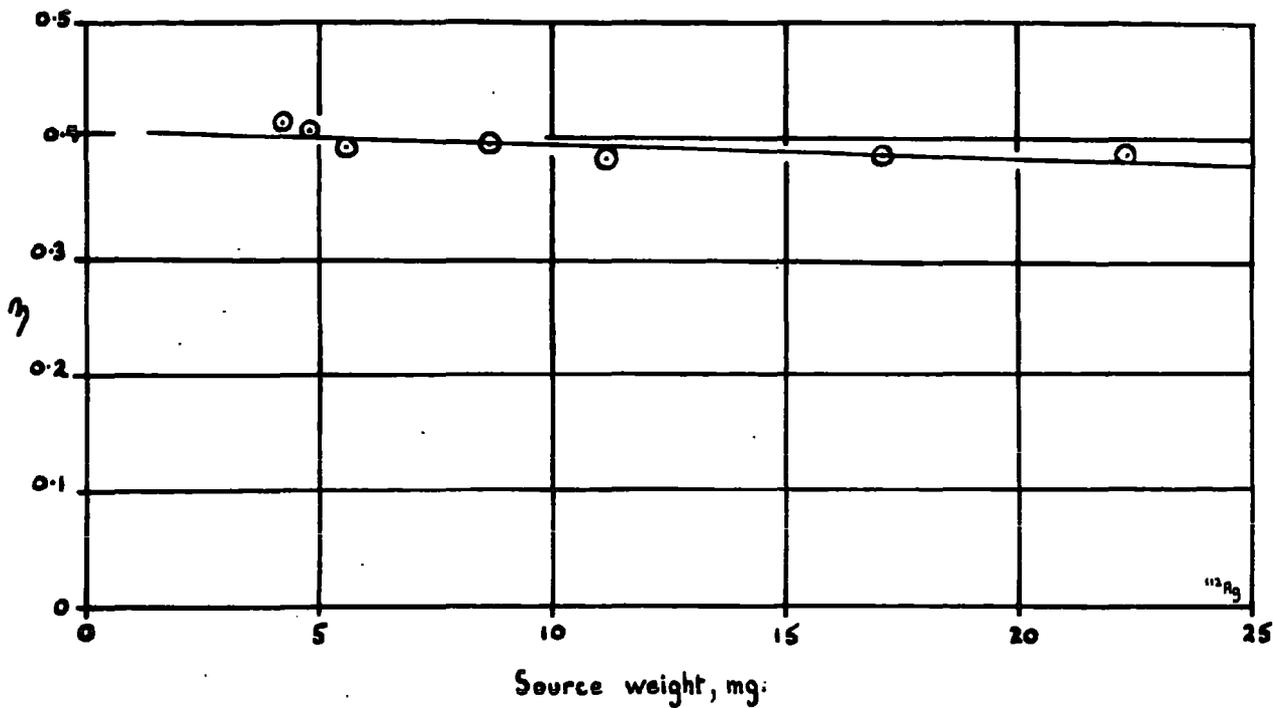
<u>Fig. 18</u>

Efficiency of the end-window counter for counting 3.2 hour ^{112}Ag in sources of different weights of silver chloride.

Results of Relative Yield Measurements for Mass Number 112

The results of the palladium - silver milking experiments are given in Table 12.

Since the silver was never permitted to come completely to equilibrium with the palladium parent, it was necessary to calculate the palladium activity in the following manner: If $^{112}Pd = 1$, $^{112}Ag = 2$, t = time interval in which the silver was growing into the decaying palladium, I_1^O = palladium activity before the silver appeared (i.e. at the time of the previous removal of silver)

$$I_1^O = I_2 \frac{(\lambda_2 - \lambda_1)}{\lambda_2 (e^{-\lambda_1 t} - e^{-\lambda_2 t})}$$

The decay curves of the silver sources were extrapolated to the time of the milking of the silver, and I_2 obtained by application of the usual chemical yield and counter efficiency corrections. I_1^O was then calculated by use of the above equation. After allowing for the chemical yield of the palladium from which the silver was milked the decay of the palladium was plotted to obtain I_{Pd} for use in the relative yield equation.

TABLE 12

Results of palladium-silver milking experiments

Run No.	Pd yield %	t (min.)	Ag yield %	η	$A^t{}_{Ag}$	$A^t{}_{Pd}$	$A^o{}_{Pd}$	$S_{Pd} \times 10^5$	$A^o{}_{Zr}$	$S_{Zr} \times 10^5$	Relative yield
	91.0	389	49.5	0.401	1.46×10^2	1.21×10^3					
24	76.4	720	48.9	0.401	1.10×10^2	1.01×10^3					
	69.7	620	45.5	0.402	6.5×10^1	6.95×10^2	1.34×10^2	2.783	4.27×10^3	2.762	0.383
	96.0	370	75.5	0.396	3.50×10^2	2.31×10^3					
25	39.8	760	62.0	0.398	1.90×10^2	1.85×10^3					
	29.0	660	70.5	0.397	9.9×10^1	1.17×10^3	2.66×10^3	8.330	9.45×10^3	8.292	0.346
	80.6	850	78.0	0.395	1.07×10^2	6.10×10^2					
29	62.7	660	89.3	0.394	5.9×10^1	3.67×10^2					
	61.6	780	85.0	0.394	3.6×10^1	2.48×10^2	6.33×10^2	4.463	2.37×10^3	4.435	0.328

Relative yield of 21 hour $^{112}Pd = 0.352 \pm 0.028$

(8) <u>Silver</u>

The relative yields of mass numbers 111 and 113 were determined by the direct separation of fission-product silver. The decay chains for these mass numbers are:-

$$5.5h.\ ^{111m}Pd \longrightarrow 74s.\ ^{111m}Ag$$

(short ^{111}Rh) with branching 0.01 to ^{111m}Pd, 0.99 to $23m.\ ^{111}Pd$, 0.75, $7.6d.\ ^{111}Ag$, Stable ^{111}Cd

$$1.4m.Pd \xrightarrow{0.10} 1.2m.\ ^{113m}Ag \qquad 1.4m.Pd \xrightarrow{0.90} 5.3h.\ ^{113}Ag \longrightarrow Stable\ ^{113}Cd.$$
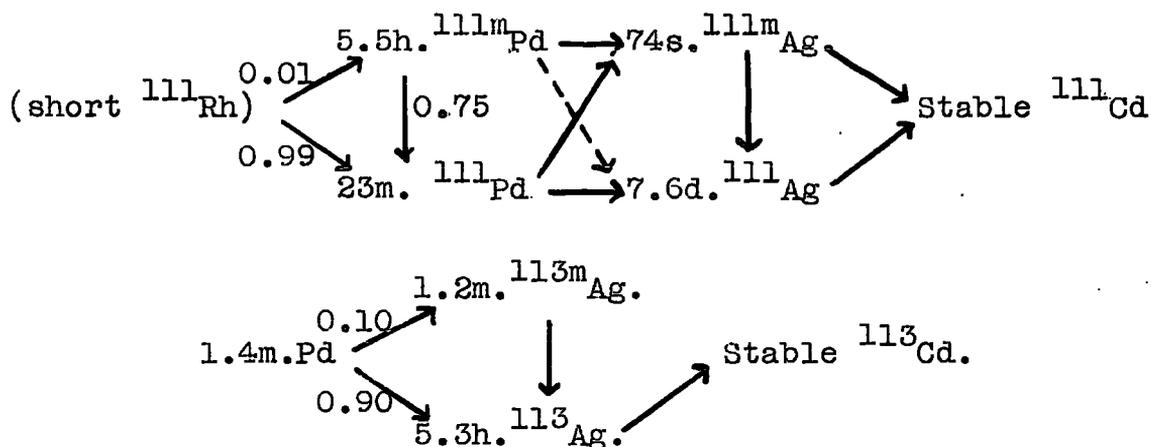
The radiochemical procedure used in the separation of fission-product silver was based upon the method of Sunderman.[38] Silver was separated from the solution of irradiated material by precipitation of silver chloride. After a scavenging precipitation of ferric hydroxide from ammoniacal solution, silver was decontaminated from fission-product halides by precipitation of silver benzotriazole from a solution containing E.D.T.A. The precipitate was dissolved in nitric acid, and silver oxide precipitated by addition of sodium hydroxide. Retained organic matter was removed and the oxide converted to sulphate by heating to dryness with sulphuric acid. The silver sulphate was dissolved in water and silver iodate precipitated for counting.

The sources prepared decayed with half-lives of 5.3 hours, edcept in those irradiations where a very high neutron flux was obtained, and then 7.6 day ^{111}Ag was also detected.

The details of the relative yield measurements of ^{113}Ag to ^{97}Zr for neutrons of different bombarding energies (as referred to in Chapter 2, page 21) are included in this section.

Estimation of the efficiency of the end-window counter for ^{111}Ag and ^{113}Ag.

The efficiency of the end-window counter for sources of silver iodate containing ^{111}Ag and ^{113}Ag was estimated by comparison with other sources, taking account of the β-energies of the nuclides concerned and the electron density of the sources.

Results of Relative Yield Measurements

The results of the relative yield measurements of 7.6 day ^{111}Ag and 5.3 hour ^{113}Ag are presented in Tables 13 and 14. The variability of the results for 7.6 day ^{111}Ag may be attributed to the low counting rates obtained.

Relative yield measurements of ^{113}Ag to ^{97}Zr for neutrons of different energies

The reason for this experiment has been given in Chapter 2 (page 21).

TABLE 13

Relative Yield Measurements of 7.6 day ^{111}Ag

Run No.	Source wt., mg.	Chemical Yield %	η	A^o obs.	A^o corr.	S_{Ag} x 10^5	A^o_{Zr}	S_{Zr} x 10^5	Relative Yield
10	6.31	21.8	0.31	2.9×10^1	4.3×10^2	4.723	9.86×10^3	4.511	0.45
12	15.99	55.1	0.30	5.0×10^1	3.0×10^2	3.532	8.74×10^3	3.393	0.35
15	11.45	39.6	0.30	3.6×10^1	3.0×10^2	1.093	8.76×10^3	1.072	0.36
18	9.15	31.7	0.31	5.9×10^1	6.2×10^2	6.192	1.39×10^4	6.052	0.47

Relative yield of 7.6 day ^{111}Ag = 0.41 $\pm$ 0.06

TABLE 14

Relative Yield Measurements of 5.3 hour ^{113}Ag

Run No.	Source wt., mg.	Chemical Yield, %	$\mathfrak{z}$	$A^o{}_{obs.}$	$A^o{}_{corr.}$	S_{Ag} x 10^5	$A^o{}_{Zr}$	S_{Zr} x 10^5	Relative Yield
5	5.84	20.2	0.377	1.11×10^3	1.46×10^4	6.998	1.66×10^4	8.353	0.326
6	18.31	63.4	0.364	1.78×10^3	7.69×10^3	1.941	7.90×10^3	2.232	0.347
8	14.65	50.7	0.368	1.60×10^3	8.54×10^3	2.349	8.20×10^3	2.634	0.362
10	6.31	21.8	0.376	8.32×10^2	1.02×10^4	4.068	9.86×10^3	4.511	0.357
15	11.45	39.6	0.374	1.28×10^3	8.62×10^3	1.025	8.76×10^3	1.072	0.322

Relative yield of 5.3 hour ^{113}Ag = 0.343 $\pm$ 0.018

Experimental

For each irradiation two packets of thorium nitrate were prepared:- a small square packet which was attached to the base of the target block, and a long narrow packet which was wrapped around the side of the target block. During irradiation these packets were bombarded with neutrons of 14.8 and 14.1 MeV respectively. After irradiation, the relative yield of silver to zirconium was determined for each sample.

Results

The results, which are presented in Table 15, indicate that any differences. in the ratio of the yields of ^{113}Ag to ^{97}Zr which might arise from small differences in the energy of bombarding neutrons are too small to be detected by the current procedure. Whilst the activities induced in samples irradiated at the side of the target can be seen to be an order of magnitude less than activities induced in samples attached to the bottom of the target block for irradiation, the results of relative yield measurements in either case are seen to be in agreement, within suggested experimental errors.
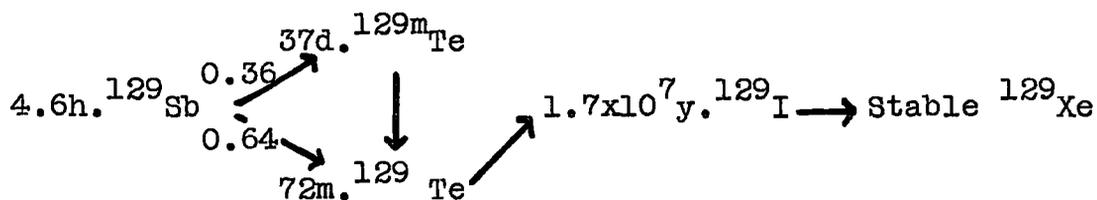
TABLE 15

Relative Yield Measurements of 5.3 hour ^{113}Ag for neutrons of different energies

Run No.	E_n	Source wt., mg.	Chemical Yield, %	γ	$A^o_{obs.}$	$A^o_{corr.}$	S_{Ag} x 10^5	A^o_{Zr}	S_{Zr} x 10^5	Relative Yield
11	14.1	10.45	36.3	0.373	1.53×10^2	1.13×10^3	3.102	1.12×10^3	3.393	0.344
12	14.8	15.99	55.1	0.367	1.85×10^3	9.15×10^3	3.102	8.74×10^3	3.393	0.355
17	14.1	4.21	14.6	0.383	1.48×10^2	2.65×10^3	5.751	2.60×10^3	6.052	0.333
18	14.8	9.15	31.7	0.376	1.65×10^3	1.38×10^4	5.751	1.39×10^4	6.052	0.324

(9) Antimony

The relative yield of mass number 129 was determined by the radiochemical separation and measurement of 4.6 hour ^{129}Sb. The decay chain for this mass number is:-

$$4.6\text{h.}\ ^{129}\text{Sb} \underset{0.64}{\overset{0.36}{\lessgtr}} \begin{array}{c} 37\text{d.}\ ^{129m}\text{Te} \\ \downarrow \\ 72\text{m.}\ ^{129}\text{Te} \end{array} \longrightarrow 1.7\times10^{7}\text{y.}\ ^{129}\text{I} \longrightarrow \text{Stable}\ ^{129}\text{Xe}$$

The separation of fission-product antimony from irradiated thorium carbonate was based upon the method used by Pappas[45] for the rapid separation of short-lived antimony fission products. Samples of irradiated thorium carbonate were dissolved in a solution containing 10mg. of antimony (III) carrier. The antimony was oxidised to the (V) state with chlorine, and extracted into di-iso-propyl ether. It was back-extracted into a saturated solution of hydrazine hydrochloride and potassium thiocyanate. After a scavenging precipitation of tellurium, metallic antimony was precipitated by addition of chromous chloride solution, and a source prepared for counting.

Trial separation of antimony from samples of unirradiated thorium nitrate produced sources contaminated by ^{212}Bi (ThC). This contamination was eliminated by removal of the thorium daughters from the samples before irradiation, as described

in Chapter 2, page 17. Sources of fission-product antimony prepared from samples of irradiated thorium carbonate decayed with the 4.6 hour half-life of ^{129}Sb.

Calibration of the end-window counter for 4.6 hour ^{129}Sb.

Fission-product antimony was separated from a sample of pile-irradiated uranium by the method described above, reduced for working with approximately 1 mg. of added carrier. The final antimony precipitate was dissolved in a few drops of nitric acid and diluted to 5 ml. to provide a solution for preparation of 4π sources, and for addition to antimony carrier for preparation of a set of sources for end-window counting.

Owing to the length of the irradiation in the pile (3 days) long-lived antimony isotopes were observed in the sources thus prepared. These were not detected in the short laboratory irradiations of thorium. However resolution of the decay curves for the 4.6 hour ^{129}Sb was possible. The absolute activity of ^{129}Sb in the 4π sources was calculated, taking account of the ^{129m}Te daughter resulting from some 64% of the antimony disintegrations. The ^{129}Sb activity of each of the solid sources was obtained by resolution of the appropriate decay curve and the efficiency of the end-window counter for counting these sources calculated. The calibration of the counter for this nuclide is given in Fig. 19. The calibration includes the correction factor for the ^{129m}Te contribution to
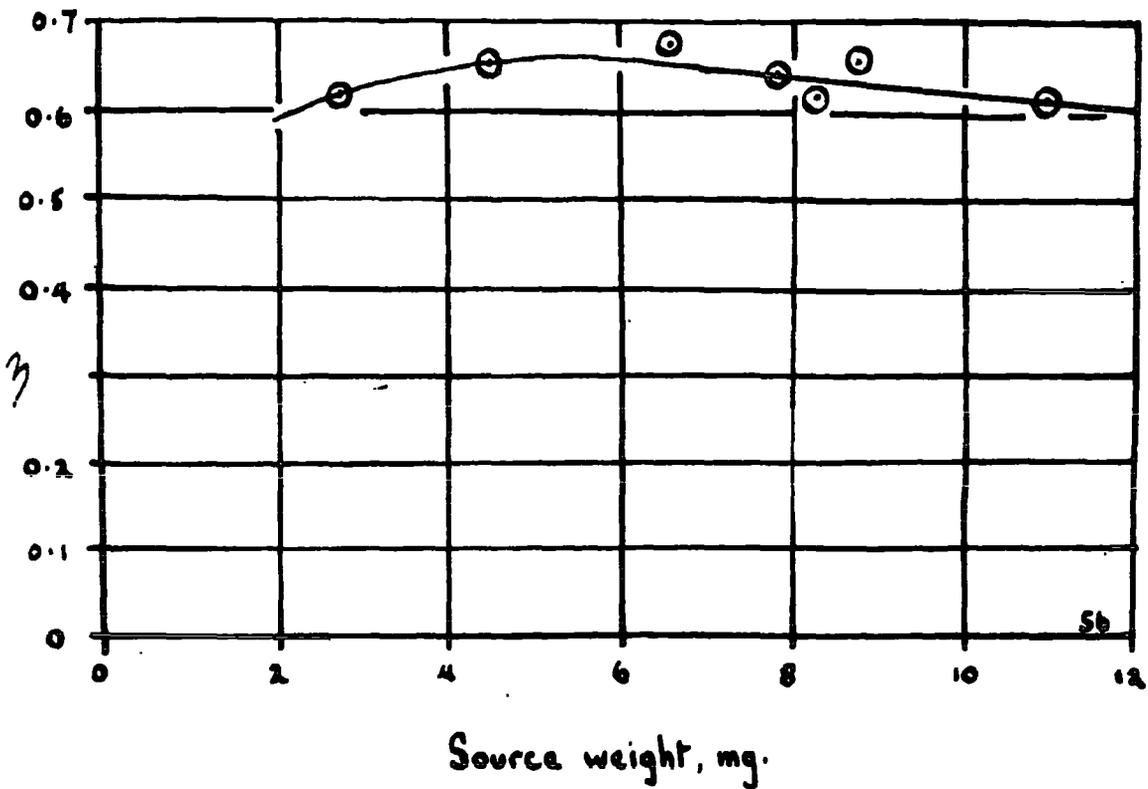
Fig. 19

Efficiency of the end-window counter for counting 4.6 hour
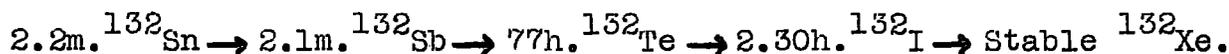^{129}Sb in sources of different weights of metallic antimony.

the counting rate of the solid sources.

Results of Relative Yield Measurements for ^{129}Sb

The results of the measurements of the relative yield of 4.6 hour ^{129}Sb to 17 hour ^{97}Zr are given in Table 16.

(10) Tellurium - Iodine

The decay chain for mass number 132 contains two nuclides with half-lives convenient for measurement in the current work. The decay chain for this mass number is:-

2.2m. ^{132}Sn $\longrightarrow$ 2.1m. ^{132}Sb $\longrightarrow$ 77h. ^{132}Te $\longrightarrow$ 2.30h. ^{132}I $\longrightarrow$ Stable ^{132}Xe.

77 hour tellurium was separated in all experiments. In the first case this was measured by preparing sources of elementary tellurium with ^{132}Te - ^{132}I in transient equilibrium. In the second case ^{132}I was milked from purified tellurium and sources of silver iodide prepared for counting. The end-window counter was independently calibrated for both types of sources counted, and so the measurements on these nuclides give an indication of the reliability of the methods.

(a) Separation and measurement of ^{132}Te

The separation of tellurium from irradiated thorium nitrate

TABLE 16

Relative Yield Measurements of 4.6 hour ^{129}Sb

Run No.	Source wt., mg.	Chemical Yield %	η	$A^{o}_{obs.}$	$A^{o}_{corr.}$	S_{Sb} x 10^5	A^{o}_{Zr}	S_{Zr} x 10^5	Relative Yield
42	3.33	25.3	0.635	6.70×10^1	4.16×10^2	1.770	3.85×10^2	1.834	0.302
43	3.75	28.5	0.650	3.97×10^2	2.14×10^3	5.061	1.74×10^3	5.371	0.351
44	3.43	26.2	0.638	4.16×10^2	2.48×10^3	3.773	2.25×10^3	3.981	0.315

Relative yield of 4.6 hour ^{129}Sb = 0.323 $\pm$ 0.025

was preceded by the redox cycle recommended by T.C. Hoering.[46]

Tellurium was precipitated with sulphur dioxide, and purified

by dissolution and reprecipitation, with scavenging precipita-

tions of ferric hydroxide, as described by Meinke.[24] Sources

containing fission-product tellurium prepared by this method

decayed with the 77-hour half-live of ^{132}Te after the initial

growing in of ^{132}I.

Calibration of the end-window counter for 77 hour ^{132}Te – 2.30 hour ^{132}I.

A solution of "carrier-free" tellurium was obtained from

the Radiochemical Centre, Amersham, and its absolute activity

determined by 4π counting of aliquot parts. Both ^{132}Te and

^{132}I were counted in transient equilibrium in the 4π counter

and the contribution from the tellurium calculated from this.

A weighed quantity of active solution was added to a

solution of tellurium carrier, and after digestion to ensure

complete isotopic exchange elementary tellurium was precipitated

with sulphur dioxide and a set of sources of different weights

prepared for the end-window counter. The efficiency of the

counter for detecting ^{132}Te in these sources was determined,

and a calibration curve of counter efficiency (including the

correction term for ^{132}I) against source weight is given in
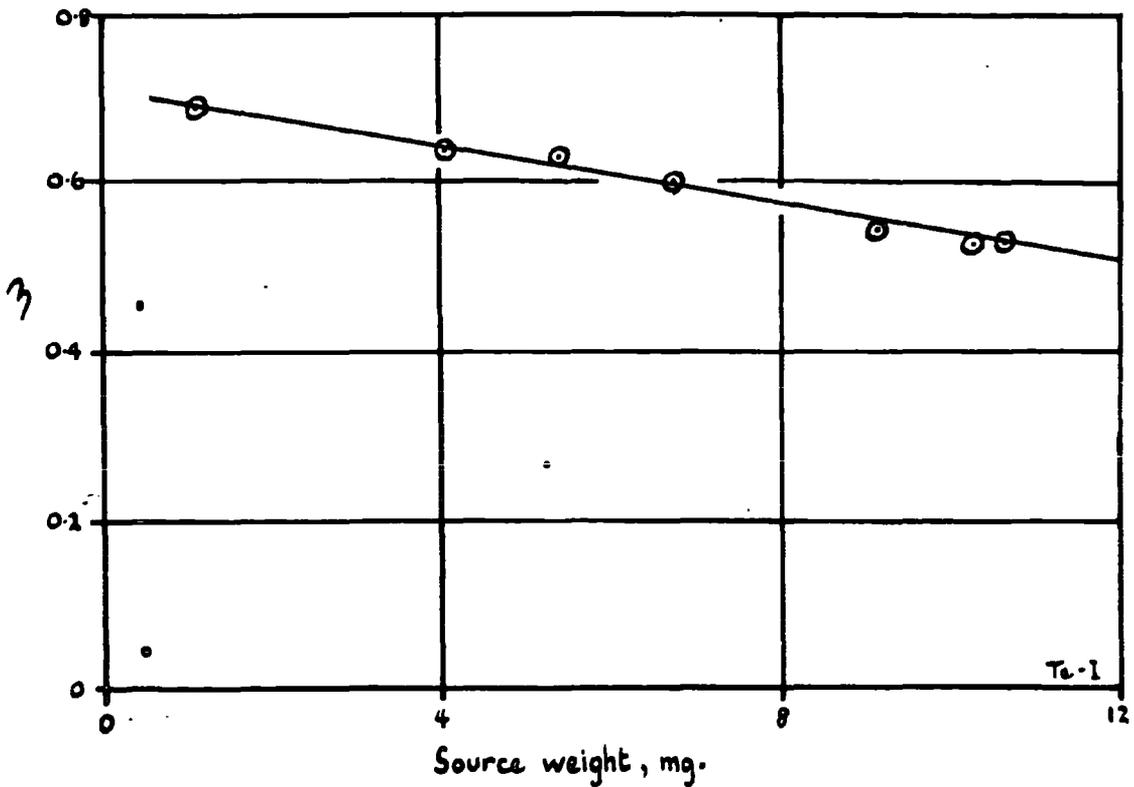
Fig. 20.

Fig. 20

Efficiency of the end-window counter for counting 77 hour ^{132}Te – 2.3 hour ^{132}I in sources of different weights of metallic tellurium.

Results of Relative Yield Measurements

The results of the measurements of the yield of 77 hour ^{132}Te relative to ^{97}Zr as determined by the separation and counting of elementary tellurium are presented in Table 17.

(b) Measurement of ^{132}Te by milking of ^{132}I

Tellurium was separated from irradiated thorium nitrate by the method described above (page 68) and a tellurium source prepared and weighed. The tellurium was then dissolved, and iodine carrier added. After a period of time sufficient for 2.3 hour ^{132}I to grow into transient equilibrium with the 77 hour ^{132}Te a redox cycle was carried out to ensure complete exchange of iodine activity and added carrier. The iodine was purified and prepared for counting by extraction into carbon tetrachloride, back extraction into sodium sulphite solution, and precipitation of silver iodide. The tellurium was recovered. and the milking procedure repeated for as many times as was. justified by the counting rates, obtained on the silver iodide sources. Complete details of the procedure are given in the appendix (page 105).

Calibration of the end-window counter for 2.30 hour ^{132}I.

A solution of iodine activity was obtained by milking a portion of the tellurium from the Radiochemical Centre , Amersham. The absolute activity of the iodine solution was determined by 4π counting of aliquot parts. A weighed quantity of the

TABLE 17

Results for 77 hour ^{132}Te

Run No.	Source wt., mg.	Chemical Yield %	η	$A^o_{obs.}$	$A^o_{corr.}$	$S_{Te} \times 10^5$	A^o_{Zr}	$S_{Zr} \times 10^5$	Relative Yield
2	1.47	14.7	0.683	9.3×10^1	9.21×10^2	1.231	4.42×10^3	1.141	0.871
13	1.58	15.8	0.682	4.52×10^2	4.18×10^3	10.176	2.31×10^4	9.510	0.765
21	2.30	23.1	0.668	1.32×10^2	8.51×10^2	2.325	4.62×10^3	2.176	0.780
32	2.51	25.4	0.664	8.56×10^1	5.07×10^2	3.048	2.62×10^3	2.953	0.850
33	2.30	23.1	0.668	1.66×10^2	1.07×10^3	5.878	5.28×10^3	5.667	0.891

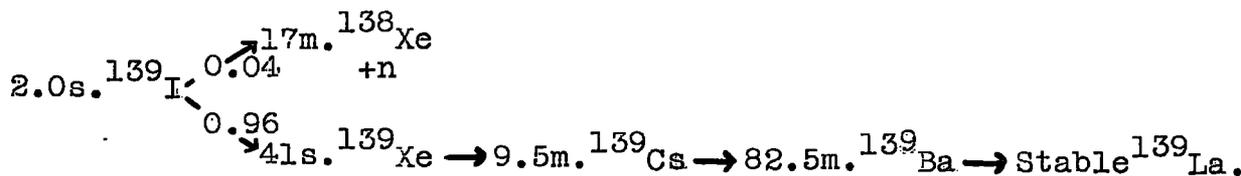Relative yield of 77 hour ^{132}Te = 0.835 ± 0.056

solution was added to a solution of iodine carrier and a set of sources of silver iodide prepared and counted in the end-window counter. The efficiency of the end-window counter for counting 2.30 hour iodine in sources of different weights of silver iodide is given in Fig. 21.

Results of Relative Yield Measurements

The results of the measurements of the relative yields of 77 hour ^{132}Te and 17 hour ^{97}Zr as determined by the milking of 2.30 hour iodine from the tellurium are given in Table 18. The relative yield determined by the counting of iodine milked from the tellurium will be seen to be within the limits of the determination by counting metallic tellurium sources.

(11) Barium

The fission yield for mass number 139 was determined by the radiochemical separation and measurement of 82.5 minute barium. The decay chain for this mass number is:-
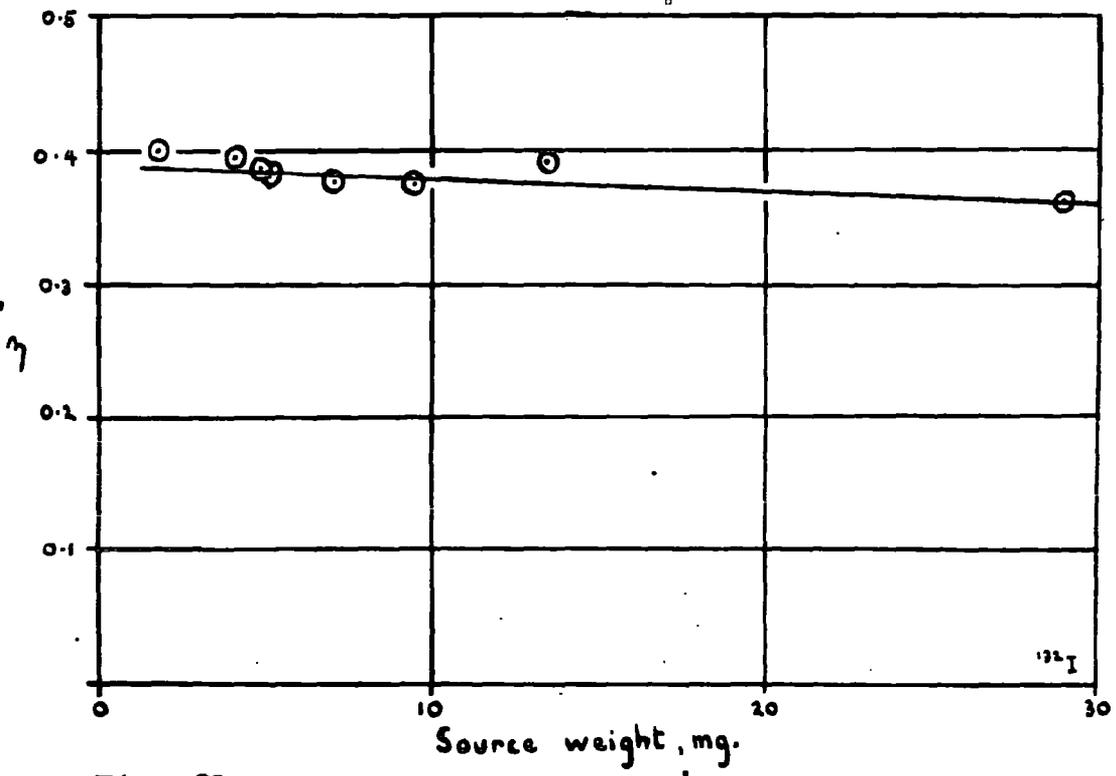
$$2.0s.^{139}I \begin{cases} \nearrow 17m.^{138}Xe \\ 0.04 \quad +n \\ \\ 0.96 \\ \searrow 41s.^{139}Xe \longrightarrow 9.5m.^{139}Cs \longrightarrow 82.5m.^{139}Ba \longrightarrow Stable^{139}La. \end{cases}$$

Fig. 21

Efficiency of the end-window counter for counting 2.3 hour
^{132}I in sources of different weights of silver iodide.

TABLE 18

Results for milking 2.3 hour ^{132}I from 77 hour ^{132}Te

Run No.	Te yield	t (hrs.)	I source wt., mg.	I yield	η	A^t_I	A^t_{Te}	A^o_{Te}
	59.6	18.0	15.40	81.9	0.375	3.52×10^2	1.94×10^3	2.27×10^3
	33.1	66.5	15.10	80.8	0.375	1.28×10^2	1.26×10^3	2.30×10^3
36	20.5	90.0	11.76	62.3	0.377	4.58×10^1	9.50×10^2	2.12×10^3
	16.7	113.0	9.24	49.3	0.380	2.7×10^1	8.55×10^2	2.29×10^3

A^o_{Te}	$S_{Te} \times 10^5$	A^o_{Zr}	$S_{Zr} \times 10^5$	Relative Yield
2.25×10^3	6.231	1.25×10^4	5.985	0.782

The separation of fission-product barium from irradiated thorium was not commenced until at least an hour after the end of an irradiation to allow for the growing-in of barium from its 9.5 minute precursor.

The contamination of sources of fission-product barium with the radium daughters of thorium and hence also the latter members of the thorium series was anticipated and steps were taken to minimise this interference. Whilst barium and radium have been separated by ion-exchange it was not found practicable to do this in the time available for the separation of 82.5 minute barium from irradiated thorium. It was more convenient to purify the thorium before irradiation by the procedure given in Chapter 2 (page 17). Barium sources produced after this still contained some contaminating activity due to the re-appearance of the thorium daughters over the period of irradiation but this was at a lower level and could be conveniently subtracted from the observed decay curves to obtain the decay of 82.5 minute barium. Since the thorium daughter activities contained several α contributions which would overload the amplifier of the counting system, the barium sources were covered with 12 mg./cm^2 aluminium foil which was sufficiently thick to stop the most energetic of the α-particles encountered and allowance made for the attenuation of the 2.27 MeV β-particles in the correction for the efficiency of the counter for 82.5 minute ^{139}Ba. (see below).

Barium and strontium were usually separated together from irradiated thorium. The initial steps are described in the section on strontium (page 49). Barium was separated from strontium by precipitation of barium chromate from an acid buffered solution. The subsequent purification of barium consisted of precipitations of barium chloride, as recommended by Sunderman[38], and sources of barium chloride were prepared for counting.

Estimation of the efficiency of the end-window counter for 82.5 minute ^{139}Ba

The efficiency of the end-window counter for counting un-covered sources of barium chloride was estimated from the measured efficiencies for sources of other nuclides, taking account of the β -energies involved and the electron density of the sources. The reduction in counting rate due to covering the sources with 12 mg./cm.^{2} of aluminium was estimated to be 7%, considering the energy of the β -particles from the barium. The correction factor for this effect was included in the overall counter efficiency for this nuclide when calcu-lating barium activities induced in thorium.

Results of Relative Yield Measurements

The results of the measurements of the relative yields of 82.5 minute ^{139}Ba and ^{97}Zr are given in Table 19. Decay curves for ^{139}Ba were obtained after subtracting the contribu-

TABLE 19

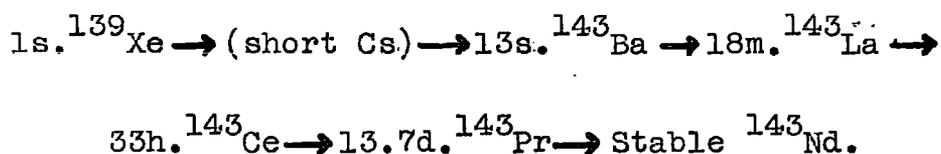Results of Relative Yield Measurements of 82.5 minute ^{139}Ba

Run No.	Source wt., mg.	Yield %	η	Parent Factor	A^o obs.	A^o corr.	S_{Ba} x 10^5	A^o_{Zr}	S_{Zr} x 10^5	Relative Yield
9	12.78	68.9	0.332	0.882	1.46×10^4	5.64×10^4	1.689	4.87×10^3	2.778	1.54
22	1.45	7.8	0.341	0.882	7.72×10^2	2.57×10^4	4.041	1.74×10^3	5.831	1.72
28	11.29	60.9	0.333	0.882	2.50×10^3	1.09×10^4	2.270	7.41×10^2	3.162	1.65

Relative yield of 82.5 minute ^{139}Ba = 1.64 ± 0.09.

tion of the thorium daughters β-emitters from the observed counting rates. The "parent factor" takes account of the decay of ^{139}Cs. and ^{139}Ba during the irradiations owing to the comparative half-lives of the two species, as described in Part b of this Chapter (page 38).

(12) Cerium

The relative fission yield for mass number 143 was determined by the radiochemical separation and measurement of 33 hour ^{143}Ce. The decay chain for this mass number is:-

1s. ^{139}Xe $\rightarrow$ (short Cs.) $\rightarrow$ 13s. ^{143}Ba $\rightarrow$ 18m. ^{143}La $\rightarrow$

33h. ^{143}Ce $\rightarrow$ 13.7d. ^{143}Pr $\rightarrow$ Stable ^{143}Nd.

The separation of fission-product cerium from irradiated thorium was not commenced until ninety minutes after the end of an irradiation to allow for the decay of eighteen minute lanthanum. 13.7 day ^{143}Pr was also observed in the sources produced.

The radiochemical separation of cerium was based upon the method of Glendenin et al.[47] in which cerium (IV) is extracted into hexone. Samples of irradiated thorium were dissolved in nitric acid containing carriers for cerium, zirconium, and other elements to be separated. After a redox procedure and

digestion to ensure complete exchange between fission-product species and added carriers, cerium was reduced to its trivalent state and the bulk of the thorium removed from the solution by precipitation of thorium iodate. Cerium hydroxide was precipitated on making the solution alkaline. The precipitate was dissolved in nitric-acid-sodium bromate solution and Ce (IV) extracted into hexone. The cerium was back-extracted into water containing a few drops of hydrogen peroxide and cerium oxalate sources prepared for counting. Sources produced by the foregoing procedure were shown to be free of contamination from thorium and its daughters when cerium carrier was separated from a sample of thorium which had not been irradiated. Sources of fission-product cerium contained 33 hour ^{143}Ce with 13.7 day ^{143}growing.in. The decay of these sources was resolved to obtain the decay of 33 hour cerium.

Calibration of the end-window counter for 33 hour ^{143}Ce

Cerium activity was separated from a sample of pile-irradiated uranium by the method of Glendenin et al. reduced for working with 1 mg. added carrier and omitting the final precipitation of cerium oxalate. The absolute activity of ^{143}Ce in the solution obtained was determined by 4π counting of aliquot parts. A weighed quantity of the solution was added to a solution of cerium carrier and a set of sources prepared for the end-window counter. The decay of the sources was resolved to

obtain the ^{143}Ce activities in them. A calibration curve was
drawn for the efficiency of the end-window counter for detecting
^{143}Ce in sources of different weights of cerium oxalate, and
is given in Fig. 22.

Results of Relative Yield Measurements

The results of the measurements of the yield of ^{143}Ce
relative to ^{97}Zr are given in Table 20. A^{o}_{corr} was obtained
from $A^{o}_{obs.}$ by application of corrections for counter efficiency
and chemical yield. The relative yield was calculated by
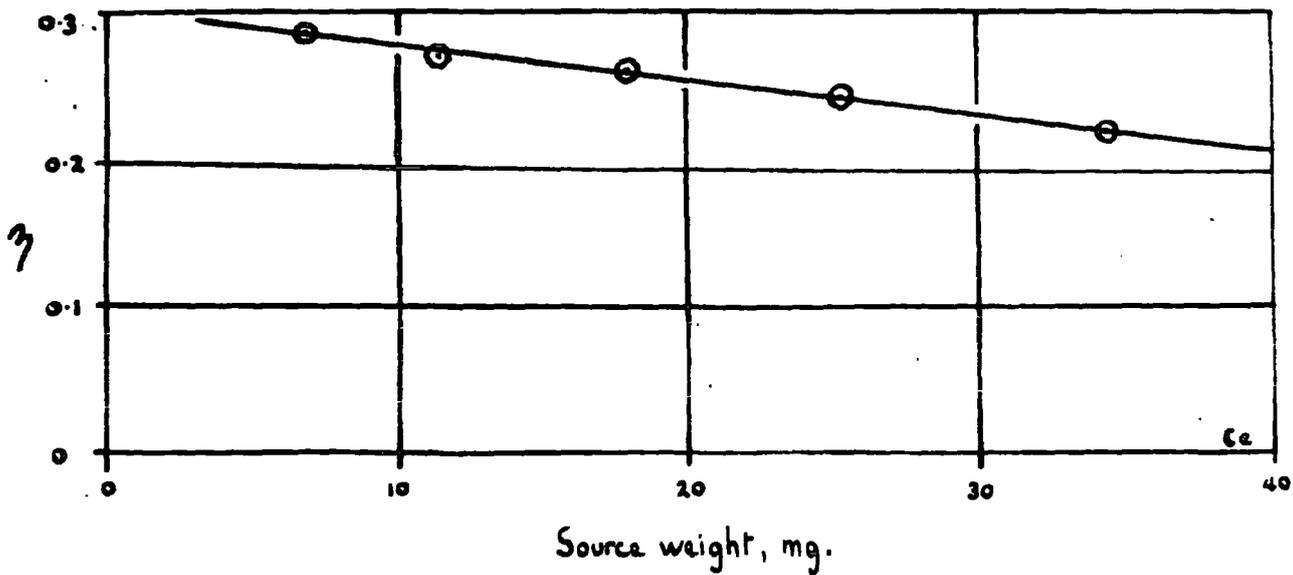application of the relative yield equation (page 38).

Fig. 22

Efficiency of the end-window counter for counting 33 hour ^{143}Ce in sources of different weights of cerium oxalate.

TABLE 20

Results for 33 hour ^{143}Ce

Run No.	Source wt., mg.	Chemical Yield %	η	$A^o_{obs.}$	$A^o_{corr.}$	$S_{Ce} \times 10^5$	A^o_{Zr}	$S_{Zr} \times 10^5$	Relative Yield
5	15.01	55.3	0.267	2.07×10^3	1.40×10^4	8.687	1.66×10^4	8.353	1.58
6	13.38	49.3	0.271	8.09×10^2	6.00×10^3	2.303	7.90×10^3	2.232	1.43
19	13.59	49.9	0.271	1.06×10^3	7.82×10^3	5.114	9.39×10^3	4.997	1.58
20	3.93	14.4	0.294	3.39×10^2	8.00×10^3	4.200	1.12×10^4	4.125	1.36
26	3.55	13.1	0.296	2.46×10^2	6.32×10^3	6.866	9.01×10^3	6.737	1.34
30	8.50	31.4	0.284	2.87×10^2	3.22×10^3	3.807	3.87×10^3	3.735	1.58

Relative yield of 33 hour ^{143}Ce = 1.48 $\pm$ 0.13

TABLE 21

Correction of measured relative yields to total chain yields by application of the hypothesis of equal charge displacement.

A	Nuclides Measured	Z_A	A^x	Z_A^x	$Z_A + Z_A^x$	Z_p	Z	$Z - Z_p$	I.Y. of successors	% measured
83	2.4h.Br	36.2	145.4	60.8	97.0	32.7	35.0	2.3	$<10^{-4}$	100.0
84	6.0m.Br	36.6	144.4	60.4	97.0	33.1	35.0	1.9	1.1×10^{-9}	99.99
	31.8m.Br									
91	9.7h.Sr	40.2	137.4	57.2*	97.4	36.5	38.0	1.5	1×10^{-3} $<10^{-4}$	99.90
93	10.3h.Y	91.0	135.4	55.8	96.8	37.6	39.0	1.4	1.5×10^{-3} $<10^{-4}$	99.85
97	17.0h.Zr	42.6	131.4	54.0	96.6	39.3	40.0	0.7	3.3×10^{-2} 3.7×10^{-4}	96.66
99	66h.Mo	43.4	129.4	53.7	97.1	39.8	42.0	2.2	$<10^{-4}$	100.0
105	4.45h.Ru	45.8	123.4	51.6	97.4	42.1	44.0	1.9	1.1×10^{-4} $<10^{-4}$	99.99
111	7.6d.Ag	48.1	117.4	50.0*	98.1	44.0	47.0	3.0	$<10^{-4}$	100.0
112	21h.Pd	48.6	116.4	49.7*	98.3	44.4	46.0	1.6	6.0×10^{-4} $<10^{-4}$	99.94
113	5.3h.Ag	49.0	115.4	49.9	98.9	44.5	47.0	1.5	1.0×10^{-3} $<10^{-4}$	99.90
129	4.6h.Sb	53.5	99.4	43.5	97.0	50.0	51.0	1.0	1.0×10^{-2} $<10^{-4}$	99.00
132	77h.Te	54.6	96.4	42.5	97.1	51.0	52.0	1.0	1.0×10^{-2} $<10^{-4}$	99.00
139	83m.Ba	57.8*	89.4	39.1*	96.9	54.3	56.0	1.7	3.7×10^{-4}	99.96
143	33h.Ce	59.9	85.4	37.1	97.0	56.4	58.0	1.6	6.0×10^{-4} $<10^{-4}$	99.94

* Average of two values, where mass numbers lie in two shell groups.

CHAPTER IV

COLLECTED RESULTS AND DISCUSSION

(a) Correction of measured yields to total chain yields

To obtain total chain yields from the measured yields
of nuclides which are one or two β-decays from the end of
the chain, it is necessary to apply a correction for the
charge distribution at the instant of fission. The hypo-
theses which have been put forward to explain the charge
distributions in the fission of many of the heavy elements
have been briefly described in Chapter I (page 5).

Alexander and Coryell[48] have measured the indepen-
dent fission yields of five products in the fission of
thorium by fast neutrons (produced in the beryllium target
of a cyclotron and containing a spread of energies up to
19 MeV). Reasonable agreement was found with the equal
charge displacement hypothesis and poor agreement with the
postulate of unchanged charge distribution. The equal charge
displacement hypothesis has been applied to correct the
measured yields in the current investigation of the fission
of thorium with 14 MeV neutrons.

As stated in Chapter I, the equal charge displacement
hypothesis may be written as

$$Z_A - Z_P = Z_A^* - Z_P^*$$

where Z_A and Z_A^* are the most stable charges of complementary fission product chains and Z_p and Z_p^* are the most probable charges for the primary fission products A and A^*. The sum of the primary charges Z_p and Z_p^* must equal the charge of the fissioning nucleus, Z_f:

$$Z_p + Z_p^* = Z_f$$

The complementary fission product masses are related by

$$A + A^* = A_f - \bar{\nu}$$

where A_f is the mass number of the fissioning nucleus and $\bar{\nu}$ the average number of neutrons emitted per fission.

The equation for the most probable charge of a fission product of mass number A is given by

$$Z_p = Z_A - \tfrac{1}{2}(Z_A + Z_A^* - Z_f).$$

Values of Z_p have been calculated for the mass chains investigated in the current work, and are given in Table 21. Values for Z_A have been taken from the data of Pappas[45]. For mass numbers in the vicinity of shell closure there is an uncertainty in the Z_A value. Where this occurs, the average of the Z_A values from the two groups has been taken, as suggested by Steinberg and Glendenin[51]. In calculating A^*, a value of 4.6 was taken for $\bar{\nu}$, as determined by Smith,

Nobles, and Cox[52]. The average number of neutrons emitted from a given fission fragment has been shown to be dependent on the mass of the fragment[53]. However, this variation occurs in such a way that the total number of neutrons from complementary fragments remains approximately constant.

After calculation of Z_p, $Z - Z_p$ was obtained for the nuclides measured and the independent yields of the remaining nuclides in the mass chains concerned obtained from the charge distribution curve of Nethaway and Wahl[49]. This curve is similar to Glendenin's[12], but gives somewhat better agreement with more recent data[50].

The fraction of the total chains represented by the nuclides isolated was found, and is given in Table 21. The correction of measured yields to total chain yields is given in Table 22. The "measured yields" are those determined in the experimental work described in Chapter III. The measured yield for mass number 84 includes both measurements of 6.0 minute ^{84}Br and 31.8 minute ^{84}Br. The results of the tellurium-iodine milking experiment have been included in the tellurium measurement.

TABLE 22

Correction of measured yields to total chain yields

Mass Number	Measured Yield	% of chain	Total Chain Yield
83	0.395 ± 0.087	100.0	0.395 ± 0.087
84	0.507 ± 0.034	99.99	0.507 ± 0.034
91	1.77 ± 0.09	99.90	1.77 ± 0.09
93	1.58 ± 0.11	99.85	1.58 ± 0.11
97	1.00	96.66	1.07
99	0.503 ± 0.024	100.0	0.503 ± 0.024
105	0.331 ± 0.026	99.99	0.331 ± 0.026
111	0.41 ± 0.06	100.0	0.41 ± 0.06
112	0.352 ± 0.028	99.94	0.352 ± 0.028
113	0.343 ± 0.018	99.90	0.343 ± 0.018
129	0.323 ± 0.025	99.00	0.326 ± 0.025
132	0.825 ± 0.054	99.00	0.832 ± 0.055
139	1.64 ± 0.09	99.96	1.64 ± 0.09
143	1.48 ± 0.13	99.94	1.48 ± 0.13

(b) The mass-yield curve for fission of thorium with
14 MeV neutrons

By imposing the condition that the sum of the yields

of all the fission products must be 200% it is possible

to normalise the measured relative yields to absolute

yields.

A curve has been drawn through the corrected yields

of the masses given in Table 22 and the yields of their

complementary masses, for a value of $\bar{\nu} = 4.6$[52], and nor-

malised by imposing the above condition. The normalised

yield curve is given in Fig. 23 and the absolute yields of

individual mass chains is given in Table 23.

Fission of thorium by 14 MeV neutrons can be seen to

be essentially asymmetric, as shown by the two maxima of the

mass-yield curve. The yields of masses in the region of the

trough show a trend to a subsidiary maximum, but since the

rise in yield involved is comparable with the deviation of

the experimental measurements a horizontal line has been

drawn through this region. Similar uncertainties exist in

the measurement of yields in the trough region for the

fission of thorium with pile neutrons and with 6 - 11 MeV

neutrons, as shown in Figs. 2 and 3 in Chapter I. The

high yield for mass number 111 has also been seen to occur
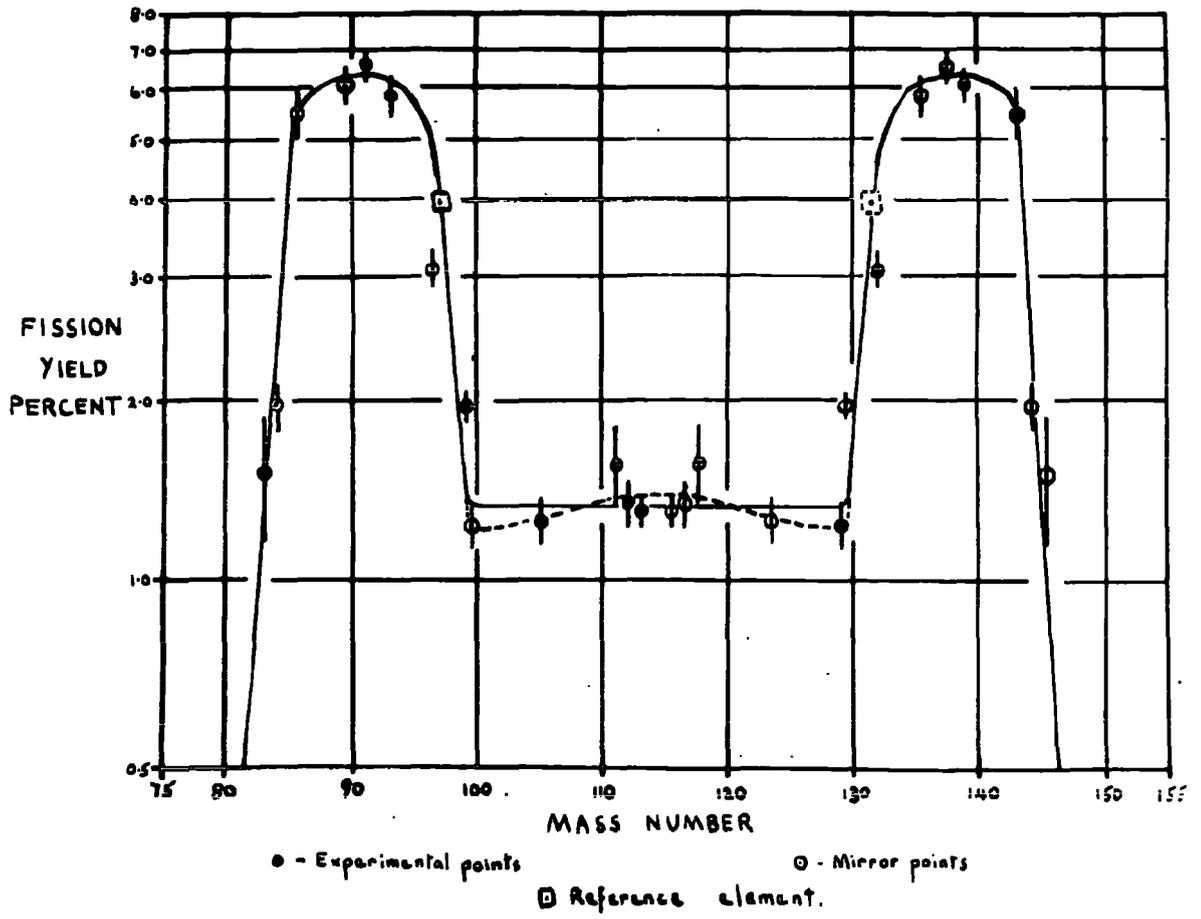
Fig. 23

The mass-yield curve for fission of thorium
with 14 MeV neutrons.

Table 23

Absolute mass yields for the fission of
thorium with 14 MeV neutrons

Mass Number	Absolute Yield
83	1.44 ± 0.32
84	1.85 ± 0.12
91	6.48 ± 0.33
93	5.80 ± 0.40
97	3.92
99	1.84 ± 0.09
105	1.24 ± 0.10
111	1.5 ± 0.2
112	1.29 ± 0.10
113	1.26 ± 0.07
129	1.19 ± 0.09
132	3.05 ± 0.20
139	6.00 ± 0.33
143	5.41 ± 0.48

in both high and low energy proton fission of ^{232}Th, ^{238}U, and ^{239}Pu[54].

The peak maxima will be seen to occur at masses of 91 and 137.4, with a peak width at half-height of 12.5 mass units. The peak-to-trough ratio is 4.85.

The mass-yield curve for fission of thorium with 14 MeV neutrons is compared with similar curves for fission of thorium with neutrons of other (less well defined) energies, and for photofission of thorium in Table 24. Whilst a different compound nucleus is produced in photofission, the distribution of the mass yields is comparable with neutron induced fission since approximately one less prompt neutron is emitted in photofission[22]. The increased occurrence of symmetric fission (decreasing peak/trough ratio) with increasing nuclear excitation is clearly demon-strated. The slight differences in the positions of the peak maxima may be attributed to the increasing number of prompt neutrons emitted with rising nuclear excitation.

In other studies of asymmetric fission it has been generally found that the individual peaks become broader as the energy of the fissioning nucleus is increased.[55] The mass-yield distribution in the 14 MeV neutron-induced fission of thorium does not appear to conform with this

Table 24

Mass-yield distributions in fission of thorium

method of fission	peak/trough	maxima		peak width m.u.	ref.
		light	heavy		
14 MeV neutrons	4.8_5	91	137.4	12.5	This work
6-11 MeV neutrons	11	91*	141*	17*	19
pile neutrons (average 2.7 MeV)	110	91	140	14*	18
69 MeV γ	10	91	138	12	22

*data taken from the mass-yield curves produced in the references quoted; these figures are not presented by the original authors.

this generalization. Whilst this difference may be due to the experimental limitations on defining this part of the mass-yield curve (see below), the similarity of the mass-yield curve with that produced in photofission is noteworthy.

Alexander and Caygill have produced a mass-yield curve for the fission of thorium with 0 - 19 MeV neutrons[48]. This investigation was primarily of the nuclear charge distribution, and a limited number of mass chains were investigated, not giving complete coverage of the mass distribution.

The mass-yield curves for the fission of several of the heavy elements by 14 MeV monoenergetic neutrons is given in Fig. 24. The broad trough for fission of thorium is conspicuous. The presence of this broad trough in the fission of thorium has been noted since the first investigation of the fission of thorium with pile neutrons[18]. The shift in the position of the light peak with the mass number of the bombarded nucleus is clearly demonstrated. The effect of a nuclear shell at mass number 132 on maintaining the position of the heavy peak was mentioned in Chapter I. The fine structure detected in the fission of ^{238}U (and also in the mass-spectrometric determination of yields in the "fast" neutron fission of ^{232}Th) was not detected in the present work.
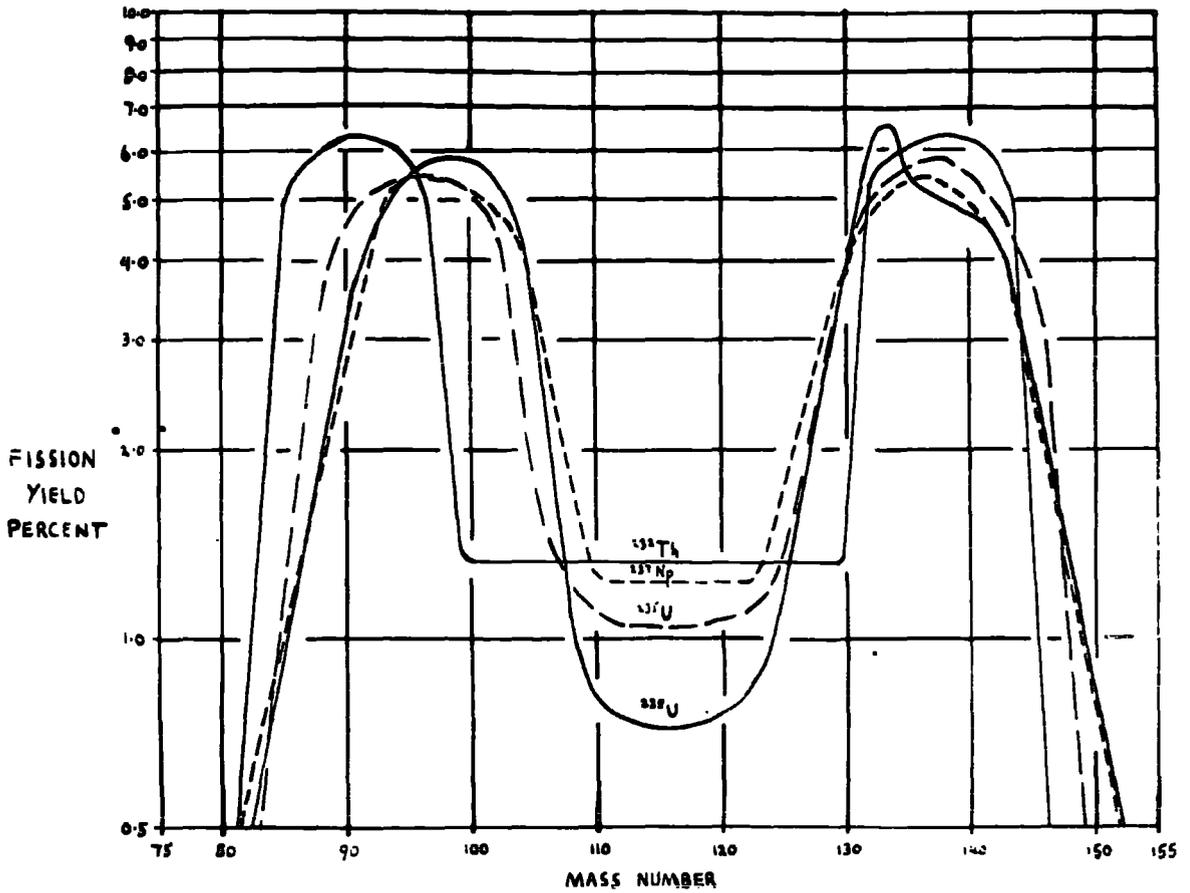
<u>Fig. 24</u>

Mass distributions for fission of heavy elements
induced by 14 MeV neutrons.

^{232}Th – this work.

^{237}Np – R.F. Coleman et al.[56]

^{235}U – S. Katcoff[11]

^{238}U – D.J. Silvester[30]

The distribution of measured yields about the curves
given in Fig. 24 can only be seen by consulting the original
references. In these, and other mass-yield distributions
which have been investigated, yield measurements of masses
in the heavy region of the trough are particularly scarce.

The number of mass chains for which the yield can be
determined radiochemically is limited by the activities
produced in the fission-product isotopes separated. This
limitation is most severe in the regions of the trough and
outer wings of the mass-yield curve. In regions of nuclear
isomerism (particularly the heavy region of the trough) the
existence of complex branched decay schemes makes it diffi-
cult to obtain the absolute activity of a specific nuclide
separated, and to correct this to a total mass yield. In
some cases the branching ratios in some of these chains
have yet to be determined. When the necessary nuclear data
becomes available yields for additional fission-product
chains may be determined and the mass-yield distribution
investigated more thoroughly.

It has been suggested[55] that some simplification might
be introduced in the analysis of mass distributions if they
were regarded as the superimposition of symmetric and
asymmetric parts. The analysis of measured mass distribu-
tions into these separate parts may become possible on

paying particular attention to measurement of yields in the trough region.

APPENDIX

DETAILS OF RADIOCHEMICAL SEPARATIONS
OF FISSION PRODUCTS

1. ZIRCONIUM.

Preparation and Standardisation of Carrier

A carrier solution of zirconium nitrate containing 10 mg. of zirconium/ml. in 1N nitric acid was prepared, and standardised by precipitation of zirconium tetramandelate by the method described by Belcher et al.[57]

Radiochemical Procedure

Step 1. The solution, containing thorium and 10 mg. of zirconium carrier and carriers for other elements to be separated, was adjusted to 3N in H Cl and 10 ml. of 1M mandelic acid solution added. The solution was heated for 20 minutes to 80 - 90°C. in a water bath, to precipitate zirconium tetramandelate. The precipitate was centrifuged down, and the supernate put to one side for the separation of other elements as required.

Step 2. The precipitate from Step 1 was transferred to a 10 ml. polythene centrifuge tube with washings of water, and dissolved with 60% HF. 0.5 ml. of lanthanum nitrate solution (containing 10 mg. of La/ml.) was added, and the solution stirred thoroughly with a polythene rod. The precipitate of lanthanum fluoride was centrifuged down. A second 0.5 ml. of lanthanum nitrate was added, and the

precipitate formed centrifuged down on top of the first. The supernate was decanted into a clean tube, and the pre-cipitate discarded.

Step 3.   1 ml. of barium nitrate solution (containing 10 mg. barium/ml.) was added, to precipitate barium zirconyl fluoride, and the solution stirred thoroughly. The pre-cipitate was centrifuged down and the supernate discarded.

Step 4.   The precipitate was suspended in 2 ml. of water, and dissolved by addition of 1 ml. of saturated boric acid and 0.5 ml. of conc. nitric acid. 1 ml. of barium nitrate solution was added and 1 ml. of 60% HF, to reprecipitate the zirconium. After stirring, the precipitate was centrifuged down and the supernate discarded.

Step 5.   Step 4 was repeated.

Step 6.   The precipitate was suspended in 2 ml. of water and 0.5 ml. of boric acid, and dissolved by the addition of 2 ml. of 6N HCl. The solution was made alkaline by addition of 6N NaOH, to precipitate zirconium hydroxide. After centrifugation the supernate was discarded. The precipitate was washed with 5 ml. of water and the washings discarded.

Step 7.   The precipitate was dissolved by addition of 3 ml. of conc. HCl and 3 ml. of water and transferred to a glass centrifuge tube with further rinses of water to make the total volume up to 10 ml. 10 ml. of 1M mandelic acid was added and the solution heated to 80 - 90°C. for 20 minutes

in a water bath, to precipitate zirconium tetramandelate.

Step 8.   The precipitate was transferred to a glass-fibre filter disc and washed with 10 ml. of 5% mandelic acid - 2% HCl mixture, then with three 5 ml. portions of ethanol, and finally with two 5 ml. portions of ether. The source prepared was dried for chemical yield determination and counting.

2. BROMINE

Preparation and Standardization of Carriers

(i)   A carrier solution containing 1.0 mg. bromine per ml. as bromate was prepared by dissolving potassium bromate in water. The bromate content of the solution was determined by addition of potassium iodide and sulphuric acid to aliquot parts, and titration of the iodine liberated with sodium thiosulphate solution.

(ii.)   A carrier solution containing 10 mg. bromine per ml. as potassium bromide solution was prepared and the bromine content determined by precipitation of silver bromide from aliquot parts.

Radiochemical Procedure

Step 1.   The irradiated thorium was dissolved in 5 ml. of dilute nitric acid containing 1 ml. each of carrier solutions for bromate, zirconium, and any other elements to be separated. 1 ml. of bromide carrier was added, and 12 drops

of saturated ceric sulphate solution, to complete the oxidation of bromide to bromine.

Step 2. The solution was transferred to a separatory funnel and the bromine extracted into 3 x 15 ml. of carbon tetrachloride. The aqueous phase was retained for the separation of other elements. The organic extracts were added together and washed with 30 ml. of water and the washings discarded. A few drops of a solution of iodine in carbon tetrachloride was added to the organic phase as a hold-back for fission-product iodine in the next extraction step.

Step 3. Bromine was back-extracted into 15 ml. of water containing a few drops of 6N hydroxylamine solution and the organic layer discarded. 2 ml. of 5M nitric acid was added to the aqueous layer and sufficient 1M potassium permanganate solution to colour the solution permanently. The bromine liberated was extracted into 2 x 10 ml. of carbon tetra-chloride and the aqueous layer discarded.

Step 4. The carbon tetrachloride was shaken with 10 ml. of water containing a few drops of 1M sodium bisulphite until both phases were colourless. The organic phase was discarded.

Step 5. The aqueous phase from Step 4 was transferred to a beaker, 1 ml. 5M nitric acid added, and the solution warmed to expel SO_2. 2 ml. of 0.1M silver nitrate was added to the

solution, to precipitate silver bromide. In order to obtain a uniform source for counting, the precipitate was transferred to a tared filter disc before it was completely coagulated. The source was washed with water, alcohol, and ether, and dried for weighing and counting.

3. STRONTIUM

Preparation and Standardisation of Carrier

A solution of strontium nitrate was prepared, containing 10 mg. strontium/ml. in 1N nitric acid. This was standardised by precipitation of strontium oxalate from aliquot parts in a similar way to which the fission-product sources were prepared.

Radiochemical Procedure

Step 1.   The irradiated basic thorium carbonate was dissolved in conc. nitric acid containing 10 mg. quantities of carriers for barium, strontium, zirconium, and any other elements to be separated. After steps to ensure complete exchange between fission products and added carriers the solution was cooled in running water and 20 ml. of fuming nitric acid added, to precipitate barium and strontium nitrates. The precipitate was centrifuged down and the supernate put to one side for the separation of other elements at a convenient time.

Step 2.   The precipitate was dissolved in 2 ml. of water and 15 ml. of nitric acid added to reprecipitate the strontium and barium. After cooling in an ice bath the mixture was

centrifuged and the supernate discarded.

Step 3. The precipitate from Step 2 was dissolved with 5 ml. of water and 1 ml. of iron carrier solution (containing 5 mg. iron/ml.) was added. A scavenging precipitation of ferric hydroxide was made by addition of 2 ml. of 6N ammonia. After centrifugation the precipitate was discarded.

Step 4. The supernate from step 3 was neutralised with 6N nitric acid and 1 ml. of 6N acetic acid and 2 ml. of 6N ammonium acetate added. The solution was heated to nearly boiling and 1.5 ml. of sodium chromate added, to precipitate barium chromate. After standing for one minute, the precipitate was centrifuged down, and reserved for the separation of barium, as described on page .

Step 5. 2 ml. of conc. ammonia were added to the clear supernate from step 4 and the solution heated to nearly boiling. 5 ml. of saturated ammonium oxalate solution were added slowly, with stirring, to precipitate strontium oxalate. The precipitate was centrifuged down and the supernate discarded. The precipitate was transferred to a tared filter disc with washings of hot dilute ammonia and washed with ethanol and ether in preparation for weighing and counting.

4.   YTTRIUM

    Preparation and Standardisation of Carrier.

    A solution of yttrium nitrate was prepared, containing

10 mg. yttrium/ml. This was standardised by precipitation

of yttrium oxalate from aliquot parts by the method described

by Ballou[58]

    Radiochemical Procedure

Step 1.   After removal of zirconium and thorium from the

solution cerium and yttrium hydroxides were precipitated by

making the solution alkaline with conc. ammonia. The pre-

cipitate was centrifuged down and the supernate discarded.

The precipitate was dissolved in 9N nitric acid containing

sodium bromate and the cerium extracted into hexone. Yttrium

was reprecipitated from the aqueous phase by making it alkaline

with ammonia again. The precipitate was centrifuged down and

the supernate discarded.

Step 2.   The precipitate of yttrium hydroxide from Step 1

was dissolved in 1 ml. of conc. nitric acid and the solution

made up to 10 ml. and transferred to a polythene centrifuge

tube. 1 ml. of zirconium holdback carrier was added and the

solution made 4N in HF to precipitate yttrium fluoride. The

precipitate was centrifuged down and the supernate discarded.

The precipitate was washed with 10 ml. of 5N HF and the

washings discarded.

Step 3.   The precipitate was dissolved in 2 ml. of saturated boric acid solution and 2 ml. of conc. nitric acid, and diluted to 10 ml.   Zirconium holdback carrier was added and yttrium fluoride reprecipitated.   The precipitate was centrifuged down and washed, as in Step 2.

Step 4.   The precipitate was dissolved in boric acid and conc. nitric acid and the solution made up to 10 ml.   Yttrium hydroxide was precipitated by addition of conc. ammonia.   The precipitate was centrifuged down and the supernate discarded.

Step 5.   The yttrium hydroxide was dissolved in 50 ml. of conc. nitric acid and the solution transferred to a separatory funnel.   10 ml. of T,B.P. reagent (60% T.B.P. in petroleum spirit) was added, and the solution shaken for five minutes, to extract the yttrium into the organic layer.   The aqueous layer was discarded and the T.B.P. phase washed twice by shaking for two minute intervals with 50 ml. of conc. nitric acid.   The yttrium was removed from the T.B.P. by shaking for one minute each with three 10 ml. portions of water.   The aqueous extracts were combined in a centrifuge tube, and yttrium hydroxide precipitated by addition of conc. ammonia. The precipitate was centrifuged down and the supernate discarded.

Step 6.   Step 5 was repeated.

Step 7.   The precipitate of yttrium hydroxide was dissolved in 2 ml. of 5N HCl and diluted to 10 ml. with water.   The

solution was transferred to a clean centrifuge tube and yttrium hydroxide reprecipitated by addition of conc. ammonia. The precipitate was centrifuged down and the supernate discarded. The precipitate was redissolved in 2 ml. of 5N HCl and diluted to 10 ml. with water. The solution was heated in a water bath and 15 ml. of saturated ammonium oxalate added. The heating was continued for ten minutes and then the solution was cooled for five minutes in an ice bath. The precipitate was transferred to a weighed filter disc and washed with water, alcohol, and ether and dried for weighing and counting.

5. MOLYBDENUM

Preparation and Standardisation of Carrier

A molybdenum carrier solution containing 10 mg. molybdenum/ml. was prepared by dissolving ammonium molybdate in water, with addition of HCl and sodium bromate. This was standardised by precipitation of molybdenum oxinate from aliquot parts, by the method described in Vogel.[59]

Radiochemical Procedure

Step 1. The sample of irradiated thorium was dissolved in 5 ml. dilute nitric acid containing 10 mg. quantities of carriers for the elements to be separated, including molybdenum. After steps to ensure complete isotopic exchange between fission products and added carriers, the other elements were

separated and the solution diluted to 20 ml. 10 ml. α-benzoin oxime reagent were added to precipitate molybdenum, and the solution stood for five minutes to allow the precipitate to coagulate. The precipitate was centrifuged down and the supernate was discarded. The precipitate was washed with 10 ml. 1M nitric acid and the washings discarded.

Step 2. The precipitate from Step 1 was transferred to a beaker with washings of fuming nitric acid and 1 ml. 70% perchloric acid added. The solution was heated, with further addition of nitric acid, to destroy the organic reagent.

Step 3. The solution was cooled and diluted to 20 ml. with water. It was then made alkaline by addition of conc. ammonia and 1 ml. iron carrier solution added, for a scavenging pre-cipitation.[*] The precipitate of ferric hydroxide was centri-fuged down and discarded. The supernate was made acid again by addition of nitric acid and molybdenum reprecipitated with -benzoin oxime. The precipitate was centrifuged down and washed with 1M nitric acid.

Step 4. The precipitate was dissolved in nitric acid - perchloric acid again and the solution heated to destroy the

[*]   Addition of iron before making the solution alkaline
     was found to reduce the yield of molybdenum, as the
     bulk of it was found to be carried down with the ferric
     hydroxide in these circumstances.

organic reagent. The solution was cooled and diluted to 30 ml. with water. 1 ml. of saturated ammonium oxalate was added to complex any technetium in the solution and molybdenum α-benzoin oxime reprecipitated on addition of 10 ml. reagent. The precipitate was centrifuged down and washed as in Step 3.

Step 5. The precipitate was digested with nitric acid - perchloric acid again and the solution diluted to 30 ml. with water. The solution was made alkaline by addition of ammonia and then just acid to methyl red by addition of a few drops of 5N sulphuric acid. 5 ml. of 2N ammonium acetate was added as a buffer and the solution heated to 90°C. Molybdenum was precipitated by addition of a 3% solution of oxine in dilute acetic acid and the solution heated until the precipitate coagulated. The precipitate was centrifuged down and the supernate discarded. The precipitate was washed with 20 ml. of hot water and transferred to a weighed filter disc. It was then washed with alcohol and ether and dried for weighing and counting.

6. RUTHENIUM

Preparation and Standardisation of Carrier

A solution of ruthenium trichloride was prepared, con-taining 10 mg. ruthenium/ml. in 1N HCl. For standardisation, aliquot parts of the solution were made alkaline with sodium hydroxide, and ruthenium dioxide precipitated on digestion

with ethanol, as in the fission-product investigation.

Radiochemical Procedure

Step 1.   Irradiated thorium nitrate was dissolved in conc.
HCl containing 10 mg. ruthenium carrier. 6 - 8 drops saturated
ceric sulphate solution was added, and the solution warmed, to
ensure complete exchange between fission-product ruthenium and
added carrier. The solution was diluted to 10 ml. with water,
and ruthenium sulphide precipitated on passing H_2S through
the solution. The precipitate was centrifuged down and the
supernate put to one side for the separation of other elements.

Step 2.   The precipitate of ruthenium sulphide was dissolved
with 0.5 ml. nitric acid and transferred with washings of
nitric acid to the distillation vessel. 5 ml. of freshly
prepared 12N sodium hydroxide was placed in the receiving
vessel, and this surrounded with ice-cold water. 10 ml. of
perchloric acid was added to the solution of ruthenium and
the flow of air through the apparatus adjusted to 2 - 3
bubbles per second. The still was heated gently until all the
ruthenium was distilled over into the alkali. (The solution
in the still lost its deep red colour, and the alkali became
orange-brown).

Step 3.   The alkaline catch solution was transferred to a
beaker, and diluted to 25 ml. 5 ml. of ethanol was added and
the solution heated to boiling to precipitate ruthenium dioxide.

The precipitate was centrifuged down and the supernate discarded.
The precipitate was transferred to a tared filter disc with
washings of water, washed with alcohol and ether, and dried
for weighing and counting.

7. PALLADIUM-SILVER-MILKING

Preparation and Standardisation of Carriers

(i) A carrier solution of palladous chloride in 1N HCl was
prepared, containing 10 mg. palladium/ml, and standardised by
precipitation of palladium dimethyl glyoxime as described by
Vogel[59)

(ii) The silver carrier used in the milking experiments was
the same as that used in the direct separation of fission-
product silver, being 10 mg./ml. silver as silver nitrate.
(See page 99).

Radiochemical Procedure

(i) Separation of Palladium

Step 1. Irradiated thorium nitrate was dissolved in HCl con-
taining 10 mg. quantities of palladium, zirconium, and any
other elements to be determined. After digestion and a redox
procedure to ensure complete isotopic exchange of fission-
products and added carriers the solution was diluted to 2N
in HCl and 2.5 ml. of 1% alcoholic solution of dimethylglyoxime
added to precipitate palladium. After standing for five

minutes the precipitate was centrifuged down and the supernate reserved for the separation of other elements.

Step 2. The precipitate of palladium dimethylglyoxime was transferred to a beaker with washings of conc. nitric acid and the solution heated to destroy the organic reagent. The solution was cooled and diluted to 10 ml. with water. 5 mg. of iron carrier was added and the solution made alkaline with ammonia. 10 mg. silver carrier was added and sufficient potassium iodide solution to precipitate all the silver. The precipitates were centrifuged down and discarded.

Step 3. The scavenging precipitations were repeated by addition of 5 mg. more iron carrier and 10 mg. of silver carrier, digesting, and centrifuging.

Step 4. The supernate was acidified with HCl and any silver chloride precipitate removed by centrifugation. 2.5 ml. of dimethylglyoxime reagent was added and the solution stood for five minutes as palladium dimethylglyoxime was precipitated. The precipitate was transferred to a tared filter disc and washed with water, alcohol, and ether. The source was dried in a desiccator and weighed.

(ii) Milking of silver from palladium

Step 1. The precipitate of palladium dimethylglyoxime was transferred to a beaker with washings of conc. nitric acid and the solution heated to destroy the organic reagent. 10 mg. of

silver carrier was added and the total volume adjusted to 10 ml. with water.

Step 2.   When sufficient time had elapsed for ^{112}Ag to grow in from the ^{112}Pd, silver chloride was precipitated at a noted time on addition of 1N HCl. The precipitate was centrifuged down and purified for counting (Steps 3 and 4) and palladium was recovered from the supernate for subsequent milking operations (Step 5).

Step 3.   The precipitate of silver chloride from Step 2 was dissolved in 3 - 4 drops conc. ammonia and the solution diluted to 5 ml. Two scavenging precipitations of ferric hydroxide were carried out on addition of 5 mg. amounts of iron carrier.

Step 4.   Silver chloride was reprecipitated on acidifying the solution with 1N HCl. The precipitate was washed with water, alcohol, and ether, and dried for weighing and counting.

Step 5.   Palladium was precipitated from the supernate from step 2. by addition of 2.5 ml. of dimethylglyoxime reagent. The precipitate was transferred to a filter disc and washed and dried in the usual way. The precipitate was weighed in preparation for the repetition of the silver milking for as long as sufficient activity was available.

8.   SILVER

Preparation and Standardisation of Carrier

A carrier solution of silver nitrate containing 10 mg. of silver/ml. was prepared and standardised by precipitation of silver iodate from aliquot parts.

Radiochemical Procedure

Step 1.   Irradiated thorium nitrate was dissolved in conc. nitric acid containing 10 mg. of silver carrier and carriers for zirconium and other elements to be separated. After digestion to facilitate exchange of fission-product species and added carriers, the solution was diluted with water and silver chloride precipitated on addition of HCl. The precipitate was centrifuged down and the supernate reserved for the separation of other elements at a convenient time.

Step 2.   The precipitate of silver chloride was dissolved in 2 ml. of conc. ammonia, and the solution diluted to 10 ml. A scavenging precipitation of ferric hydroxide was carried out, and the precipitate discarded.

Step 3.   5 ml. of 40% E.D.T.A. in ammonia was added to the solution and the mixture stirred. 1 ml. of 2.5% benzotriazole was added, and the solution stood for five minutes for the precipitation of silver benzotriazole. The precipitate was centrifuged down and the supernate discarded.

Step 4.   The precipitate was dissolved on warming with 1 ml.
of conc. nitric acid and the solution diluted to 10 ml. Silver
chloride was precipitated on addition of 1 ml. of 1M HCl, and
the precipitate centrifuged down.

Step 5.   Steps 2 and 3 were repeated.

Step 6.   The precipitate of silver benzotriazole was dissolved
on warming with 1 ml. of conc. nitric acid. The solution was
made alkaline with 6N NaOH, and three drops excess added to
precipitate silver oxide. The precipitate was centrifuged down
and the supernate discarded. The silver oxide was dissolved in
4 drops of conc. sulphuric acid and the solution heated to dry-
ness.

Step 7.   After cooling, the residue was dissolved in 20 ml. of
water and 1 ml. of 2M HIO_3 added to precipitate silver iodate.
The precipitate was centrifuged down and the supernate discarded.
The silver iodate was dissolved in 4 drops of conc. ammonia,
the solution centrifuged, and transferred to a clean tube.

Step 8.   3 drops of conc. sulphuric acid were added to the
solution which was then diluted to 10 ml. to reprecipitate
silver iodate. The precipitate was transferred to a tared
filter disc, washed with water, alcohol, and ether, and dried
for weighing and counting.

9. ANTIMONY

Preparation and Standardisation of Carrier

A carrier solution containing 10 mg. of antimony/ml. in

6N HCl was prepared and standardised by precipitation of metal-
lic antimony with chromous chloride, as described by Kleinberg.[25]

Radiochemical Procedure

Step 1.   Irradiated thorium carbonate was dissolved in 5 ml.
of conc. HCl, and carriers for zirconium and antimony (III)
added. Chlorine was passed through the solution to oxidise
antimony to the (V) state to facilitate complete isotopic ex-
change. The solution was heated to expel excess chlorine.

Step 2.   The solution was diluted to 25 ml. and saturated with
H_2S to precipitate antimony sulphide. The precipitate was
centrifuged down and the supernate reserved for the recovery
of zirconium. The precipitate was washed with water and the
washings discarded.

Step 3.   The precipitate was dissolved in 5 ml. of conc. HCl
and evaporated down to 1 - 2 ml. to eliminate the presence of
sulphide. The solution was diluted to 10 ml. with conc. HCl
and saturated with chlorine, to ensure that all the antimony
was in the (V) state. Excess chlorine was expelled by heating,
and the solution cooled and transferred to a separatory funnel.

Step 4.   The antimony was extracted into 25 ml. of di-isopropyl
ether, which had previously been equilibrated with conc. HCl,
and the aqueous layer discarded. The antimony was back-extracted
into a saturated solution of hydrazine hydrochloride and potas-
sium thiocyanate, and the organic layer discarded. The aqueous
layer was washed with a further 25 ml. of di-isopropyl ether

and the washings discarded. The aqueous layer was transferred
to a centrifuge tube.

Step 5. A few drops of tellurium carrier were added to the
aqueous solution from Step 4. and tellurium precipitated on
heating. The precipitate was removed by centrifugation.

Step 6. Chromous chloride solution was added to the clear
supernate from Step 5. to precipitate metallic antimony. This
precipitate was transferred to a weighed filter disc, washed
with water, alcohol, and ether, and dried for weighing and
counting.

10 (a) TELLURIUM

Preparation and Standardisation of Carrier

A carrier solution containing 10 mg. of tellurium/ml. in
HCl was prepared and standardised by precipitation of elementary
tellurium from aliquot parts by saturation with SO_2, as described
by Glendenin[60]

Radiochemical Procedure

Step 1. Irradiated thorium nitrate was dissolved in 10 ml. of
nitric acid containing carriers for tellurium, zirconium, and
other elements to be investigated. To facilitate complete
isotopic exchange, tellurium was oxidised by addition of
potassium permanganate solution, and then excess permanganate
removed by addition of hydrogen peroxide. The solution was
evaporated down to half-volume, with addition of HBr, and

diluted once more to 10 ml. Tellurium was precipitated on passing SO_2 through the solution. The precipitate was centrifuged down and the supernate reserved for the separation of other elements.

Step 2.   The tellurium was dissolved in 5N nitric acid and 10 ml. of conc. HCl added. The solution was evaporated to near-dryness to get rid of nitric acid. A further 10 ml. of conc. HCl was added and the evaporation repeated. The solution was diluted to 3N in HCl and tellurium reprecipitated on passing SO_2 through the solution.

Step 3.   The tellurium precipitate was dissolved in nitric acid and evaporated down with HCl as in Step 2. The solution was made up to 5 ml. with water and 6N ammonia added until the precipitate of telluric acid which formed redissolved, and a further 10 drops excess ammonia added. The solution was scavenged twice with precipitations of ferric hydroxide and these precipitates discarded. The solution was made 3N in HCl and tellurium precipitated with SO_2. The precipitate was centrifuged down and the supernate discarded.

Step 4.   The tellurium was redissolved and reprecipitated as in Step 2. The final precipitate was transferred to a weighed filter disc with washings of water, washed with alcohol and ether, and dried for weighing and counting.

10 (b) UNDERLINE MILKING OF IODINE FROM TELLURIUM

Preparation and Standardisation of Carrier

A carrier solution of potassium iodide was prepared, containing 10 mg. of iodine/ml. and standardised by precipitation of silver iodide from aliquot parts.

Radiochemical Procedure

Step 1. Tellurium was separated from irradiated thorium by the procedure given above;. After weighing, the tellurium source was dissolved in nitric acid, and the solution evaporated down, with additions of HCl. 10 mg. of iodine carrier were added and the solution stood until the 2.3 hour iodine had grown into equilibrium with the tellurium (at least 12 hours).

Step 2. The solution was made alkaline with ammonia, 5 - 6 drops of sodium hypochlorite added, and the solution warmed. The solution was made acid with HCl, 1 ml. of 6% hydroxylamine hydrochloride added, and the solution cooled with running water. Iodine was extracted into 2 x 10 ml. carbon tetrachloride. The aqueous layer was reserved for the recovery of tellurium for subsequent milkings, as described in Step 6.

Step 3. The organic layer from Step 2 was shaken with 10 ml. of water containing a few drops of sodium bisulphite solution until both phases were colourless. The organic layer was discarded.

Step 4. 1 ml. of 6M nitric acid was added to the aqueous layer from Step 3. together with a few drops of 1M sodium nitrite.

The iodine liberated was extracted into 15 ml. of carbon tetra-chloride.

Step 5. The iodine was back-extracted into 10 ml. of water containing sodium bisulphite, and the organic phase discarded. The aqueous layer was transferred to a beaker and 1 ml. of 6M nitric acid added. The solution was warmed to remove SO_2. 1 ml. of 0.1 N silver nitrate was added to precipitate silver iodide. The precipitate was transferred to a weighed filter disc, washed with water, alcohol, and ether, and dried for weighing and counting.

Step 6. Tellurium was reprecipitated from the aqueous layer from Step 2, on saturation with SO_2. The precipitate was trans-ferred to a weighed filter disc and washed, dried and weighed in the usual manner. For as long as the silver iodide sources produced contained sufficient activity for counting, the tel-lurium was redissolved and the milking procedure repeated.

11. BARIUM

Preparation and Standardisation of Carrier

A carrier solution of barium nitrate containing 10 mg. of barium/ml. was prepared and standardised by precipitation of barium chloride with HCl – ether reagent, as described by Glendenin.[61]

Radiochemical Procedure

Barium and strontium were usually separated together from

irradiated thorium. After two precipitations of barium and strontium nitrates with nitric acid, barium was separated from strontium by precipitation of barium chromate from a buffered solution. These steps are given in detail in the procedure for strontium, page 89. The following procedure commences with the precipitate of barium chromate.

Step 1. The precipitate of barium chromate was washed with 10 ml. of hot water and the washings discarded. The precipitate was dissolved in 1 - 2 ml. of 6N HCl, and 15 ml. of HCl - ether reagent (20% ether, 80% HCl) added. The solution was stirred for two minutes as barium chloride was precipitated. The precipitate was centrifuged down and the supernate discarded.

Step 2. The precipitate was dissolved in 1 ml. of water and then reprecipitated on addition of 15 ml. of HCl - ether reagent. The precipitate was centrifuged down and the supernate discarded. The precipitate was transferred to a weighed filter disc with washings of 4% HCl in alcohol, washed with alcohol and ether, and dried for weighing and counting.

12. CERIUM.

Preparation and Standardisation of Carrier

A solution of cerous nitrate was prepared containing 10 mg. of cerium/ml. This was standardised by precipitation of cerium oxalate from aliquot parts in a similar way to which the fission-product sources were prepared.

Radiochemical Procedure

Step 1.   Irradiated thorium nitrate was dissolved in 4 ml. of 10N nitric acid containing 10 mg. each of carriers for cerium, zirconium, and other elements to be separated. 6 – 8 drops of saturated sodium bromate solution was added and the solution warmed to oxidise cerium to the (IV) state. The solution was cooled and 5 ml. of 6% hydroxylamine hydrochloride solution added to reduce the cerium to the (III) state. Zirconium was precipitated on addition of mandelic acid and the precipitate separated for purification of zirconium. Thorium was precipitated on addition of 25 ml. of $2M.HIO_3$, and the precipitate removed by centrifugation.

Step 2.   The supernate from Step 1 was made alkaline with 6N NaOH to precipitate cerium hydroxide. The precipitate was centrifuged down and the supernate discarded. The precipitate was dissolved in 1 ml. of conc. nitric acid and the solution made up to 10 ml. with 9N nitric acid and 2 ml. of sodium bromate solution. Cerium (IV) was extracted into hexane which had previously been equilibrated with nitric acid – sodium bromate solution, and the aqueous phase discarded. The organic layer was washed with 10 ml. of nitric acid – sodium bromate solution and the washings discarded.

Step 3.   The cerium was back-extracted into 2 x 5 ml. of water containing 0.25 ml. of 60% hydrogen peroxide. The cerium solution was made just alkaline by addition of conc. ammonia, and

then 1.5 ml. of 6N nitric acid added. The solution was heated
to nearly boiling and 10 ml. of saturated ammonium oxalate
added, to precipitate cerium oxalate. The solution was cooled,
the precipitate centrifuged down, and the supernate discarded.
Step 4.   The precipitate was dissolved in 1 ml. of conc.
nitric acid and the solution diluted to 10 ml. with water. The
solution was heated and cerium oxalate precipitated as in Step
3. The precipitate was transferred to a weighed filter disc,
washed with water, alcohol and ether, and dried for weighing
and counting.

REFERENCES

1. E. Fermi, Nature 133, 898. (1934)

2. O. Hahn and F. Strassman, Naturwiss. 27, 89. (1939)

3. L. Meitner and O.R. Frisch, Nature 143, 239. (1939)

4. F. Joliot, Compt. Rendus, 208, 341. (1939)

5. L.A. Turner, Rev. Mod. Phys. 12, 1. (1940)

6. C.D. Coryell and N. Sugarman (Eds.) "Radiochemical Studies: The Fission Products", National Nuclear Energy Series, Div. IV, Vol. 9. (McGraw-Hill, New York, 1951).

7. N. Bohr and J.A. Wheeler, Phys. Rev. 56, 426. (1939)

8. R.D. Hill, Phys. Rev. 98, 1272. (1955)

9. P. Fong, Phys. Rev. 102, 434. (1956)

10. E.K. Hyde, A Review of Nuclear Fission. U.C.R.L. 9036, 9065. (1960)

11. S. Katcoff, Nucleonics 18, No. 11, 201. (1960)

12. L.E. Glendenin, C. Coryell, R.R. Edwards. Paper 52, p. 489 of Ref. 6.

13. L.W. Roeland, L.M. Bollinger, G.E. Thomas, U.N.I.C.P.U.A.E. A/CONF. 15/P/551. (1958)

14. G.N. Walton, Quart. Rev. 15, 88. (1961)

15. E.K. Hyde, U.C.R.L. 9036, 9065. (1960)

16. R.C. Jenson and A.W. Fairhall, Phys. Rev. 109, 942. (1958)

17. N.E. Ballou et al. page 1410 of Ref. 6.

18. A. Turkevitch and J.B. Niday, Phys. Rev. 84, 52. (1951)

19. A. Turkevitch, J.B. Niday, and A. Tomkins, Phys. Rev. 89, 552. (1953).

20. A.S. Newton, Phys. Rev. 75, 17. (1949)

21. H.A. Tewes and R.A. James, Phys.Rev. 88, 860. (1952)

22. D.M. Hiller and D.S. Martin, Phys.Rev. 90, 581. (1953)

23. T.J. Kennett and H.G. Thode, Can.J.Phys. 35, 969. (1957)

24. W.W. Meinke, Chemical Procedures used in Bombardment work at Berkeley, AECD - 2738. (1949)

25. J. Kleinberg. (ed.). Radiochemical Procedures. LA - 1566. (1953)

26. G. Schwarzenbach, Complexometric Titrations, page 75. (Methuen, London, 1957)

27. E.B.M. Martin, Handbook for Cockcroft-Walton accelerator, Londonderry Laboratory for Radiochemistry.

28. E.J. Wilson and C. Evans, Atomics 9, 238. (1958)

29. J.H. Davies, Ph.D. Thesis, Durham University, 1960.

30. D.J. Silvester, Ph.D. Thesis, Durham University, 1958.

31. T.S. Ma and A.A. Benedetti-Pichler, Anal.Chem. 25, 999. (1953)

32. R.C. Hawkins, W.F. Merritt, and J.H. Craven. Proceedings of Symposium on Maintainance of Standards, N.P.L. May, 1951. (H.M.S.O.)

33. B.D. Pate and L. Yaffe, Can.J.Chem., 33, 15. (1955)

34. A.N. Protopopov et al. J. Nucl. Energy, 9, 157. (1961)

35. Nuclear Data Cards. (Nuclear Data Group, N.R.C., Washington).

36. R.B. Hahn and R.F. Skomieczmy, Nucleonics 14, No. 2, 56. (1956).

37. L.E. Glendenin, R.R. Edwards and H. Gest. Paper 232, page 1451 of Ref. 6.

38. D.N. Sunderman, Radiochemical Separation Procedures for Ba,Ca,Sr,Ag, and In. AECU - 3159. (1956)

39. W.W. Wendlandt, Anal.Chem. 30, 58 (1958).

40. Page 74 of Ref. 26.

41. N.E. Ballou. Paper 257, page 1538 of Ref. 6.

42. G. Charlot and D. Bezier. Quantitative Inorganic
     Analysis, page 65 (Methuen, London, 1957).

43. R.P. Larsen, L.E. Ross, G. Kesser. The Determination
     of fission-product Ruthenium. ANL - 5810 (1957).

44. L.E. Glendenin, Paper 265, page 1575 of Ref. 6.

45. A.C. Pappas. A Radiochemical Study of Fission Yields
     in the Region of Shell Perturbations. AECU - 2806 (1953).

46. T.C. Hoering, Procedure for Tellurium in "Collected
     Procedures" (H.L. Finston, ed.) B.N.L. (1956).

47. L.E. Glendenin, K.F. Flynn, R.F. Buchanan, and
     E.P. Steinberg. Anal. Chem. 27, 59 (1955).

48. J.M. Alexander and C.D. Coryell, Phys.Rev. 108, 1274
     (1957).

49. Data of Nethaway and Wahl produced in page 184 of Ref. 10.

50. Page 183 of Ref. 10.

51. E.P. Steinberg and L.E. Glendenin, Paper P/614, Vol. 7,
     U.N.I.C.P.U.A.E. (1955).

52. A.B. Smith, R.G. Nobles, S.A. Cox. Phys. Rev. 115,
     1242 (1960).

53. J.S. Fraser and J.C.D. Milton, Phys. Rev. 93, 818, (1954).

54. J.P. Butler, B.J. Bowles, and F. Brown, Paper P/6, Vol. 15,
     U.N.I.C.P.U.A.E. (1958).

55. I. Halpern. Ann. Rev. Nucl. Sci. 9, 245. (1959).

56. R.F. Coleman, B.E. Hawker, and J.L. Parkin, J.I.N.C.
     16, 8 (1961).

57. R. Belcher, A. Sykes, and J.C. Tatlow, Analytica
     Chimica Acta Vol. 10, No. 1. p.34 (1954).

58. N.E. Ballou. Paper 292 of Ref. 6.

59. A. Vogel. Quantitative Inorganic Analysis.

60. L.E. Glendenin. Paper 274 of Ref. 6.

61. L.E. Glendenin. Paper 236 of Ref. 6.

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