A STUDY OF FISSION YIELDS
WITH
ISOTOPE DILUTION AND THE MASS SPECTROMETER

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SCOPE AND CONTENTS: The relative abundances of the stable and long-lived isotopes of rubidium, cesium, strontium, cerium, neodymium, and samarium resulting from the thermal neutron fission of U^{235} and Pu^{239} were determined mass spectrometrically. Special precautions were taken to eliminate or at least minimize contamination of the sub-microgram quantities of fission products with the naturally occuring elements. By using isotope dilution the yields of isotopes of different elements were related with very good precision. Sufficient information was available to evaluate from such results the absolute cumulative yields of twenty-seven mass chains for U^{235} fission.

It was possible from the results of the present study to make a quantitative comparison between the yields of the heavy fragments for U^{235} and Pu^{239} fission, with special attention being given to the fine structure supposedly resulting from the influence of nuclear shells involving 50 and 82 neutrons.

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TABLE OF CONTENTS

Table of Contents (Cont'd)

LIST OF TABLES

LIST OF ILLUSTRATIONS

GENERAL INTRODUCTION

One of the most spectacular and certainly one of the most complex of nuclear transformations is the fission of heavy nuclei. The fission process involves the breakdown or splitting of a nucleus of high atomic weight into two main fragments with the simultaneous release of a tremendous amount of energy.

All nuclei with more than 83 protons and 126 neutrons are unstable. Through a complicated series of decay chains involving the emission of both alpha- and beta-particles, they finally reach stability either as isotopes of lead or (in a few cases) as Bi^{209}. Spontaneous alpha-emission is generally a much more probable process than spontaneous fission; although the latter has been observed among the isotopes of some naturally occurring elements, notably those of thorium and uranium. Fission only becomes favourable when excitation energies greater than 6 Mev. are provided.

The simplest way of exciting nuclei is through bombardment with neutrons. A neutron, unlike a charged particle, is not influenced by the powerful long range Coulomb field about the nucleus, and hence can come within the shorter range of the even more powerful nuclear forces without the necessity of much kinetic energy. Once within this range, the neutron interacts strongly with the nuclear field. It is frequently incorporated with the rest of the nucleons to form a nucleus qualitatively differing from the original only by one unit of mass. However, this new nucleus is in a highly excited state due to the binding energy of the added neutron. In the low mass region, this binding energy is usually released as gamma-radiation. However, if sufficient to overcome the threshold energy of 6 Mev., it will promote de-excitation of a heavy nucleus through the fission process.

Only nuclei with an even number of protons (92 or greater) and an odd number of neutrons are known to undergo fission to any appreciable extent by the singular effect of the binding energy of a captured neutron. For similar nuclei containing an even number of neutrons, this binding energy is significantly less than the fission threshold value. Only when pairing with an odd neutron can occur, will the capture of a slow (or thermal[#]) neutron result in fission.

Several nuclei that undergo fission by thermal neutrons are known. The most common of these are U^{235}, and Pu^{239}. The isotope of uranium is found in nature[##], whereas the natural abundance of Pu^{239} is virtually negligible. This isotope is generally prepared through a series of reactions

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[#] The term 'thermal' refers to neutrons with a kinetic energy spectrum similar to that of the molecules of a gas at room temperature.

[##] Natural uranium has the following composition: U^{234} 0.0058%, U^{235} 0.715%, and U^{238} 99.28%.

resulting from the capture of a thermal neutron by U^{238}, which is very abundant.

At present, U^{235} and Pu^{239} (and to some extent probably U^{233}) are being used as nuclear fuels. As such, they have been the subject of numerous experimental studies, many of which have been concerned with determining the yields of the various fission products. The accumulation of knowledge concerning the fission products and their individual yields has played an extremely important role in guiding nuclear reactor design and improving efficiency of operation.

The importance of this knowledge, however, extends far beyond the scope of just technical operations. It has had considerable influence on the course of current theories of nuclear structure, and stands as a final body of facts to be explained by any quantitative theory. From this point of view alone, the determination of the most accurate fission yield data possible is indeed a very worthwhile venture.

The variation of yield with both the charge on a primary fission fragment nucleus and its mass are of fundamental importance to the complete understanding of the fission process. A quantitative yield vs. charge study, however, is hindered experimentally by the fact that the primary fragments have a neutron-to-proton ratio much too great for stability in their respective mass regions, and de-excite very rapidly by the emission of beta-particles. Thus any significant data on the variation of yield with nuclear charge can be directly obtained only through the use of physical methods capable of resolving nuclei of different charge virtually immediately after fission. Unfortunately, no such methods have yet been successfully applied.

The other type of fission yield correlation, namely yield vs. mass, happens to remain fairly constant with time. Beta-emission from the fission products has no appreciable effect. On the other hand, delayed neutron emission, occurring after beta decay has started, has been found limited to comparatively few nuclides. Besides, the characteristics of these delayed neutron emitters have been fairly well established and their influence on the observed fission yields may be estimated with considerable certainty.

All methods of determining the variation of yield with mass have shown that the formation of pairs of fragments with equal mass is not very significant in the fission of any nucleus, unless the energy of excitation is over 100 Mev. For example, in the thermal neutron fission of U^{235} the yield of identical fragments (mass 117 or thereabouts) is virtually negligible compared to the yields of fragments around mass 95 and 139. The corresponding regions of preference in the thermal neutron fission of Pu^{239} are situated about masses 98 and 139.

The variation of yield within these most probable regions has been the subject of much investigation. Early radiochemical data indicated that for the thermal neutron fission of U^{235}, for example, the yield-mass relationship might be a regular one, starting with very low yields for identical pairs of fragments, then rising smoothly until the peak due to the corresponding masses quoted above was reached, and finally descending regularly and rapidly with increasing asymmetry of fission. Similar trends were reported for the thermal neutron fission of Pu^{239}, as illustrated in Figure I.

However, with the advent of more accurate techniques, such as mass spectrometry, numerous irregularities, indicating fine structure, have been found. It is of considerable interest to determine whether this fine structure is characteristic of the primary fission act or is due to post-fission processes that affect the yields individually, apart from delayed neutron emission. Such details can be definitely established only after sufficient accurate fission yield data is available.

At present, mass spectrometrically determined fission yields are considered the most reliable. However, only precise relative yields of the isotopes of isolated fission product elements have been reported to date as having been obtained by direct measurement. These have all been expressed in terms of the total yield of fission products, through the use of radiochemically determined data as normalization points.

The many calibrations involved in counting measurements make it often difficult to assess the accuracy of the final result. An accurate method of fission product analysis, completely independent of counting techniques, would, therefore, seem highly desirable.

This thesis reports a successful attempt at measuring fission yields with the combined use of isotope dilution and mass spectrometry. This method of quantitative analysis, although not quite as sensitive as radiochemical techniques for work with fission products formed in low yield, has been found capable of accurate results in several important regions of the mass yield distribution. The absolute (cumulative) fission yields for the thermal neutron fission of U^{235} at masses 85, 87, 88, and 90, which constitute part of the light-fragment distribution, and at masses 133, 135, 137, 142 to 152, and 154 have been determined with a precision close to 1%. For this work, the total yield of fission products in a known weight of irradiated uranium was calculated from the results of a neutron flux monitoring experiment employing BF_3. The B^{10}/B^{11} ratio before and after irradiation had been determined mass spectrometrically, and the average neutron flux during the irradiation calculated using the best available value of the B^{10} capture cross-section for thermal neutrons.

Values for the fission yields in the same mass regions for the thermal neutron fission of Pu^{239} have also been obtained with the use of isotope dilution. However, no direct measurement of the total yield of fission products was made in this case. Consequently, the results can be expressed only relative to one another, unless they are normalized at a radiochemically determined point. Even without this normalization, however, enough information is available to reveal many of the trends in the heavy mass region, especially with reference to those found for the fission of U^{235}.

HISTORICAL INTRODUCTION

A. The Discovery of Fission and Related Phenomena

The interaction of neutrons with uranium to produce nuclei undergoing beta-decay was first observed by Fermi and co-workers in 1934 (1). Fermi at that time assumed nuclei of atomic number 93 or higher were being formed, Noddack (2), on the other hand, did not find the evidence sufficiently convincing, and suggested that possibly a split in the uranium nucleus might have occurred to form nuclei of lower atomic number. However, her speculation seemed to have had very little effect on future developments. Further work during the years 1937 and 1938, mainly carried out by Meitner, Strassmann, and Hahn (3) (4) in Germany, and Curie and Savitch (5) (6) in France, continued to be interpreted in terms of transuranic element formation. However, evidence for the production of isotopes resembling Ba and La in chemical properties, aroused suspicion of the current interpretations, and prompted Hahn and Strassmann in 1939 to undertake a very careful chemical investigation of the problem. This resulted in the conclusive proof that Ba and La isotopes were actually being formed during the irradiation of uranium with neutrons (7). Soon isotopes of I, Br, Xe, Kr, Cs, and Rb were found (8) and the splitting of the uranium nucleus became an accepted fact. This newly acknowledged nuclear phenomenon was given the name 'fission' by Meitner and Frisch in the same year. (9)

It was first pointed out by Meitner and Frisch (9) that the division of a heavy nucleus, such as that of uranium or thorium, into two lighter fragments of equivalent size would involve the release of a tremendous amount of energy, due to the mutual repulsion of the charges on the two fragments, once the latter were separated. This was soon experimentally confirmed by Frisch (10) and Joliot (11) independently. Frisch observed great pulses of ionization when the fission fragments passed through a gas, while Joliot showed that the fragments had sufficient kinetic energy to be ejected from the surface of an irradiated sample of uranium and had a maximum range in air of about 3 cm.

Soon after, Jentschke and Prankl (12) found that the energetic pulses from fission fragments could be divided according to magnitude into two groups at about 60 and 100 Mev. A little later, more elaborate experiments by Booth, Dunning, and Slack (13), carried out with very thin electrically deposited layers of uranium metal, showed a continuous distribution of size of pulse with two pronounced maxima at 100 Mev. and 72 Mev. Here was then direct evidence that asymmetric fission was the favoured process.

Meanwhile, von Halban, Joliot and Kowarski (14) (15) as well as Anderson, Fermi and Hanstein (16) found that, in water containing a neutron source, the thermal neutron density was increased in the presence of uranium. Szilard and Zinn (17) reported that neutrons were emitted with considerable energy and apparently instantaneously when uranium was bombarded with neutrons. Before this instantaneous emission had been discovered, Roberts, Meyer and Wang (18) found a delayed emission of neutrons which apparently followed a short-lived beta-active product. Szilard and Zinn (17) showed quite conclusively that the instantaneous emission was very much stronger than the delayed and assumed it corresponded to a direct ejection of neutrons from the fission fragments. Their measurements yielded a value of 2.3 neutrons emitted per fission (19), which was consistent with the previously determined less accurate data of Anderson, Fermi and Szilard (20) and von Halban, Holiot and Kowarski (21).

The problem as to which isotope of uranium was undergoing fission by thermal neutrons was first seriously considered by Bohr in 1939 (22). On the basis of calculations concerning critical energies for fission of the known isotopes of uranium and the binding energy released due to the absorption of a neutron, Bohr came to the startling conclusion that the comparatively rare isotope, U^{235}, was responsible for the thermal neutron fission of uranium. This was later confirmed experimentally by Nier, Booth, Dunning and Grosse (23) who worked with the separated isotopes of uranium.

Thus, within a year after the revelation of fission by Hahn and Strassmann (7), many of the salient features of this process were known in surprising detail. Since that time, the extended research in this field has been enormous. Fission has been observed in dozens of nuclei under various modes of excitation. These studies, for example, range from the 190 Mev. deuteron fission of Bi^{209} (24) to the 3-hour spontaneous fission of an isotope of element 100 with mass 254 (25).

In particular, the fission of U^{235} and of Pu^{239} has been very thoroughly investigated. Since the results of the previous studies concerning the thermal neutron fission of these two nuclei are of direct interest to the investigations reported in this thesis, the discussion in the following sections of the Historical Introduction has been restricted chiefly to them; especially since excellent reviews dealing with other types of fission are available (26) (27) (28).

B. Characteristics of the Thermal Neutron Fission of U^{235} and Pu^{239}

From the experimental data accumulated during the course of fission studies, it became apparent that the sequency of events following the capture of a thermal neutron by U^{235}, say, could in general be expressed as follows:

$$\begin{tikzcd}
 & {}_{92}U^{235} \quad + \quad {}_0n^1 \arrow[r] & {}_{92}U^{236} \arrow[dl] \arrow[dr] & & \\
 & (Z_1,A_1) \arrow[dl] \arrow[d] & (a) & (Z_2,A_2) \arrow[d] \arrow[dr] & \\
v_1({}_0n^1) & (Z_1,A_1-v_1) \arrow[d, dotted] & (b) & (Z_2,A_2-v_2) \arrow[d, dotted] & v_2({}_0n^1) \\
 & (Z_{1s},A_1-v_1) & (c)\ \text{with release of 3 beta-particles} & (Z_{2s},A_2-v_2) &
\end{tikzcd}$$

where ${}_{92}U^{236}$	is the excited compound nucleus,
(Z_1,A_1) and (Z_2,A_2)	are the primary fission fragments, the subscript 1 and 2 referring to light and heavy mass respectively,
v_1 and v_2	are the neutrons emitted from the primary fragments,
(Z_1,A_1-v_1) and (Z_2,A_2-v_2)	are the fission products undergoing beta decay,
(Z_{1s},A_1-v_1) and (Z_{2s},A_2-v_2)	are the stable fission products.

It is now generally conceded that thermal neutron fission is a relatively slow process (24). After the capture of a neutron, there is enough time for considerable rearrangement of the nucleons before separation into fragments takes place. The division into two fragments, namely binary fission, has been shown to be the most important process by far. Ternary and quaternary fissions occur only 3×10^{-3} and 2×10^{-4} times as often, respectively (29).

The emission of neutrons from the primary fission fragments (reaction (b) above) has been found to take place for the major part within 10^{-14} sec. of the actual fission act (a) (30). The latest figure for the number of neutrons emitted per fission is 2.5 ± 0.1 (31); thus suggesting that v_1 and v_2, the number of neutrons emitted from corresponding fragments, may be 1 or 2 (or possibly even 0) depending on the nature of the fragments. Fraser (30) has shown, through a study of the angular distribution of the prompt neutrons, that on the average the light fragment group emits 30 per cent more neutrons than does the heavy. Recent work (48) indicates that neutron emission from the light fragment predominates at low mass ratios, whereas at high mass ratios neutron emission from the heavy fragment is more probable.

In addition to the release of neutrons from the primary fragments, some emission of neutrons can occur after beta-decay (reaction (c)) has started. Certain nuclides, after the ejection of a beta-particle or more, find themselves in an excited state favourable for the immediate release of a neutron. However, these delayed neutron emitters account for only 1.0 ± 0.2% of the total number of neutrons emitted (32). Hence, the figure, 2.5, for the average number of neutrons released per fission may be taken as representative of prompt neutron emission within experimental error.

The average amount of energy released per fission is about 190 Mev. (33). Of this, 160 Mev. is released as kinetic energy of the two main fragments, 5 Mev. is radiated as gamma-rays, 5 Mev. is carried off as kinetic energy by the prompt neutrons, and about 20 Mev. results from the beta-decay of the fission products. On the average, the emission of 3 beta-particles from each fragment is necessary before stability is reached. Thus each beta decay may be considered to release approximately 3 Mev. However, this is not exactly the case; the release of energy accompanying beta-emission as low as 0.076 Mev. (for Sm^{151} decay) and as high as 6.5 Mev. (for I^{136} decay) has been recorded (34) (35).

The details of the thermal neutron fission of Pu^{239} are very similar to those discussed above, except for the fact that more neutrons (3.0 ± 0.1 per fission) are released on the average, and the probability of fission is higher for this nuclide than for U^{235}. The fission cross-section of Pu^{239} is 664 barns, whereas that of U^{235} is 549 barns# (31).

A barn, by definition, is 10^{-24} cm.^{2}.

The preferred asymmetry of fission has already been mentioned in the General Introduction and illustrated in Figure I, which shows the fission yield curves for U^{235} and Pu^{239} obtained through radiochemical studies (36). Such studies reveal that the yield of the most probable mode relative to that of the symmetrical one (the so-called peak-to-valley ratio) is 550:1 for the thermal neutron fission of U^{235}, and only 150:1 for Pu^{239} (37) (38).

The variation of the peak-to-valley ratio with excitation energy of the compound nucleus has been a subject of considerable interest. From a comparison of the fragmentary data for different compounds at various energies of excitation, it has been shown (38) (39) that one can obtain a strong correlation between the energy of excitation and the peak-to-valley ratio over a considerable range of values. This correlation shows that the peak-to-valley ratio decreases very rapidly with increase in excitation energy. Such a plot can be interpreted as an excitation curve for the formation of asymmetric products relative to symmetric ones for the fission of heavy elements in general. It indicates, for example, that the yield of symmetric products in spontaneous fission would be immeasurably low, as has been indicated to be the case from spontaneous fission yield studies to date (40) (41) (42).

Another interesting fact revealed in comparing the fission yield patterns of U^{235} and Pu^{239} is that, while the light mass peak is displaced to higher masses for Pu^{239}, the position of the heavy mass peak compared to that of U^{235} remains virtually unaffected. This reluctance of the heavy mass peak to shift position seems to be characteristic of asymmetric fission in general. For example, the thermal neutron fission of U^{233} (43), the fast neutron fission of U^{238} (44) (45) and of Th^{232} (46), and the spontaneous fission of Cm^{242} (47)--to mention only a few cases--all result in a heavy mass peak at practically the same position, especially with regard the side favouring lighter masses. Concurrent with a change in mass of the fissioning nuclide, however, is a change in the breadth and shape of the peaks. Thus, for Pu^{239}, the yields of highly asymmetric fissions (though still not very large) are much more significant than for U^{235}.

C. The Yields of Fission Products

In 1941 Anderson, Fermi, and Grosse (49) measured the number of beta-disintegrations of a suitable member of a radioactive series resulting from the fission of uranium after a quantitative chemical separation and under specified geometry conditions. Since then this technique, although vastly improved, has been applied by many others to some member or members of practically every mass chain produced in fission, and has resulted in fairly quantitative results where the half-lives concerned have been more than a few hours but less than

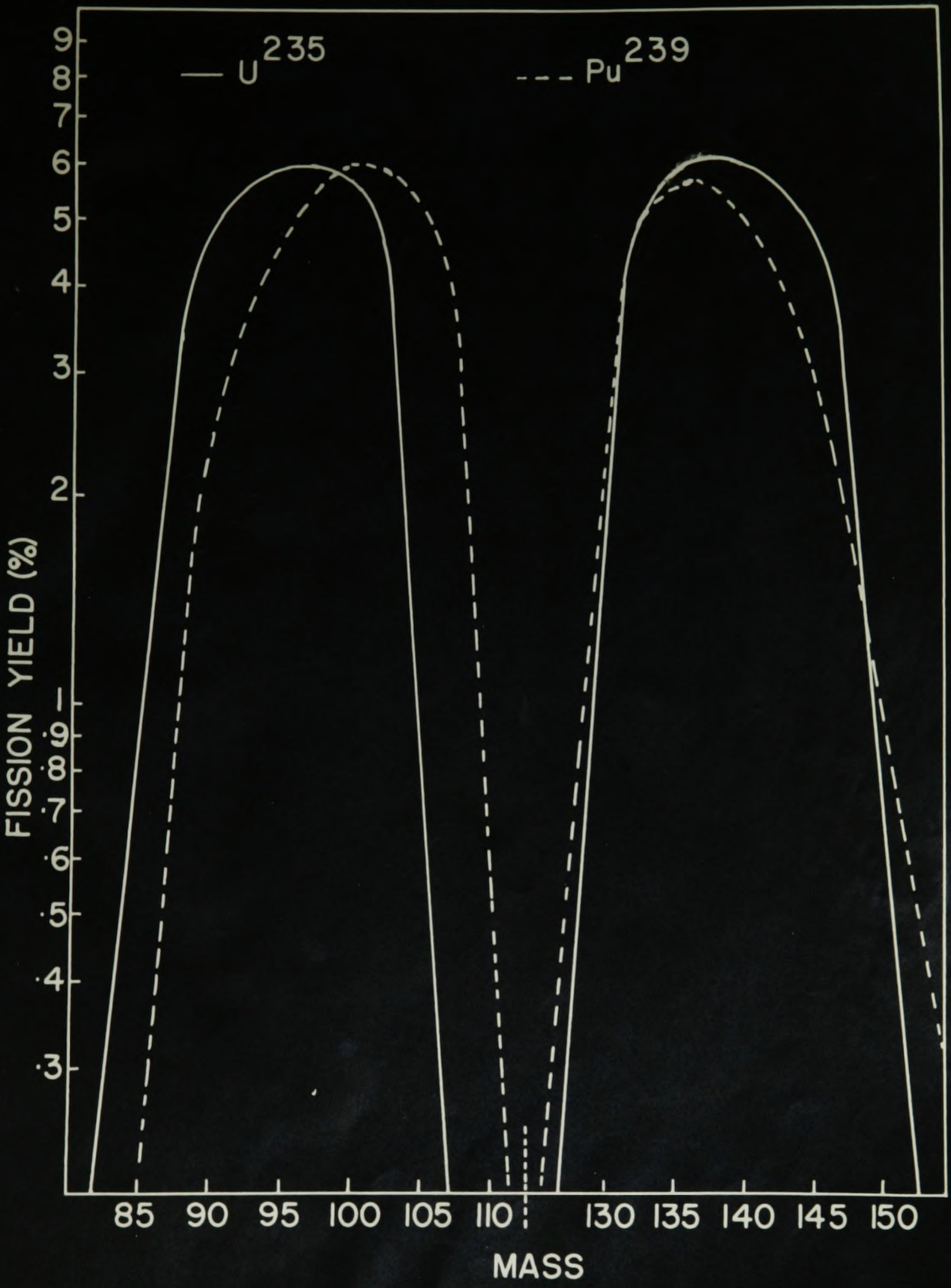

FIGURE 1· RADIOCHEMICAL FISSION YIELD CURVES a year. The radiochemical fission yields for U^{235} and Pu^{239} obtained prior to 1949 have been conveniently assembled by Coryell and Sugarman (36). On examining these results one can see that the reproducibility obtained, although sufficiently good to establish the main features of the mass-yield distribution, was not generally better than ± 10% and in several cases not good enough to establish with certainty the yields of some masses within even 30%. Hence it was quite justifiable, on the strength of this information, to draw a curve of best fit through the data and thus obtain smooth yield-mass curves for the various fissile elements studied.

(a) Fine Structure in the Mass Yield Distribution

The first attempt at measuring fission yields with a mass spectrometer by Thode and Graham in 1945 (50) resulted in data that could not be reconciled with a smooth mass yield curve. Further work by Macnamara, Collins and Thode (51) confirmed the fact that, of the stable xenon isotopes that resulted from the thermal neutron fission of U^{235}, Xe^{134} was formed in a yield about 30% higher than expected from a smooth curve. Furthermore, they were able to show that the yield of Xe^{133} was over 20% higher than expected on the same basis. By that time considerable experimental evidence for nuclear shell structure was available (52) and the fact that the observed anomoly occurred in the vicinity of the 82-neutron shell was soon realized. Glendenin (53) attempted to explain the favoured yields at masses 133 and 134 entirely on the assumption that nuclei with 83 neutrons formed either as primary fragments or resulting from the emission of a neutron by a primary fragment would have a good probability of "boiling off" a neutron to form the very favourable 82-neutron configuration. This mechanism, although increasing the yield at masses 133 and 134 as required, caused a corresponding decrease in the yields of masses 135 and 136. The fact that this had not been observed experimentally led Wiles et al (54) (55) to suggest that, in addition to the Glendenin mechanism, a favoured yield of 82-neutron fragments was characteristic of the primary fission process. By assuming that this added effect was a function of the distance of the nuclide from the Bohr-Wheeler stability curve, and therefore increased in going from mass 131 to 136, it was found possible to construct a semi-empirical curve fairly well in line with the experimental data.

Since then, Glendenin and co-workers (56) have examined the stable molybdenum isotopes from fission mass spectrometrically and have found an enhanced yield for Mo^{100}. Wiles (57) has also done radiochemical work in this region and, although his results are not quite as accurate as the mass spectrometric data, they do indicate that the yield of Mo^{101} is also abnormally high.

By folding the fission yield curve in such a way as to superimpose the light mass peak over the heavy (on the assumption that the masses of complementary fragments added to 233.5), it has been shown (56) that the observed fine structure in both mass regions coincided, but was more pronounced for the heavy mass peak. This seemed to be good confirmation of the original suggestion by Wiles et al (55) that part of the fine structure in the heavy mass region was characteristic of the primary fission process.

Pappas (58) has recently made a study of the neutron binding energies in the region of closed shells (in particular the 50, 82, and 126 neutron configurations). The results of his analysis indicate that, in addition to the high probability of neutron emission by fragments with 51 and 83 neutrons (original postulate of Glendenin), the probability of neutron emission by fragments with 3, 5 and 7 neutrons more than closed shells is also significantly high. On this basis, Pappas predicted that in addition to the sub-peak at mass 134, there should be pronounced, but smaller, sub-peaks at masses 136, 138, 142, and 144. Using the results of his own radiochemical study in this mass region, the best available information concerning delayed neutron emitters, and the available mass spectrometric data normalized at suitable points, Pappas claimed good agreement between the experimental data and his predicted yield - mass curve. The quoted fission yields, however, were in many cases not accurate enough to establish whether this agreement was actually real.

Recently (59) Fleming has mass spectrometrically determined the relative fission yields of xenon and krypton isotopes from the thermal neutron fission of U^{233} and Pu^{239}. These results were compared with the corresponding data for U^{235} and U^{238} obtained in this laboratory (60), and it was concluded that fine structure in the mass region 131 to 137 was mainly due to a primary preference for certain nuclei, probably as a result of the extra stability of the 82 neutron configurations. The effect originally suggested by Glendenin and later extended by Pappas (as discussed above) could not be reconciled with the new data, and was considered to be of secondary importance, if it existed at all.

Thus one can conclude that the problem of fine structure in the yield mass curve is still open to a great deal of investigation. It seems quite certain that some of the difficulties in explaining observed fission yields to date may be directly the result of inaccurate fission yields. Over thirty mass-chains from the fission of U^{235} have been examined with the mass spectrometer through the combined efforts of Thode and co-workers in this laboratory and Ingrham's group at the Argonne National Laboratory. These are given in Tables I and II.

Although the precision of the mass spectrometric measurements themselves is exceedingly good, subsequent corrections# to the data may lead to erroneous results for the fission yields.

These will be discussed later in connection with the investigations of this thesis.

TABLE I

Mass Spectrometrically Determined Relative Fission Yields Compared to Smooth Curve Values
(U^{235}-Light Mass Region

Isotopes Compared		Relative Fission Yields		
		Mass Spectrometric		From Smooth Curve (63)
Kr	83	0.270 (60)		0.21
	84	0.506 #		0.34
	85	0.643		0.68
	86	1.000		1.00
Rb	85	0.475 (55)	0.542 (61)	0.50
	87	1.000	1.000	1.00
Sr	88	0.68 (55)	0.607 (61)	0.74
	90	1.00	1.000	1.00
Zr	91	0.890 (56)		0.87
	92	0.911		0.94
	93	0.974		0.97
	94	1.000		1.00
	96	0.997		1.02
Mo	95	1.000 (56)		1.00
	97	0.949		0.97
	98	0.944		0.97
	100	1.034 #		0.94

acknowledged "fine structure".

TABLE II

Mass Spectrometrically Determined Relative Fission Yields Compared to Smooth Curve Values (U^{235}-Heavy Mass Region)

Isotopes Compared	Relative Fission Yields		
	Mass Spectrometric		From Smooth Curve (63)
Cs 133	1.091 #(55)		0.73
135	1.054 #		0.95
137	1.000		1.00
Xe 131	1.000 (60)		1.00
132	1.497 #		1.29
133	2.264 #		1.61
134	2.739 #		1.96
136	2.182		2.18
Nd 143	1.000 (61)	1.000 (62)	1.00
144	0.927	0.859	0.98
145	0.660	0.670	0.87
146	0.499	0.520	0.74
148	0.279	0.304	0.37
150	0.112	0.122	0.17
Sm 147	1.95 (62)		1.86
149	1.000		1.00
151	0.405		0.39
152	0.254		0.21
154	0.083		0.064

acknowledged "fine structure".

These undoubtedly account for some of the large differences in the values reported in Table I. Moreover, uncertainties soon arise when attempts at normalization are made. Several efforts have been made to improve the radiochemical techniques to the extent that they give excellent reproducibility. However, the results of independent laboratories frequently do not agree. For example, the yield of I^{131} (one of the most extensively studied radioactive fission products) has been given values ranging from 2.8% (64) to 3.28% (65). At present, a value of 3.14% is favoured (66). Since I^{131} is chosen as a normalization point for the mass spectrometrically determined yields of the xenon isotopes, this variation has had a considerable influence on the magnitude of the fine structure in the mass region 131-137 in terms of the mass yield curve in general. Hence, it would seem very important to either establish once and for all the yield of a particular mass in the region of fine-structure or to accurately fix it with respect to a yield in the neodymium mass region, say, where mass spectrometric data is again available (61) (62).

(b) Delayed Neutron Emitters

Although the contribution of delayed neutrons to the yield of neutrons in fission has been shown to be small (32), the effects of delayed neutron emitters on individual chain yields may be of considerable consequence. All the available information concerning delayed neutron emitters identified among the fission products of U^{235} and Pu^{239} is given in Table III.

TABLE III

Yields of Delayed Neutrons in Thermal Neutron Fission[#]

Half-life	Delayed Neutron Emitter	Contribution to Chain Yield (%)	
		U^{235}	Pu^{239}
0.05 s.		0.063	
0.43 s.	As^{85}	0.21	
1.13 s.			0.43
1.52 s.	Sb^{135} (?)	0.60	
4.51 s.	$Br^{(89)}$	0.53	0.36
22.0 s.	I^{137}	0.42	0.26
55.6 s.	Br^{87}	0.063	0.039
0.8 m.	Sb^{134} (?)		
3.0 m.		5.8×10^{-6}	
12 m.		5.5×10^{-8}	
125 m.		3.0×10^{-8}	

[#] From data compiled by Pappas (58).

EXPERIMENTAL

The main objectives of this work were twofold: 1) to determine the absolute fission yields of the stable and long-lived isotopes of cesium, rubidium, strontium, neodymium, and samarium in the thermal neutron fission of U^{235} and 2) to determine the accurate relative yields of the isotopes of each of these elements in the thermal neutron fission of Pu^{239}, and, if possible, to correlate the yields of the various elements without the need of radiochemical data.

This was to be done with the combined use of isotope dilution and mass spectrometric analysis.

A. Isotope Dilution

The technique of isotope dilution as applied to the present problem can be best illustrated by means of a simulated example.

Suppose a sample of uranium has been irradiated and the relative fission yields of the isotopes of element X have been determined mass spectrometrically. In particular, let us consider the isotopes X^1 and X^2 whose ratio in fission is much different from that in nature (provided the isotopes are found in nature). Let the isotope ratio in fission ($[X^1]_f/[X^2]_f$) be R_f. We now add a known amount of the natural element to an aliquot of the fission product solution. Suppose the resulting ratio for X^1 and X^2 is R_{fn}. Then R_{fn} can be expressed as follows

$$R_{fn} = \frac{[X^1]_f + [X^1]_n}{[X^2]_f + [X^2]_n}$$

where $[X^1]_f$ is the no. of atoms of X^1 in the fission product solution,

$[X^1]_n$ is the no. of atoms of X^1 added,

and so on.

$$\text{Now} \quad \frac{[X^1]_f}{[X^2]_f} = R_f$$

$$\text{Therefore} \quad R_{fn} = \frac{R_f \, [X^2]_f + [X^1]_n}{[X^2]_f + [X^2]_n} \quad \ldots\ldots\ldots (1$$

Since $[X^1]_n$ and $[X^2]_n$ are known from the amount of the standard solution added and the normal isotopic composition of the natural element (as given in the literature), a mass spectrometric evaluation of R_f and R_{fn} gives $[X^2]_f$ directly.

This can be used to calculate the fission yield of X^2 provided the number of fissions per gram of uranium is known, and the appropriate corrections for decay of X^2 or incomplete decay of its precursors can be made. In addition, external factors such as contamination, neutron capture, and delayed neutron emission have to be taken into account. Once the fission yield of one isotope is known, the yields of the other isotopes observed can be evaluated directly from the mass spectrometric abundance data, after applying all of the necessary corrections above.

B. Mass Spectrometry

The mass spectrometer used for all the fission product analyses was a six-inch-radius 90-degree-sector instrument (67) with magnetic scanning and a hot filament source. This instrument had been recently equipped with a vibrating reed d.c. amplifier (Model 30E, Applied Physics Corporation) and a Brown Electronics recorder with a half-second response (Minneapolis-Honeywell Reg. Co.).

A platinum-plated tungsten filament, 0.001 in. thick and 0.030 in. wide, was found to be more efficient than one of plain tungsten. With such a filament as little as 0.001 microgram of cesium, rubidium and neodymium and 0.01 microgram of samarium and strontium could be analyzed with a precision of 1 or 2%. In general, however, the samples taken for analysis contained between 0.01 and 0.1 microgram of each of the fission products. The precision for these was consequently better than ± 1% in most cases. The alkali metals (cesium and rubidium) gave especially reproducible results (± 0.2%).

Before each analysis a new filament was prepared from tungsten ribbon of the dimensions above, and electroplated with a very thin layer of platinum from a 1% solution of chloroplatinic acid. The coating obtained was usually dark and nonmetallic in appearance. Nevertheless, by heating the filament under vacuum at about 2000°C, a metallic surface with a dull luster was obtained. The heat treatment was usually extended for about an hour to drive off any alkali metal impurities that might be on the surface of the filament. On occasion the filament after preparation was inserted directly into the mass spectrometer and the various mass regions scanned with increasing filament current. At no time were any ions found in the fission product regions. However, small amounts of Na^+ and K^+ were often detected, but these caused no difficulties during fission product analysis.

The fission product solutions for analysis were in all cases evaporated to near dryness, and a drop transferred to the filament. This was taken to dryness by heating the filament with a current sufficient to promote rapid evaporation but not large enough to cause spattering.

It was found fairly early in the course of this work that separation of the fission products was unnecessary for mass spectrometric analysis of the various elements. These could be individually studied by virtue of their different isotopic masses and their different ion-emission characteristics. Cesium, rubidium, strontium, and barium for example, were always emitted as the singly charged ions (i.e. Cs^+, Rb^+, Sr^+, and Ba^+), and in that sequence with increasing filament current. NdO^+ peaks were obtained at temperatures very near or slightly higher than those necessary for the emission of Sr^+ and Ba^+. The NdO^+ peaks were invariably the most prominent for neodymium, but, on occasion, Nd^+ ion currents were also observed. These, however, could always be made to disappear by lowering the filament current slightly.

Samarium was always observed both as Sm^+ and SmO^+ ions. The ion currents due to the former were usually larger by a factor of two at least. Since the heaviest mass of Sm^+ was 154 as compared to 158 for the lightest mass of NdO^+, the isotopic abundances of samarium based on the Sm^+ peaks required no correction for neodymium undercutting. However, the peak due to $La^{139}O^+$ (mass 155) was usually large enough to undercut the $(Sm^{154})^+$ peak quite seriously. Hence, the Sm^{154}/Sm^{152} ratio was measured in the SmO^+ region.

Cerium was emitted as CeO^+ entirely. At temperatures most favourable for the emission of NdO^+, only very small $Ce^{140}O^+$ peaks were seen (less than 5% the height of the $Nd^{142}O^+$ peak). Hence the corrections to the peaks of $Nd^{142}O^+$ and $Nd^{144}O^+$ were generally very small and not of serious consequence.

When sufficient measurements were made on the isotope ratios of samarium and neodymium, the filament temperature was raised until the peaks of CeO^+ grew to satisfactory heights. By that time the peaks due to NdO^+ usually began to fade. However, by continuously measuring all masses from (140 + 16) to (146 + 16) it was possible to apply a fairly accurate correction to the peaks of $Ce^{142}O^+$ and $Ce^{144}O^+$ from the previously determined neodymium isotope ratios. Thus, a reasonably precise value (± 2%) for $Ce^{140/142}$ and $Ce^{144/142}$ could be obtained.

C. Uranium-235 and Fission Products

Two samples of uranium metal (A and B) which had been irradiated with thermal neutrons (in a nuclear reactor) and had been allowed to "cool" for several years were chosen for this part of the investigation. The details concerning the irradiation of each sample and the chemical techniques used in preparing the fission products for mass spectrometric analysis are given below.

(a) Irradiation

The irradiation data concerning the two samples is given in Table IV.

The flux during the irradiation of Sample A was only approximately known from pile data. Hence, this sample was only useful for the evaluation of relative fission yields. In particular, it was used for the mass spectrometric determination of the fission yields of neodymium and samarium isotopes. The relative fission yields of the isotopes of cesium, rubidium, strontium, xenon, and krypton in this sample had been previously determined (55) (60).

Sample B (to be used for absolute fission yield studies)

TABLE IV

Irradiation Data for Uranium Samples

Sample	Weight (grams)	Nuclear Reactor	Irradiation Time (days)	Average Neutron Flux {n./cm.^{2}/sec. x 10^{12}}	No. of Fissions per gram (x 10^{16})
A #	30	Oak Ridge	18	0.6	0.9
B ##	2.966	NRX (Chalk River)	36	2.30	7.55

\# A disk of uranium metal 3 cm. in diameter and 0.4 cm. thick.

\## A block of metal 10.4 cm. x 0.4 cm. x 0.8 cm. cut from a disk similar to Sample A.

was irradiated under conditions that permitted a fairly accurate measurement of the thermal neutron flux. Although this flux measurement was not a product of the present work, the details concerning it have been given here, since the results will be discussed in connection with absolute fission yield calculations.

(b) Flux Measurement with BF_3

Sample B, along with four other samples of uranium weighing between 0.6 gram and 6.7 grams, was placed in a self-serve irradiation container beside a quartz capsule containing boron trifluoride. The capsule was provided with a "break-seal" and was filled to a pressure of about 30 cm. of mercury. The sample was inserted in a self-serve position of the Chalk River pile and irradiated for 36 days.

After the irradiation, the relative abundances of B^{10} and B^{11} of the boron were determined with a 180 degree direction-focusing mass spectrometer equipped with a vibrating reed d.c. amplifier and speedomax recorder. The ratio of B^{10}/B^{11} before irradiation to that after irradiation was found to be 1.029 ± 0.001. This was based on the assumption that the B^{10}/B^{11} ratio for this sample of boron before irradiation was 0.2321 as given by Inghram (68) for natural boron.

By assuming the only significant reaction resulting in the observed change of the B^{10} and B^{11} relative abundances was $B^{10}(n, \alpha)Li^7$, and using the best value of the cross-section of boron relative to that of uranium given in the literature, it was possible to calculate the number of fissions per gram of uranium to be 7.55×10^{16} as given in Table IV. Further details concerning this calculation are given in Appendix A.

(c) <u>Chemical Procedures</u>

(i) <u>Treatment of Sample A</u>

M.J. Parker (61) has already discussed in detail the relative merits of various methods of preparing carrier-free samples of fission products for mass spectrometric study. The method adopted for Sample A was based on one reported in her thesis employing solvent extraction and ion-exchange.

Sample A was rinsed with dilute nitric acid until a clean shiny surface was obtained. The disk was then dissolved in a minimal volume of 6N HNO_3, which had been prepared from reagent grade nitric acid by distillation in pyrex apparatus.

The uranium was extracted from the solution with portions of freshly distilled ether saturated with 6N HNO_3. The aqueous phase, containing most of the fission products and a small quantity of uranium, was then taken to dryness, the residue dissolved in about 1 ml. of distilled water, and transferred to an 11 cm. x 1 sq. cm. cylindrical pyrex column filled with clean Dowex-50 (100-200 mesh) resin.

The aqueous phase was then displaced with ether, and the uranium removed with ether saturated with 6N HNO_3. After flushing with pure ether again, fission product tellurium and molybdenum were eluted with ether saturated with 6N HCl. The HCl was then removed by further flushing with ether and fission product rubidium and cesium eluted with a 1.0 N aqueous solution of HCl, and strontium with 2.0 N HCl. By this time the band of rare-earths on the column showed considerable broadening. Hence all the rare earths were desorbed with 5% ammonium citrate solution at a pH of 4.0 and re-adsorbed at a pH of about 1.5. The citrate solution was adjusted to a pH of 2.9 and the rare earths eluted in sequence. The yttrium was efficiently separated from samarium and promethium, which in turn were collected separately from neodymium, praseodymium, and lanthanum.

In all cases the rate of flow was about 1 ml/min. and the volume of eluent needed to effect adequate separation between 100 and 300 ml.

All the solutions, apart from those containing the rare earths, yielded on evaporation a barely visible residue. The carbonaceous residue remaining from the citrate solutions had to be destroyed with perchloric acid and the ammonium salts oxidized with aqua regia.

The pyrex beakers containing the various separated fission products were carefully kept under cover until it was convenient to analyze the fission products with the mass spectrometer.

(ii) Treatment of Sample B

With Sample B an attempt was made to minimize the number of reagents and quantity of each required to separate the fission products carrier-free from the bulk of uranium matrix. This was done to eliminate the danger of contaminating the fission rubidium and cesium isotopes with the naturally occurring elements. Contamination of the isotopes of strontium, neodymium, and samarium was a less likely matter. Thus, once the alkali metal fission products could be separated without contamination, it was justifiable to assume that the abundances of the other fission isotopes had not been altered either.

First of all, the rather tedious column separations were abandoned in favour of a simple technique involving the precipitation of uranium as $UO_4 \cdot 2H_2O$. This method consisted of dissolving the irradiated uranium metal with a minimum volume of nitric acid, evaporating the solution to dryness, then redissolving the uranyl nitrate (and fission products) in a few cc. of distilled water to which were then added a few drops of 30% hydrogen peroxide. At a pH of 7 or thereabouts the precipitation of $UO_4 \cdot 2H_2O$ was practically complete and very few of the fission products were carried down. All the alkali metals, alkaline earths and rare earths of interest were found to be retained in over 70% yield in the supernatant solution. This solution had merely to be evaporated to dryness, the residue taken up with a few drops of water and transferred to the filament of the mass spectrometer for evaporation. The various elements could be studied separately by virtue of their different ion-emission characteristics as discussed before.

In detail the treatment of Sample B was as follows. The surface of the uranium was cleaned with diluted nitric acid, then rinsed with distilled water, and dried by pressing the sample between pieces of filter paper and gently warming under a heat lamp. After this the sample was accurately weighed and transferred to a clean vycor crucible, to which a total of 4 cc. of HNO_3 and 1.5 cc. of HCl were added. Each reagent had been prepared by distilling the reagent-grade acid (available commercially) directly into a polythene vessel; thus avoiding contact with glass#.

\# For the effect of acids and bases on pyrex and vycor glass see reference (69), page 176.

About 1 gram of the uranium was allowed to dissolve, then the solution was carefully transferred to a 50 ml. volumetric flask with a capillary pipette. The uranium remaining was washed several times with distilled water, the washings transferred to the flask also, and the volume of solution brought up to the mark with distilled water. The undissolved uranium was carefully dried and weighed; hence the concentration of the solution was accurately known.

In exactly the same way, and employing the same amounts of reagents, 50 ml. of solution containing 1 gram of unirradiated uranium was prepared. This solution was obtained by partially dissolving a 3-gram piece of uranium cut from the same disk from which Sample B had been obtained.

Immediately after both solutions were prepared, three 15 ml. aliquots of each were transferred to separate clean polythene bottles in order to minimize the time of contact with glassware.

One 15 ml. aliquot of the solution containing uranium and its fission products (B-1) was used for the determination of the relative fission yields of the isotopes of cesium, rubidium, strontium, neodymium, and samarium. The uranium was separated from the fission products by precipitation with H_2O_2 as described previously. An accurate account of the quantity of each reagent used was kept.

Another 15 ml. aliquot of irradiated uranium solution was combined with 15 ml. of solution containing unirradiated uranium and the isotopic ratios of the fission products redetermined. This solution (B-2) was treated in exactly the same manner as B-1. The proportion of the reagents to total weight of uranium was identical for the two samples also.

Another 0.6 gram of metal was dissolved from the fragment of unirradiated uranium in the same manner as before, but the solution this time was transferred directly to a tared polythene bottle and accurately weighed. About half of this solution was then poured into another tared bottle and weighed. The other half was reweighed. Thus the concentrations of the two solutions were known accurately without the need of having to calibrate volumetric apparatus. To each of these solutions were added known weights of standard solutions of the elements rubidium, cesium, strontium, neodymium, and samarium. The uranium was then separated from each of the resulting solutions (B-3 and B-4) by the method used for samples B-1 and B-2, with care being taken to keep the reagents in the same proportion to the amount of uranium present as before. The relative abundances of the various isotopes were then redetermined with the mass spectrometer.

(d) Standard Solutions for Isotope Dilution

These solutions were prepared from spectroscopically pure samples of CsCl, RbCl, $SrCO_3$, and Sm_2O_3 purchased from Johnson and Matthey Co. Limited, and highly purified neodymium metal prepared by F.H. Spedding# and obtained through the courtesy of Dr. H.E. Duckworth of this University. The final

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concentration of each of these solutions was intended to be such that 100-200 ml. of each would be sufficient to effect the most favourable change in the isotope ratios of the fission products in 0.3 gram of irradiated uranium. The calculations of the necessary concentrations were based on the fission yields reported by Coryell and Sugarman (36) and the known number of fissions per gram of uranium (from the BF_3-monitor results).

Each of the reagents was heated to constant weight at 110° C., and an appropriate amount (0.1-0.3 gram) weighed out to the nearest 0.01 mg. This was dissolved in 50 ml. of 2 N HCl and diluted to 1000 ml. with distilled water. The specific gravity of the resulting solution was determined by weighing 5 ml. aliquots delivered by a calibrated pipette. Then 1 ml. was transferred to a tared 120 ml. polythene bottle and weighed. This was diluted to the appropriate concentration with 2 N HCl, the whole solution weighed, and the specific gravity determined as before.

The concentrations of the various solutions used for isotope dilution in connection with the analysis of fission products in both the uranium and plutonium samples are given in Table V.

TABLE V

Standard Solutions for Isotope Dilution

Reagent	Concentration (g./g.soln.)	Isotope	Concentration (Atoms/g. soln.) x 10^{15}
CsCl	1.295_8	Cs 133	4.633
RbCl	1.292_0	Rb 85	4.642[a]
		87	1.792
$SrCO_3$	2.536_5	Sr 86	1.020[b]
		88	8.54_2
Nd metal	12.48_5	Nd 142	14.139[c]
		143	6.360
		144	12.446
		145	4.326
		146	8.956
		148	2.982
		150	2.919
Sm_2O_3	6.97_9	Sm 147	3.631[d]
		148	2.716
		149	3.335
		150	1.800
		152	6.418
		154	5.429

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[a] Assuming natural isotopic abundances given by Nier (71)

[b] Assuming natural isotopic abundances given by Nier (72)

[c] Assuming natural isotopic abundances given by Inghram (73)

[d] Assuming natural isotopic abundances given by Inghram (74)

D. Plutonium-239 and Fission Products

(a) Plutonium Samples for Irradiation

Two plutonium samples were irradiated with thermal neutrons (Table VI). One of these (Sample C) was in the form of a Pu-Al alloy weighing approximately 200 mg. and containing 20.2 mg. of plutonium. This was supplied by O.J.C. Runnalls of the Atomic Energy Company of Canada Limited at Chalk River. The sample was irradiated in one of the self-serve positions of the NRX reactor. Approximately one year after irradiation the fission product gases were extracted (59) and the sample was made available for the study of the other fission products.

Sample D was prepared from Sample C by separating the aluminum and fission products from the plutonium on an anion-exchange column complexed with concentrated HCl. It was found that plutonium adhered very efficiently to a column of Dowex-1 (50-100 mesh) anion exchange resin conditioned with 8 N HCl, whereas aluminum and the fission products of interest passed through readily. The acidity of the elutriant was decreased, but no appreciable desorption occurred until 4 N HCl was used. By this time only zirconium and ruthenium activities were detected on the column. Hence, to keep the volume of solution to a minimum, distilled water was used to remove the remaining plutonium. Two such column separations were made in all. The resulting plutonium was completely free from aluminum and had negligible quantities of the fission products to be studied later.

A small sample of this purified plutonium (as PuO_2) was sealed in a quartz capsule and irradiated in the Chalk River pile (NRX). The sample was allowed to "cool" for about two months before fission product studies were undertaken.

TABLE VI

Irradiation Data for Plutonium Samples

Sample	Chemical Form	Weight of Pu (mg.)	Nuclear Reactor	Irradiation Time (hours)	Average Neutron Flux (n./cm^2/sec.)
C	Pu-Al alloy	20.2	NRX (Chalk River)	67	6×10^{12}
D	PuO_2	1.65	NRX	329	2.9×10^{13}

(b) Chemical Procedures

(i) Treatment of Sample C

Data provided by O.J.C. Runnalls (75) on the purity of the plutonium used to make the Pu-Al alloy showed that barium, calcium, and sodium were each present to about 0.02% by weight of plutonium. This meant that the fission products were likely badly contaminated with natural cesium, rubidium, and strontium, and also possibly the rare earths. Hence, no unusual steps were taken to keep contamination from reagents to the low limits required for the analysis of uranium Sample B, for example.

The alloy was dissolved in a small volume of conc. HCl and the solution evaporated to dryness. The residue was dissolved with distilled water and $Al(OH)_3$ (as well as $Pu(OH)_4$) precipitated by the addition of sufficient quantities of NH_3. The supernatant solution, after centrifugation, contained enough cesium, rubidium, and strontium for mass spectrometric analysis. This was evaporated and the fission products transferred to the mass spectrometer in the usual manner. The hydroxide precipitate was washed with distilled water and dissolved with 8 N HCl. The solution was transferred to a pyrex column, 1 sq. cm. in diameter, packed to a height of 15 cm. with 50-100 mesh Dowex-1 anion exchange resin conditioned with 8 N HCl. Complete removal of the plutonium was achieved. The eluent, containing the bulk of aluminum and fission products, was evaporated to dryness. The residue was taken up with distilled water, and a solution containing 3 mg. of $FeCl_3$ added. Sufficient NaOH solution was added to precipitate $Fe(OH)_3$ and to dissolve the $Al(OH)_3$. After separation of the $Fe(OH)_3$ by centrifuging and washing with dilute NaOH, it was found that the bulk of the rare earth activities had been coprecipitated. The iron was removed from the rare earth fission products on a small (0.1 sq. cm. x 5 cm.) column containing Dowex 1 resin conditioned with 8 N HCl (76). The rare earths were analyzed with the mass spectrometer in the usual manner.

(ii) Treatment of Sample D

The quartz capsule containing the irradiated PuO_2 was carefully washed on the outside with a solution of HCl, then rinsed with distilled water, and transferred to a clean polythene bottle, where it was broken with a sturdy glass rod. A few cc. of concentrated HCl (specially purified) were added and the bottle heated in a water bath for several hours. No appreciable dissolution of the PuO_2 occurred. An investigation of the literature revealed that PuO_2, prepared by igniting $PuCl_4$ (as this had been), resulted in a product which was chemically very inert (77), and that prolonged treatment with H_2SO_4 and/or HBr was required. This was indeed found to be the case. After more than a week of treatment, alternately with 5 cc. of H_2SO_4 (reagent grade) and 5 cc. of HBr (reagent grade distilled directly into polythene), only about one half of the total activity in the capsule was taken into solution. This was diluted to 60 ml. in a graduated polythene bottle, and 10 ml. aliquots taken for analysis.

The separation of plutonium from its fission products was successfully achieved by precipitating the plutonium as PuO_4 with 30% H_2O_2. In order to get more efficient separation about 40 mg. of pure uranium were added to 10 ml. of fission product solution before precipitation. The comparatively large amount of UO_4 precipitated served as a very efficient carrier and blanket for the plutonium. Most of the fission products were retained in excellent yield in the supernatant solution. The latter was evaporated in a clean vycor beaker to a drop which was then transferred to the filament of the mass spectrometer, evaporated to dryness, and the various fission product elements analyzed in sequence as discussed before.

(c) Isotope Dilution

Two 10 ml. aliquots of Sample D were taken for isotope dilution. One of these was used solely for the purpose of estimating the concentration of each of the fission products to be studied, since it was not sufficiently well known how much of the irradiated plutonium sample had actually gone into solution. The results of this analysis were used to plan the next isotope dilution in a way that would lead to much more accurate results. The procedure used in connection with this latter sample was as follows. Samples of the standard solutions given in Table V, weighing between 0.6 gram and 4 grams (depending on the element), were weighed directly into a tared polythene bottle and well mixed. Approximately 0.1 gram of this solution was weighed into another polythene bottle, then 10 ml. of fission product solution and 1 ml. of solution containing 40 mg. of uranium were added. The resulting solution was well agitated and, after standing for sufficient time to ensure complete equilibration of the various ionic species, was transferred to a vycor crucible and evaporated to dryness. The residue was dissolved with 2-3 ml. of distilled water, the solution transferred to a 15 ml. centrifuge tube, and 2 drops of H_2O_2 (30%) added. The precipitate was centrifuged out, and the solution, after being tested for complete removal of uranium by the addition of another drop of H_2O_2, was prepared for mass spectrometric analysis in the usual manner.

Another 10 ml. aliquot of fission product solution was treated in identical fashion apart from the addition of the standard reagents. The isotope ratios obtained for this sample were used as the reference points for the isotope dilution results in making the fission yield calculations.

EXPERIMENTAL RESULTS

A. Fission Yields of Uranium-235

The relative yields of the isotopes of cesium, neodymium, and samarium in both Samples A and B, and also those of strontium and rubidium isotopes in Sample B were determined with high precision. A fairly good measurement of the relative yields of cerium isotopes was also achieved. In addition isotope dilution was carried out on Sample B as described in the Experimental Section, and excellent reproducibility obtained. The characteristics of the various parts of Sample B used in connection with this work are given in Table VII. The weights of standard solutions taken for isotope dilution are given in Table VIII.

The total number of fissions per gram of uranium (Sample B) was determined from the results of the BF_3-monitor experiment described in the Experimental Section. All fission yields reported in the present section as per cents have been based on this value, namely 7.55×10^{16} fissions per gram of uranium (see Appendix A). A critical evaluation of the accuracy of this result has been reserved for the Discussion.

TABLE VII

Samples of BF_3-Monitored Uranium Used for Determination of Fission Yields

Sample	Characterization	Weight of U (gram)	No. of Fissions# ($\times 10^{16}$)
B-1	For Relative Fission Yields	0.3261	2.462
B-2	For Contamination Correction	0.9148	2.462
B-3	For Isotope Dilution	0.3669	2.770
B-4	For Isotope Dilution	0.3051	2.304

\# Based on BF_3 results

TABLE VIII

Isotope Dilution Data for BF_3-Monitored Uranium Samples

Element Involved in Isotope Dilution	Weight of Standard Soln. Added (gram)		No. of Atoms of Element Added ($\times 10^{15}$)	
	Sample B-3	Sample B-4	Sample B-3	Sample B-4
Rubidium	0.2046	0.2045	1.316	1.316
Cesium	0.2046	0.2053	0.948	0.951
Strontium	0.1029	0.1009	1.065	1.044
Neodymium	0.1005	0.1039	5.240	5.415
Samarium	0,1020	0.1004	1.229	1.209

(a) Cesium

(i) Relative Fission Yields

The results of mass spectrometric analyses of the relative abundances of the cesium isotopes from fission in both Samples A and B have been recorded in Table IX along with their respective Calendar Times[#].

The cesium isotopes in Sample A were determined several years ago by Wiles et al (55). The average of the data given for sample runs 1-1 and 1-2 of reference 55 has been included in Table IX for comparison. It is readily seen that, although the agreement between the present data and that of Wiles is excellent with regard the Cs 133/135 ratio, the Cs 137/135 ratio has changed considerably due to the decay of Cs^{137}. The half-life of Cs^{137} has been given as 33 years (78) (55). To be consistent with the present data, the half-life must be no more than 30 years. For example, correction of the 133/137 ratio using 33 yr. as the half-life gives 1.109 as the final value for this ratio, which is about 3% higher than that obtained for younger samples (55) (79). A direct calculation using the present data and that of Wiles (in comparing 137/135 for the two) gives a value of 29.6 yr. A critical examination of all cesium results obtained in this laboratory indicates a value between 28 and 29 yr. With 29 yr. as the half-life the corrected 133/137 ratio for Sample A becomes 1.083 while the

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[#] In all cases the Calendar Time has been taken to mean the time from the beginning of the irradiation period to mass spectrometric analysis.

TABLE IX

Relative Fission Yields of Cesium Isotopes

Sample	Calendar Time (years)	Cs Isotope	Mass Spec. Isotope Ratio	Ratio Corr.for Decay	Ratio Corr.for Capture
A	7.91	133	1.108 ± 0.003[a]	1.083	1.083
		135	1.000	0.980	1.050[b]
		137	0.844 ± 0.003	1.000	1.000
A	4.66	133	1.110 ± 0.005[c]	1.089	1.089
		135	1.000	0.981	1.050[b]
		137	0.913 ± 0.005[c]	1.000	1.000
B-1	2.36	133	1.398 ± 0.003	1.080	1.080
		135	1.000	0.773	1.050[b]
		137	1.223 ± 0.003	1.000	1.000
B-2	2.37	133	1.399 ± 0.005	1.079	1.079
		135	1.000	0.771	1.050[b]
		137	1.226 ± 0.004	1.000	1.000

[a] Standard deviation of a series of mass spectrograms.

[b] Cs^{135}/Cs^{137} obtained for thermal column sample with only very small correction necessary (79).

[c] The average of data given for Samples 1-1 and 1-2 in Table IV of ref. 55.

corresponding ratio for sample B is 1.080. These results not only agree extremely well between themselves, but are also in excellent agreement with the value 1.080 recently obtained by Melaika (79) for a comparatively young sample.

The 133/135 ratio as obtained mass spectrometrically has to be corrected for neutron capture in Xe^{135}, a 9.13 hour

(80) isotope with a cross-section reported to be 3.5×10^6 barns (31). This can be done in either of two ways: 1) by comparing the measured Xe^{136}/Xe^{131} ratio for this sample with the corresponding ratio for a sample in which there was supposedly no neutron capture in Xe^{135}, assuming a yield of Xe^{135} relative to Xe^{136} or 2) by making a direct calculation using the known flux, the time of irradiation, and the value of the cross-section. In this laboratory, method 1) has been employed with considerable success. Using samples in which the capture was fairly small, Wiles et al (55) have been able to evaluate the 133/135 ratio as 1.035. Recently Melaika (79), using samples in which the change in the 133/135 ratio due to neutron capture was less than 1%, determined this ratio to be 1.029, which not only agrees with the value above, but also is likely to be very accurate.

In the present case, no attempt was made to improve this value. Instead, by adopting the value of 133/135 = 1.029, and taking advantage of the known flux as given by the BF_3 monitor, it was possible to calculate the cross-section of Xe^{135}. The value obtained was $(3.3 \pm 0.2) \times 10^6$ barns, in excellent agreement with the only value reported in the literature (31). The details concerning this calculation are given in Appendix B.

(ii) <u>Results of Isotope Dilution</u>

From the mass spectrometric data for Samples B-1 and B-2 given in Table IX, it is readily seen that there was no appreciable Cs^{133} in the unirradiated uranium or in the reagents. Hence, the Cs^{133}/Cs^{135} value obtained is the fission ratio uncorrected for capture in Xe^{135}. The effects of isotope dilution on this ratio can be used to evaluate the Cs^{133} yield directly. The mass spectrometric results needed for the calculation of the Cs^{133} yield are given in Table X.

TABLE X

The Fission Yield of Cs^{133}

Sample	Cs^{133}/Cs^{135}		No. of atoms Cs^{133} added (x 10^{14})	Fission Yield[a] (%)
	Before i.d.	After i.d.		
B-3	1.398	2.167	9.48	6.22
B-4	1.398	2.330	9.51	6.19
			Average	6.21 ±0.02

[a] Based on BF_3 results

(b) Rubidium

(i) Relative Fission Yields

The mass spectrometric data for Sample B is given in Table XI.

The difference in the Rb^{85}/Rb^{87} ratio for B-1 and B-2 could be due to the presence of a small amount of natural rubidium in the uranium or in the reagents or both. Actually, it was found that most of it was in the uranium. The uranium and reagents were separately analyzed using isotope with a standard solution of fission rubidium (Rb^{85}/Rb^{87} = 0.495). The results

TABLE XI

Mass Spectrometric Data for Rubidium Isotopes in BF_3-Monitored Uranium Samples

Sample	Calendar Time (days)	Rb Isotope	No. of atoms of Isotope added[1]	Mass-Spectrometric Isotope Ratios
B-1	902	85		0.4370 ± 0.0013
		87		1.000
B-2	908	85		0.4589 ± 0.0037
		87		1.000
B-3	932	85	9.497×10^{14}	1.207 ± 0.003
		87	3.666×10^{14}	1.000
B-4	939	85	9.479×10^{14}	1.308 ± 0.002
		87	3.659×10^{14}	1.000

---

[1] Assuming for natural rubidium, Rb^{85} = 72.15%, Rb^{87} = 27.85% (71).

obtained are given in Table XII.

TABLE XII

Concentration of Natural Rubidium in Uranium Metal and Reagents

Reagent	Amount	No. of atoms of Rb^{85}	No. of atoms of Rb^{87}
HCl (evap. in vycor)	1 ml.	2.6×10^{11}	1.0×10^{11}
H_2O_2(30%)	1 ml.	2.1×10^{12}	8.0×10^{11}
Uranium	1 gm.	3.6×10^{13}	1.4×10^{13}

The actual ratio of Rb^{85}/Rb^{87} in sample B, had there been no contamination, was determined in two ways: 1) by using the results of B-1 and B-2 in the manner of Wiles et al (55) and Parker (61) and 2) by making use of the data in Table XII and the total concentration of rubidium in B-1 based on the results of isotope dilution (B-3 and B-4). The two results obtained were as follows:

$$Rb^{85}/Rb^{87} = \begin{array}{l} 1)\ 0.423 \\ 2)\ 0.418 \end{array}$$

To get the actual fission yield of Rb^{85}, a correction had to be applied due to the following properties of Kr^{85}, the precursor of Rb^{85} in the decay chain. This isotope (Kr^{85}) has two isomers; one with a half-life of 4.36 hours (81) and the other with a half-life of 10.27 years (82). The amount decaying through the 10.27 yr. isomer has been measured to be 21.9% of the total yield of Kr^{85} (83). Since this had only partially decayed in the present sample, the yield of Rb^{85} observed was substantially less than the actual yield of mass 85 in fission. The appropriate correction factor was found to be 1.226.

The calculated fission yields of Rb^{85} and Rb^{87} are given in Table XIII.

TABLE XIII

The Fission Yields of Rb^{85} and Rb^{87}

Sample	Calendar Time (years)	Rb Isotope	Observed No. of atoms ($\times 10^{14}$)	No. of atoms from fission only ($\times 10^{14}$)[a]	Calculated Fission Yield (%)
B-3	2.55	85	2.879	3.410	1.23
		87	6.589	6.551	2.36
B-4	2.57	85	2.354	2.786	1.21
		87	5.387	5.356	2.32
				Average 85	1.22 ± 0.01
				87	2.34 ± 0.02

[a] After correction for contamination (from results of B-1 and B-2) and for Kr^{85} branching as discussed in text.

(c) Strontium

The pertinent mass spectrometric data for the calculation of the fission yields of Sr^{88} and Sr^{90} in Sample B are given in Tables XIV and XV. The results for B-1 and B-2 indicate that a significant amount of natural strontium was present. However, the amount of Sr^{88} from contamination by the natural element could be evaluated through the observed relative abundance of Sr^{86}, which is not formed in fission.

(d) Neodymium

(i) Relative Yields

Sample A (Oak Ridge) was especially interesting in connection with the relative yields of the neodymium isotopes be-

TABLE XIV

Relative Fission Yields of Strontium Isotopes

Sample	Calendar Time (days)	Sr Isotope	Mass.Spec. Ratio	Corrected for Contamination[1]	Corrected for Decay[2]
B-1	903	86	0.0100 ± 0.0003	.....	.....
		88	0.740 ± 0.007	0.656	0.602
		90	1.000	1.000	1.000
B-2	909	86	0.0241 ± 0.0008	.....	.....
		88	0.858 ± 0.012	0.656	0.602
		90	1.000	1.000	1.000

[1] Assuming for natural strontium, $Sr^{88}/Sr^{86} = 8.37$ (72).

[2] Assuming half-life for Sr^{90} to be 19.9 yr. (84).

TABLE XV

The Fission Yield of Sr^{90}

Sample	Calendar Time (days)	Sr^{88}/Sr^{90} Before i.d.	Sr^{88}/Sr^{90} After i.d.	No. of atoms Sr^{88} added ($\times 10^{14}$)	Fission Yield[a] (%)
B-3	933	0.740	1.376	8.79	5.44
B-4	940	0.740	1.464	8.62	5.64
				Average	5.54 ± 0.10

[a] Corrected for decay assuming half-life of 19.9 yr. (84).

cause of its age (8 years). In this sample Ce^{144}(half-life 282 days (85)) had completely decayed to Nd^{144}. Hence no decay correction to the latter had to be applied. The mass spectrometric data and calculated relative fission yields of the neodymium isotopes for Sample A are given in Table XVI. Also included in this table are the corresponding results for Sample B. The latter, being considerably younger, required a correction to mass 144 due to the fact Ce^{144} had only partially decayed. Sample B, however, had the virtue of being free from natural neodymium whereas Sample A was appreciably contaminated. Nevertheless, the final corrected results for the two samples are in excellent agreement.

(ii) Results of Isotope Dilution

Since the yields of the various neodymium isotopes relative to Nd^{143} were accurately known (Table XVI), it was only necessary to evaluate the fission yield of the latter by isotope dilution. The results obtained are given in Table XVII.

TABLE XVI

Relative Fission Yields of Neodymium Isotopes

Sample	Calendar Time (days)	Nd Isotope	Mass Spec. Ratio	Corrected for Contamination[1]	Corrected for decay[2]
A	2950	142	0.0168 ± 0.0006	.....	.....
		143	1.000	1.000	1.000
		144	0.931 ± 0.002	0.923	0.923
		145	0.666 ± 0.002	0.666	0.666
		146	0.514 ± 0.002	0.507	0.507
		148	0.284 ± 0.001	0.282	0.282
		150	0.113 ± 0.001	0.110	0.110
B-1	903	142	....	.....	.....
		143	1.000	1.000	1.000
		144	0.819 ± 0.010	0.819	0.924
		145	0.667 ± 0.008	0.667	0.667
		146	0.503 ± 0.006	0.503	0.503
		148	0.278 ± 0.004	0.278	0.278
		150	0.106 ± 0.002	0.106	0.106
B-2	910	142	....	.....	.....
		143	1.000	1.000	1.000
		144	0.820 ± 0.006	0.820	0.923
		145	0.665 ± 0.008	0.665	0.665
		146	0.504 ± 0.006	0.504	0.504
		148	0.280 ± 0.004	0.280	0.280
		150	0.110 ± 0.002	0.110	0.110
			Average	143	1.000
				144	0.923
				145	0.666
				146	0.505
				148	0.280
				150	0.109

---

[1] Assuming isotopic abundance data given by Inghram (73).

[2] Assuming half-life of Ce^{144} to be 282 days (85).

TABLE XVII

The Fission Yield of Nd^{143}

Sample	Nd Isotope	Ratio before i.d.	No.of atoms of isotope added (x 10^{15})	Ratio after i.d.	Calculated Fission Yield Nd^{143} (%)
B-3	142	.....	1.421	0.664	5.42
	143	1.000	0.639_2	1.000	
	142	.....	1.421	0.572	5.43[a]
	144	1.000	1.251	1.000	
	142	.....	1.421	0.857	5.43[b]
	146	1.000	0.900_1	1.000	
B-4	142	.....	1.469	0.761	5.51
	143	1.000	0.660_6	1.000	
	142	.....	1.469	0.631	5.47[a]
	144	1.000	1.206	1.000	
	142	.....	1.469	0.949	5.32[b]
	146	1.000	0.930_3	1.000	
				Average	5.43 ± 0.04

[a] Using the 144/143 ratio given in Table XVI.

[b] Using the 146/143 ratio given in Table XVI.

(e) Samarium

(i) Relative Fission Yields

Because of the long cooling period of Sample A, most of the fission product Pm^{147} (half-life 2.6 years (85)) had decayed to Sm^{147}; thus necessitating only a minor correction to the mass spectrometrically observed yield at this mass. Also, because of the fact that this sample had been irradiated under conditions of low neutron flux (6×10^{11} neutrons/cm.^{2}/Sec.), the fission yield observed at mass 149 had not been seriously influenced by neutron capture in Sm^{149} ($\sigma_{149} \doteq 50{,}000$ barns (86)) nor was there significant capture in Sm^{151} ($\sigma_{149} \doteq 7{,}000$ barns (86)). In addition, the sample was sufficiently old to show appreciable decay in Sm^{151}(half-life 73 years (87)).

The BF_3-monitored sample (B), on the other hand, had the following characteristics. Due to the higher flux (2.3×10^{12} neutrons/cm.^{2}/sec.), there had been considerable capture in both Sm^{149} and Sm^{151}. However, the sample was fairly young (calendar time 2.5 years); consequently the Pm^{147} was only half gone as a result of decay whereas the decay of Sm^{151} was virtually negligible.

These large differences in the characteristics of the two samples made it possible, by comparing the mass spectrometric data for the two, to calculate the half-life of Pm^{147}, the capture cross-sections of Sm^{149} and Sm^{151} to pile neutrons, and an approximate half-life for Sm^{151}. The results obtained are given below, but the details of the calculations have been relegated to part C of the Appendix.

1) The half-life of Pm^{147}	2.52 ± 0.09 yr.
2) The capture cross-section of Sm^{149} to pile neutrons	66,200 ± 2,500 barns
3) The capture cross-section of Sm^{151} to pile neutrons	15,000 ± 5,000 barns
4) The half-life of Sm^{151}	90 yr. (approx.)

This information was used in making the corrections to the mass spectrometric data for samarium as given in Table XVIII.

TABLE XVIII

Relative Yields of Samarium Isotopes

Sample	Calendar Time (years)	Sm Isotope	Mass spec. Isotope Ratio	Corrected for contamination	Corrected	
					For Capture	For Decay
A	2950	147	1.891 ± 0.038	1.903	1.864	2.096[a]
		148	0.013	.....	.....	.....
		149	1.000	1.000	1.000	1.000
		150	0.030 ± 0.007	0.021	.....	.....
		151	0.375 ± 0.010	0.381	0.373	0.397[b]
		152	0.285 ± 0.008	0.256	0.251	0.251
		154	0.095 ± 0.018	0.069	0.068	0.068
B-1 and B-2	910	147	1.286 ± 0.015	1.286	1.025	2.097[a]
		148	.....	.....	.....	
		149	1,000	1.000	1.000	1.000
		150	0.255 ± 0.004	0.255	.....	.....
		151	0.468 ± 0.013	0.468	0.389	0.396[b]
		152	0.335 ± 0.008	0.335	0.251	0.251
		154	0.085 ± 0.003	0.085	0.068	0.068

[a] Assuming half-life of Pm^{147} to be 2.52 years (see text)

[b] Assuming half-life of Sm^{151} to be 90 years (see text)

(ii) Results of Isotope Dilution

The mass spectrometric data used for the calculation of the absolute yield of Sm^{149} are given in Table XIX. The yield was calculated directly using the 149/148 ratio and indirectly from the 147/148 ratio making use of the mass spectrometric value of Sm^{147}/Sm^{149} for Sample B given in Table XVIII. The yields reported in Table XIX have been corrected for capture in Sm^{149} by adding together the observed yields for Sm^{149} and Sm^{150}.

TABLE XIX

The Fission Yield of Sm^{149}

Sample	Sm Isotope	Ratio before i.d.	No. of atoms of isotope added ($\times 10^{14}$)	Ratio after i.d.	Calculated Fission Yield Sm^{149} (%)
B-3	147	1.000	3.704	1.000	1.094
	148	.....	2.770	0.407	
	148	.....	2.770	0.478	1.083
	149	1.000	3.402	1.000	
B-4	147	1.000	3.645	1.000	1.053
	148	.....	2.726	0.445	
	148	.....	2.726	0.516	1.056
	149	1.000	3.348	1.000	
				Average	$1.07_2 \pm 0.01_7$

(f) Cerium

Preliminary values for Ce^{140}/Ce^{142} and Ce^{144}/Ce^{142} have been obtained. These are given in Table XX.

TABLE XX

Relative Fission Yields of Cerium Isotopes

Ce Isotope	Mass Spec. Ratio	Corrected for decay
140	1.05	1.05
142	1.00	1.00
144	0.101	0.89_4[a]

[a] Assuming half-life of Ce^{144} to be 282 days (85).

B. Fission Yields of Plutonium-239

The Pu-Al alloy (Sample C) was found to be badly contaminated with natural cesium, rubidium, and strontium. The Cs^{133}/Cs^{137} ratio, for example, was approximately 16 whereas the Rb^{85}/Rb^{87} ratio was 1.6. The strontium separated from the sample was predominantly the natural element. The rare earth fission products, on the other hand, suffered comparatively little contamination. Hence, quite accurate measurements of the yields of neodymium and samarium isotopes were possible.

Very good fission yield data were obtained with the purefied plutonium sample (D) with regards the rare earth fission products and strontium. However, the rubidium was still contaminated and also to a certain degree the cesium.

(a) Strontium

Several independent mass spectrometric analyses of the strontium isotopes in Sample D were made. The results are given in Table XXI.

Since measurements were made at various intervals over a period of a few weeks, it was possible to follow the decay of the Sr^{89}/Sr^{90} ratio and thus evaluate the half-life of Sr^{89}. The data for this is shown in Table XXII. The value obtained (52.8 days) was used in making the decay correction for the Sr^{89} yield in Table XXI.

TABLE XXI

Relative Fission Yields of the Strontium Isotopes

Sample	Calendar time (hours)	Sr Isotope	Mass spec. ratio	Corrected for contamination[a]	Corrected for Decay[b]
D-1	1745	86	0.186 ± 0.002	.....	
		88	2.242 ± 0.020	0.685	0.680
		89	0.327 ± 0.004	0.327	0.775
		90	1.000	1.000	1.000
D-2	2122	86	0.205 ± 0.006	.....	.....
		88	2.407 ± 0.040	0.690	0.685
		89	0.268 ± 0.003	0.268	0.780
		90	1.000	1.000	1.000
D-3	2150	86	0.201 ± 0.004	.....	.....
		88	2.382 ± 0.060	0.700	0.694
		89	0.266 ± 0.005	0.266	0.786
		90	1.000	1.000	1.000
				Average 88	0.686 ± 0.005
				89	0.780 ± 0.004
				90	1.000

[a] Assuming Sr^{88}/Sr^{86} in nature is 8.37 (72).

[b] Assuming half-life of Sr^{89} is 52.8 days and for Sr^{90}, 19.9 years (84).

TABLE XXII

The Half-life of Sr^{89}

Sr^{89}/Sr^{90}	Symbol	Calendar Time (hours)	Ratio N/N_0[1]	Elapsed time, t (hours)	Half-life, $T_{\frac{1}{2}}$ (days)
0.327	(a)	1745	(a)/(e)	423	49.8
0.303	(b)	1892	(a)/(d)	405	55.8
0.268	(c)	2122	(a)/(c)	377	54.6
0.266	(d)	2150	(b)/(e)	276	47.3
0.256	(e)	2168	(b)/(d)	258	56.7
				Average	52.8 ± 3.4

[1] From decay equation $N/N_0 = e^{-0.693t/T_{\frac{1}{2}}}$

(b) Neodymium

Accurate measurements of the relative fission yields of the neodymium isotopes in both Samples C and D were made. The results are given in Table XXIII.

TABLE XXIII

Relative Fission Yields of Neodymium Isotopes

Sample	Calendar Time (days)	Nd Isotope	Mass Spec. Ratio	Corrected for contamination	Corrected for Decay and Capture
C	565	142	0.322 ± 0.002	.....	.....
		143	1.000	1.000	1.000
		144	0.821 ± 0.002	0.628	0.836[a]
		145	0.685 ± 0.004	0.685	0.685
		146	0.674 ± 0.001	0.550	0.550
		148	0.385 ± 0.002	0.371	0.371
		150	0.246 ± 0.002	0.211	0.211
D	88	142	0.118	.....	.....
		143	1.000	1.000	1.000[b]
		144	0.250	0.154	0.845[a]
		145	0.690 ± 0.003	0.690	0.686
		146	0.616 ± 0.003	0.571	0.568
		148	0.385 ± 0.003	0.380	0.378
		150	0.232 ± 0.001	0.219	0.217

[a] Assuming half-life of Ce^{144} is 282 days (85).

[b] Assuming capture cross-section of Nd^{143} is 334 barns (95).

(c) Samarium

The relative fission yields of the samarium isotopes in Samples C and D are given in Table XXIV.

TABLE XXIV

Relative Fission Yields of Samarium Isotopes

Sample	Calendar Time (days)	Sm Isotope	Mass spec. ratio	Corrected for contamination	Corrected for Capture and Decay
C	567	147	0.573 ± 0.007	0.537	1.464[a]
		148	0.053 ± 0.004	.....	.....
		149	1.000	1.000	1.000
		150	0.091 ± 0.005	0.060	.....
		151	0.674 ± 0.013	0.721	0.694[b]
		152	0.632 ± 0.012	0.542	0.497[b]
		154	0.284	0.178	0.168
D	88	147	0.123	0.119	1.418[a]
		148	0.004	.....	.....
		149	1.000	1.000	1.000
		150	0.399 ± 0.003	0.398	.....
		151	0.794 ± 0.014	0.798	0.619[b]
		152	0.766 ± 0.014	0.760	0.496[b]
		154	0.290 ± 0.006	0.283	0.202

[a] Assuming half-life of Pm^{147} to be 2.52 years (Appendix C).

[b] Assuming σ_{149} to be 66,200 barns and σ_{151} to be 15,000 barns (Appendix C).

(d) Cesium

The mass spectrometric data for the Cesium isotopes in samples C and D are given in Table XXV.

Several factors prevented a very accurate measurement of the yields of the cesium isotopes. In both samples (C and D) there was considerable neutron capture in Xe^{135}. This was especially large in Sample D since the flux during irradiation was over 10^{13} neutrons/cm^2/sec.

In addition, the Cs^{133}/Cs^{137} ratio for Sample D was found to change with time due to contamination during handling and sample preparation. The lowest value found was 1.168. Since this was much higher than expected on the basis of the xenon data for same sample obtained by Fleming (59), the following little experiment was done. The irradiated plutonium which had not dissolved during the preparation of Sample D for analysis was treated with 5 cc. of HBr (freshly distilled into polythene) and the cesium isotope ratios in the resulting solution (D') determined using the same technique as for Sample D. The Cs^{133}/Cs^{137} ratio for Sample D' was found to be 0.821. In addition, the Cs^{135}/Cs^{137} ratio was found to be 0.367 ± 0.004 as compared to 0.384 ± 0.002 for Sample D. This difference in the Cs^{135}/Cs^{137} ratios was considered to be significant and possibly indicative of some escape of Xe^{135} (9.13 hour) during sample irradiation. If some Xe^{135} had escaped from the plutonium and, on decaying, deposited on the walls of the quartz capsule as Cs^{135}, incomplete dissolution of the plutonium would have resulted in a solution slightly enriched in Cs^{135} as observed. On this basis, one would expect the escape of Xe^{133} to be very significant because of its comparatively long half-life (5.27 days). This might account for the large discrepancy (about 30%) between the Cs^{133}/Cs^{137} ratios for Samples D and D'.

Hence, only a rough estimate of the Cs^{133}/Cs^{137} fission

TABLE XXV

Relative Fission Yields of Cesium Isotopes

Sample	Calendar Time (years)	Cs Isotope	Mass Spec. Isotope Ratio	Corrected Relative Yields
C	1.44	133	15.7	....
		135	0.866 ± 0.002	1.04[a]
		137	1.000	1.00[b]
D	0.20	133	1.168 ± 0.002	0.90 ±0.10[c]
		135	0.384 ± 0.002	1.01[d]
		137	1.000	1.00
D'	0.20	133	0.821 ± 0.009	0.90 ±0.10[c]
		135	0.367 ± 0.004	1.01[d]
		137	1.000	1.00

[a] Corrected for capture using corresponding Xe data (59) and assuming fission yield of mass 135 to be equal to that of mass 136.

[b] Corrected for decay assuming half-life of Cs^{137} to be 29 years.

[c] See text.

[d] Assuming neutron flux to be 3.53×10^{16} neutrons /hr. (based on samarium data) and cross-section of Xe^{135} to be 3.3×10^{6} barns.

ratio could be made. The average of the two results (D and D') was 0.995. This was likely a little high due to contamination. Therefore the true Cs^{133}/Cs^{137} ratio was taken to be 0.90 ± 0.10. On the other hand, the true Cs^{135}/Cs^{137} ratio was taken to be $(0.367 + 0.384)/2$ or 0.376.

The Cs^{135}/Cs^{137} ratio for Sample C was corrected in the following manner. The Cs^{133}/Cs^{137} ratio for this sample was assumed to be the same as that for Sample D, namely 0.90 after correction for decay in Cs^{137}. The yield of Cs^{133} was arbitrarily taken to be 6.2% from a plot of the xenon isotope yields using the data of Fleming (59) given in Table XXVI. The corresponding yield for Cs^{137} was, therefore, 6.9%, and the observed yield of Cs^{135}, 5.8%. Then it was assumed that actual fission yield of Cs^{135} was the same as that for Xe^{136}. On this basis, the Cs^{135} yield should have been half the sum of the observed yields of Cs^{135} and Xe^{136}, namely $(5.8 + 8.6)/2$ or 7.2%. This gives a value of 1.04 for the final Cs^{135}/Cs^{137} fission ratio (Table XXV).

A more direct method of correcting the Cs^{135}/Cs^{137} was adopted for Sample D. In this case the neutron flux during irradiation could be calculated with fair accuracy from the corresponding samarium data on the basis of the observed amount of capture in Sm^{149} (as evidenced by the amount of Sm^{150} formed), assuming a cross section of 66,200 barns (see Appendix C). The amount of capture to be expected in Xe^{135} as a result of this flux (3.53×10^{16} neutrons/cm^2./hour) and a cross-section of

3.3×10^6 barns was then calculated with the use of equation 1 of Appendix B. The Cs^{135}/Cs^{137} ratio on correction became 1.01, in satisfactory agreement with the value above (Table XXV).

TABLE XXVI

Fission Yields of Xenon Isotopes

Isotope	Fission Yield (%)[a]
131	3.61
132	5.04
134	7.16
136	8.58

[a] Taken from data given by Fleming (59).

(e) Cerium and Barium

Preliminary values for Ce^{144}/Ce^{142} and Ba^{140}/Ba^{142} were obtained. These are given in Table XXVII. The error in these results may be as much as 5%.

TABLE XXVII

Relative Fission Yields of Cerium and Barium Isotopes

Sample	Calendar Time (days)	Isotope	Mass Spec. Isotope Ratio	Corrected for Contamination	Corrected for Decay
D	79	Ce 140	2.59	.....	.....
		142	1.00	1.00	1.00
		144	0.59_9	0.59_9	0.71_7[b]
D	73.2	Ba 134	0.0223	.....	.....
		135	0.0580	.....	.....
		136	0.0732	.....	.....
		137	0.1013	.....	.....
		138	1.000	1.000[a]	1.000
		140	0.00796	0.0227	0.8_{32}[c]

[a] Assuming natural isotopic abundances given by Nier (96).

[b] Assuming half-life of Ce^{144} to be 282 days (85).

[c] Assuming half-life of Ba^{140} to be 12.80 days (97).

(f) Results of Isotope Dilution

The amount of Cs^{133}, Nd^{143}, and Sm^{149} in an aliquot of fission product solution (D) was determined by isotope dilution in the manner outlined in the Experimental Section. The results obtained are given in Table XXVIII.

TABLE XXVIII

Isotope Dilution Data for Sample D

Isotopes Compared	M.S. Isotope Ratio		No. of atoms added (x 10^{14})	Fission Yield		
	Before i.d.	After i.d.		Iso-tope	No. of atoms (x10^{14})	Relative to Nd^{143}
Cs 133	1.229	2.283	2.100	Cs 137	1.992	2.67
137	1.000	1.000	.....			
Nd 142	0.118	1.228	1.870	Nd 143	0.761	
143	1.000	1.000	0.841			
Nd 144	0.250	1.163	1.646	Nd 143	0.732	
143	1.000	1.000	0.841			
Nd 146	0.613	1.036	1.185	Nd 143	0.742	
143	1.000	1.000	0.841			
			Average	Nd 143	0.745 ± 0.011	1.000
Sm 147	0.123	0.826	0.491	Sm 149	0.235[a]	
149	1.000	1.000	0.451			
Sm 148	0.004	0.592	0.367	Sm 149	0.236	
149	1.000	1.000	0.451			
Sm 151	0.794	0.211	.....	Sm 149	0.228	
149	1.000	1.000	0.451			
Sm 152	0.778	1.620	0.868	Sm 149	0.226	
149	1.000	1.000	0.451			
			Average	Sm 149	0.231 ± 0.004	0.310

[a] Corrected for neutron capture in Sm^{149}.

DISCUSSION

A critical examination of the conditions existing during the irradiation of Sample B, has shown that the total number of fissions calculated on the basis of the BF_3 data is subject to several small corrections. These arise as follows:

1) During the irradiation there was some fission of U^{238} due to the presence of a small but nevertheless significant percentage of fast neutrons. It is estimated that this accounted for about 2.5% of the fission products observed in Sample B.

2) A calculation taking into account the neutron energy distribution in the position of the NRX pile where Sample B was irradiated and the variation of the cross-sections for boron and uranium with neutron energy has shown (99) that the number of fissions based on the data given in Appendix A was high by about 2%.

3) The absorption of neutrons by the uranium made the thermal neutron flux within the sample somewhat lower than that a few centimeters away. It is impossible to determine just how this flux was related to that within the capsule of boron trifluoride. However, a simplified calculation treating the sample as a sphere of equivalent dimensions has indicated that the flux inside the sample might have been lower than that influencing the boron by as much as 3%.

4) Approximately 0.5 per cent of the U^{235} originally present in the sample was consumed during the irradiation.

Although some of these factors were mutually compensating, the overall result was to make the calculated number of fissions about 3 per cent too high. Therefore, the fission yields reported in the previous section should, on this basis, all be raised by 3 per cent.

The values obtained on making this correction are given in the first column of Table XXIX. The limits of error quoted for these figures are based entirely on the statistical error in the mass spectrometric measurements of the B^{10}/B^{11} change. The actual error may be even larger.

Hence, in view of the fact that this group of fission products accounts for more than 75 per cent of the total fission yield in the heavy mass region, it becomes attractive to calculate the individual yields by normalizing the whole group to the difference between 100 per cent and the sum of the yields of the heavy fragments. Values for the latter as reported in the literature are given in Table XXX. When these are taken for the normalization, the results listed in the second column of Table XXIX are obtained.

The fact that the two sets of data agree within the probable error in the flux measurement is a good

TABLE XXIX

The Yields of Heavy Fragment Masses in the Thermal Neutron Fission of U^{235} From the Present Work

Isotope	Fission Yield (%)	
	Based on BF_3 flux measurement (corrected)	Normalized to a total yield of 100%
Xe 131	2.83 ± 0.10[a]	2.92
Xe 132	4.23 ± 0.14	4.37
Xe Cs 133	6.40 ± 0.22	6.61
Xe 134	7.74 ± 0.26	8.00
Cs 135	6.22 ± 0.21	6.43
Xe 136	6.17 ± 0.21	6.37
Cs 137	5.93 ± 0.20	6.13
Ce 140	6.30[b]	6.30
Ce 142	6.00 ± 0.18	6.00
Nd 143	5.59 ± 0.19	5.77
Nd 144	5.16 ± 0.18	5.33
Nd 145	3.72 ± 0.13	3.84
Nd 146	2.82 ± 0.10	2.91
Sm 147	2.31 ± 0.08	2.39
Nd 148	1.57 ± 0.05	1.62
Sm 149	1.10 ± 0.04	1.14
Nd 150	$0.60_9 \pm 0.02_1$	0.629
Sm 151	$0.43_7 \pm 0.01_5$	0.451
Sm 152	0.276 ± 0.009	0.285
Sm 154	0.075 ± 0.003	0.077
Total	75.5 ± 2.3	77.6

---

[a] Xenon isotope ratios (60) normalized at mass 133.

[b] Assuming yield of Ba^{140} to be 6.30% (98).

indication that the fission yields as obtained by isotope dilution are likely to be quite accurate relative to one another. Unless the data taken from the literature is on the whole out by more than 10 per cent, it is also likely that the absolute fission yields obtained by the normalization procedure above are accurate to within 2 or 3 per cent.

Of particular interest is the fact that the resulting yield of Xe^{131} is considerably less than the presently favored radiochemical value of 3.14 per cent (66), but is fairly consistent with earlier data (64). On the other hand, the value of 6.61 per cent for the yield of Cs^{133} is in excellent agreement with the yield of 6.62 per cent for Xe^{133} reported by Katcoff and Rubinson (99). However, the Nd^{143} yield of 5.77 per cent obtained here is significantly higher than the radiochemical value of 5.4 per cent reported for Ce^{143} (100).

The new values of the fission yields in the heavy mass region are plotted in Figure 2 along with the hypothetical fission yield curve deduced by Pappas. This curve was obtained by assuming a smooth yield mass curve (also given in Figure 2) for the primary fission fragments and satisfying the requirement that all primary fragments with 83, 85, 87, and 89 neutrons emitted a neutron to form the energetically favourable 82, 84, 86,

TABLE XXX

Reported Yields of Fission Products in the Heavy Mass Region for U^{235}

Mass	Fission Yield (%)	Remarks
117 - 129	1.8	Taken from Sullivan Chart (63)
130	2.1	Reported by Pappas (58)
138	6.2	Taken from Sullivan Chart (63)
139	6.4	Reed and Turkevich (101)
141	5.7	Burgus and Ballou (102)
153	0.15	Taken from Sullivan Chart (63)
155- 162	0.06	Taken from Sullivan Chart (63)
Total	22.4	

and 88 neutron configurations respectively.

It is readily apparent that the dip predicted at mass 143 is not borne out by the present results. Since no accurate values for the fission yields at masses 138, 139, and 141 have been obtained, it cannot be established whether or not neutron emission by fragments with 3 and 5 neutrons more than the 82-neutron shell is significant. However, in view of the fact that the yields of masses 140, 142, 143, and 144 as obtained from the present work

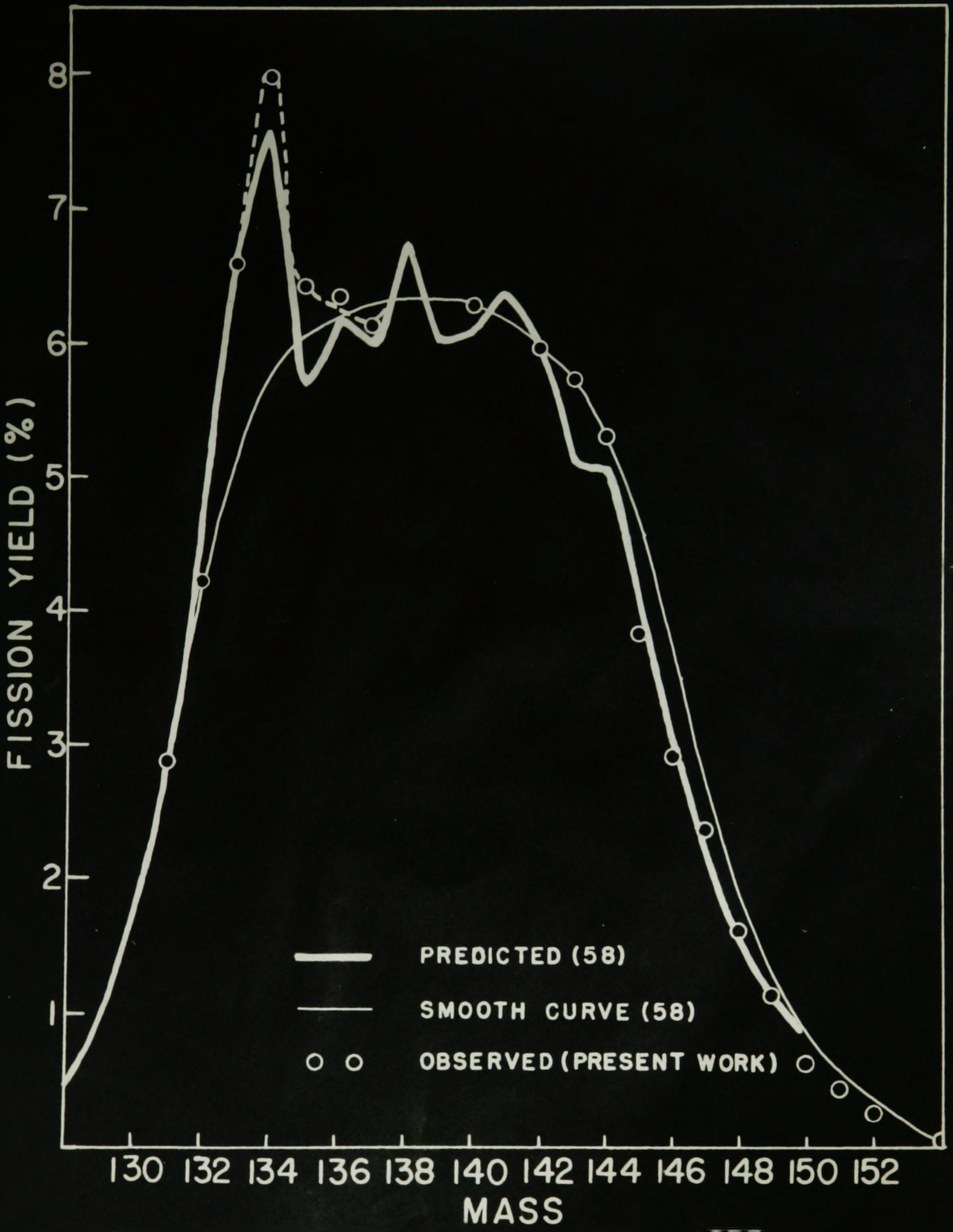

FIGURE 2 · HEAVY MASS HUMP — U^{235} FISSION lie on a smooth curve it does not seem likely that the rather marked peaks predicted at masses 138 and 141 are actually present. Nevertheless, an accurate evaluation of the yields of masses 138, 139, and 141 is really necessary before a final decision is reached.

It has already been shown (54) that neutron emission from primary fragments with 83 neutrons does not account for all the fine structure observed at mass 134. To get agreement with experimental data, one has to assume a preferential yield in fission for fragments with 82 neutrons as originally suggested by Wiles et al (55). This is included under the dotted line in Figure 2.

Any preference in the primary fission act should be revealed as fine structure in both humps of the mass yield distribution. Glendenin (56) has already indicated that the observed fine structure at masses 100 and 101 coincided with that at masses 133 and 134 provided one assumed 2.5 neutrons were emitted from each pair of fragments.

It is of interest to carry out such a comparison between the two humps now that more accurate data is available. The yields of fission products in the light mass region that were obtained from the present work are given in Table XXXI. These have been plotted in Figure 3 along with the best available radiochemical data

TABLE XXXI

The Yields of Light Fragment Masses in the Thermal Neutron Fission of U^{235} From the Present Work

Isotope	Fission Yield	
	Based on BF_3 Flux measurement (corrected)	After Heavy mass yields normalized to 100%
Kr 83	$0.52_9 \pm 0.01_8$[a]	0.54_7
Kr 84	$0.99_2 \pm 0.03_4$	1.02_6
Kr Rb 85	1.26 ± 0.04	1.30
Kr 86	1.96 ± 0.07	2.03
Rb 87	2.41 ± 0.08	2.49
Sr 88	3.44 ± 0.12	3.56
Sr 90	5.71 ± 0.20	5.90
Total	16.30 ± 0.55	16.86

[a] Krypton isotope ratios (60(normalized at mass 85.

and the mass spectrometric results of Glendenin et al (56) for the relative yields of the isotopes of molybdenum and zirconium (Table II), normalized at Zr^{94} =. 6.18% and Mo^{95} = 6.25%. Tha actual data chosen for the plot are given in Table XXXII.

In Figure 4, the light peak and the heavy peak have been plotted together on the basis of two neutrons

TABLE XXXII
Reported Yields of Fission Products in the Light Mass Region for U^{235}

Mass	Element Involved	Fission Yield (%)	Remarks
72 - 80		0.15	Taken from Sullivan Chart (63)
81	Se	0.13	Radiochemical (103)
82		0.26	Taken from Sullivan Chart
89	Sr	4.75	Radiochemical (104) rel. to Ba^{140} = 6.30%
91	Zr	5.50	Mass spectrometric (56) normalized at Zr^{94} = 6.18%
92	Zr	5.63	
93	Zr	6.02	
94	Zr	6.18	
95	Mo	6.25	Mass spectrometric (56) normalized at Mo^{95} = 6.25%
96	Zr	6.16	
97	Mo	5.93	
98	Mo	5.90	
100	Mo	6.46	
99	Mo	6.0	Radiochemical (57) rel. to Ba^{140} = 6.30%
101	Mo	5.6	
102	Mo	4.1	
105	Mo	1.35	
103		3.7	Taken from Sullivan Chart (63)
104		2.0	
106		0.52	Radiochemical (105)
107 - 117		0.4	Taken from Sullivan Chart
Total		83.0	

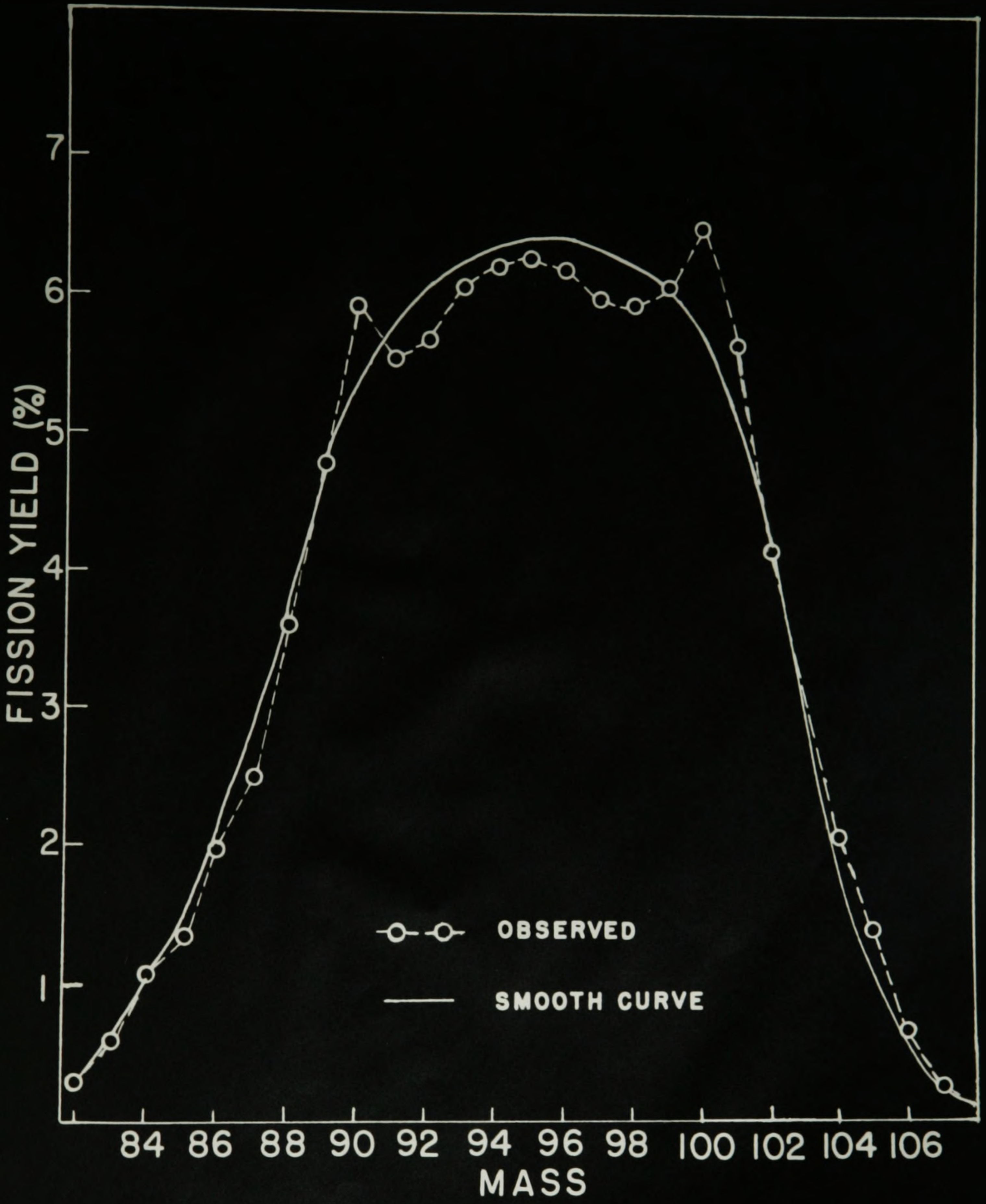

FIGURE 3 · LIGHT MASS HUMP — U^{235} FISSION

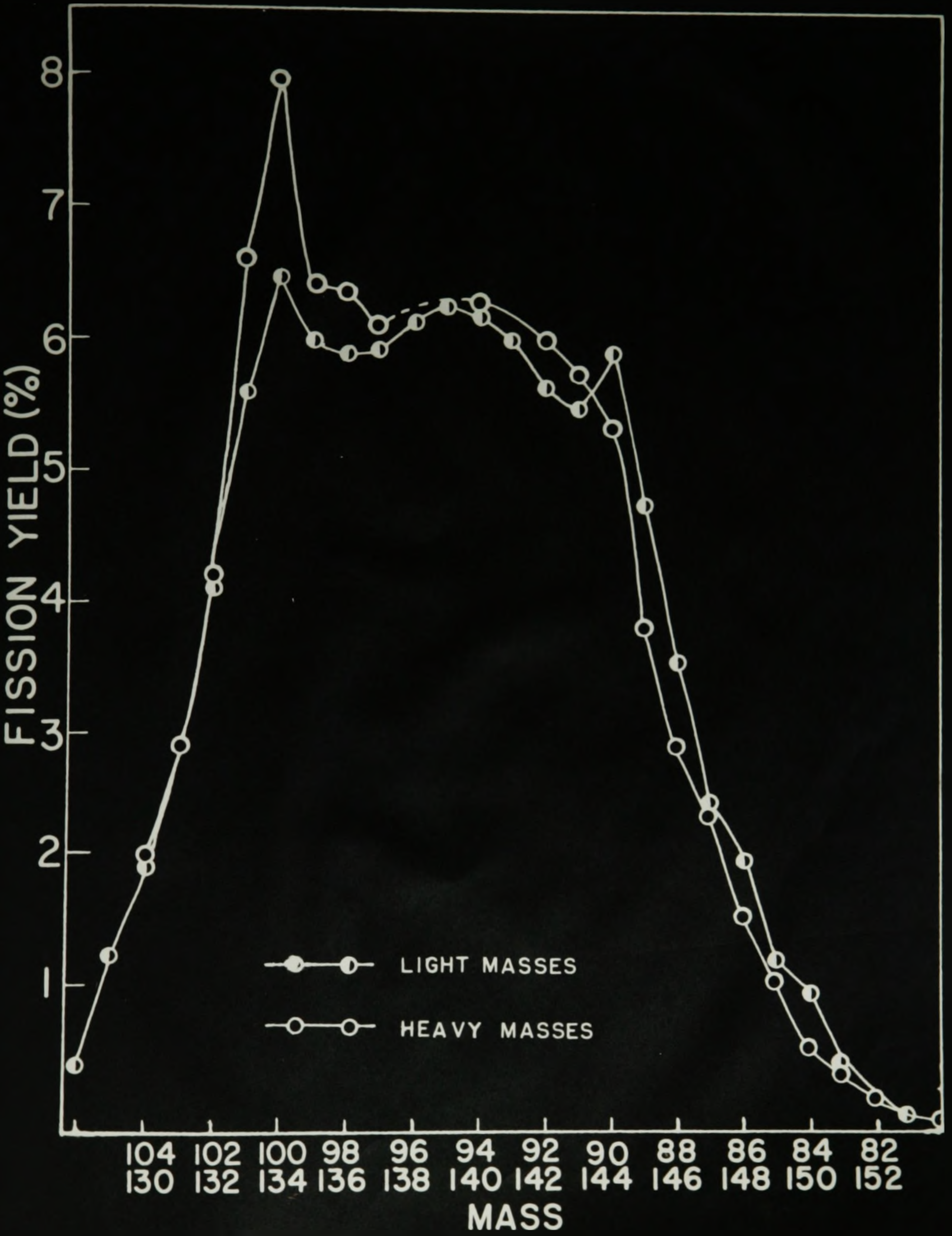

FIGURE 4 · COMPARISON OF LIGHT AND HEAVY MASS YIELDS IN THERMAL NEUTRON FISSION OF U^{23}

emitted per fission. It is readily seen that the light is somewhat broader than the heavy peak. Another interesting feature is that the yields of complementary fragments with mass ratio up to 132/102 seem to correlate satisfactorily on the basis of two neutrons emitted per fission. For higher mass ratios, however, the correlation is by no means straight-forward. It appears that primary light fragments formed a considerable distance from any nuclear shell still have a significant probability of emitting more than one neutron. Therefore it is possible that in the light mass region, the mechanism postulated by Pappas, as applied to the 50-neutron shell may actually be quite significant. In fact, Pappas (58) has predicted that if primary fragments with 51, 53, 55, and 57 neutrons "boil-off" a neutron, then the observed result would be a slightly developed fine structure in the mass region 82 to 88, the mass region 90 through 100 (the top of the light peak) would show a depressed yield and a small indentation would be expected to show up around mass 92. This is essentially what has been observed except that the depression starts at mass 91 and the yield of mass 90 is considerably enhanced. Such a result is more consistent with the postulate that only fragments with 51, 53, and 55 neutrons "boil-off" a neutron. In other words, it appears that the emission of an extra neutron from a fragment with 57 neutrons does not occur to any appreciable extent.

One way to assess the importance of nuclear shells in producing fine structure through a post-fission process such as that suggested by Pappas is to compare the yield mass curves for different fissioning nuclei. If the fine structure observed in the different cases occurs in more or less the same region and is of comparable magnitude, then a mechanism involving the emission of neutrons in the region of closed shells would be substantiated. On the other hand, any preference for certain nuclear configurations for the fission fragments should be quite strongly dependent on the excitation energy and the binding energy of the fragments in the parent nucleus. Thus for Pu^{239}, for example, where the peak-to-valley ratio is considerably lower than for U^{235} (that is, 150 as compared to 550 respectively), one would expect that fine structure due to a primary fission process would be considerably smaller than observed for U^{235}. Fine structure based on a mechanism such as that suggested by Pappas, however, should still be quite pronounced, if it exists at all or is as extensive as Pappas indicates.

The fission yields of Pu^{239} obtained relative to

Nd^{143} by isotope dilution as given in Table XXVIII have been plotted in Figure 5 and the relative yields of xenon, cesium, neodymium, and samarium isotopes normalized at these points. The resulting curve (Figure 5) shows no marked fine structure; the region from mass 140 to 150 being exceptionally regular. Once again, preferential emission of neutrons from fragments with 5 and 7 neutrons beyond the closed shell of 82 is not borne out. The relatively small fine structure at mass 134 also indicates that preferential emission of neutrons from fragments with 83 and 85 neutrons cannot be very significant. In fact it may be due entirely to structural preference in the primary fission process, as suggested by Fleming (59).

Fleming (59) has also observed that the yields of Kr^{84} and Kr^{85} in Pu^{239} fission are somewhat higher than would be indicated by a smooth curve drawn through the yields of Sm^{149}, Nd^{150}, and Sm^{154}, suggesting that an enhanced yield in this region, probably due to a preference for 50 neutron configurations, is characteristic of the primary fission process. Accurate absolute fission yield data are necessary, however, to make further comparisons worthwhile.

The yield of mass 137 relative to 143, although not relevant to the above discussion of the observed fine structure, is nevertheless of considerable interest in that

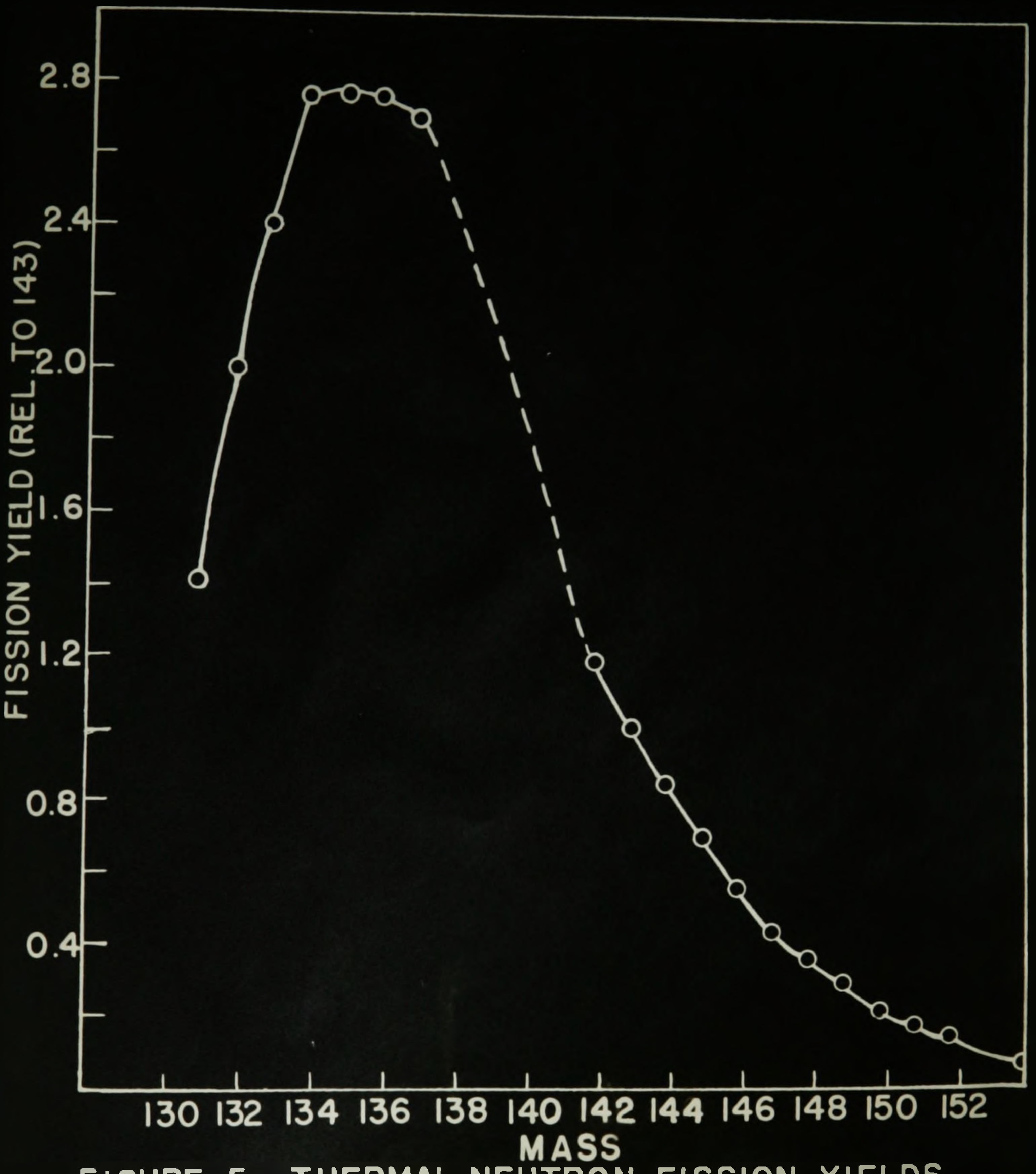

FIGURE 5 · THERMAL NEUTRON FISSION YIELDS IN Pu^{239}

it disagrees markedly with what one would expect on the basis of radiochemical data. The ratio obtained by isotope dilution was 2.67 whereas the value corresponding to the radiochemical fission yield curve for Pu^{239} is about 1.7. Since the present result is based on only one set of isotope dilution data, it conceivably may be in error, but the reason for this is not apparent at the moment. However, samples of plutonium have been irradiated since this work was done and it should be possible to check this value in the near future.

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APPENDIX

A. Results of the Flux-Measurement with BF_3 Monitor

The details of the irradiation of natural uranium with BF_3 as monitor have been discussed in the Experimental Section. The ratio of B^{10}/B^{11} before irradiation to that after irradiation was found to be 1.029 ± 0.001. By assuming that this change had been caused only by the reaction $B^{10}(n, \alpha)Li^7$, the effective flux of thermal neutrons may be calculated as follows:

At any time, t, during irradiation,

$$\frac{dN}{dt} = - N f \sigma_B$$

$$\text{or} \quad N = N_0 \exp(- f \sigma_B t)$$

where N is the number of B^{10} atoms present at time, t

f is the thermal neutron flux

σ_B is the thermal neutron capture cross-section of B^{10}

N_0 is the number of B^{10} atoms present when $t = 0$

$$\text{Now,} \quad \frac{N_0}{N_0 \exp(- f\sigma_B t)} = 1.029$$

$$\text{or} \quad \exp(f \sigma_B t) = 1.029$$

$$\text{whence} \quad f \sigma_B t = 0.0286$$

$$\text{and} \quad f = \frac{0.0286}{\sigma_B t} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1$$

Since t is known, the flux can be calculated directly from equation 1 provided σ_B is known. However, for the calculation of the number of fissions occurring in the uranium during the irradiation we can proceed as follows.

The number of fissions per gram of uranium at any time, t, is given by

$$N_f = f.t.\sigma_f.N_{235} \quad \ldots\ldots\ldots\ldots\ldots\ldots \ (2$$

where f is the thermal neutron flux, as before

σ_f is the cross-section for fission of U^{235} to thermal neutrons

N_{235} is the number of atoms of U^{235} per gram of natural U.

Substituting equation 1 in equation 2, we get

$$N_f = 0.0286 \ \frac{\sigma_f}{\sigma_B} \ N_{235} \quad \ldots\ldots\ldots\ldots \ (3$$

If the per cent abundance of U^{235} in natural uranium is taken to be 0.715 (88),

$$N_{235} = \frac{6.023 \times 10^{23}}{238.07} \times 0.00715$$

$$\text{or} \quad N_{235} = 1.808 \times 10^{19} \ \text{atoms}$$

$\sigma_{B_{Natural}}/\sigma_f$ can be given the value 1.29, this being the average of three literature values (89) (90) (91). For our sample, the per cent abundance of B^{10} in boron before irradiation is 18.84; the same as reported by Inghram (92) for natural boron.

Hence,

$$\sigma_f/\sigma_B = \frac{1}{1.29} \times 0.1884$$

$$= 0.1460$$

On substitution of the above values for N_{235} and σ_f/σ_B in 3:

$$\underline{N_f = 7.55 \times 10^{16} \text{ fissions/gram U.}}$$

This value was used to calculate the number of fissions in each of the samples listed in Table VII.

B. Neutron Capture in Xe^{135}

The decay chain involving Xe^{135} is as follows:

$$\begin{tikzcd}
 & & \substack{Xe^{135m} \\ 15.3 \text{ m.}} \arrow[dd] & & \\
\substack{Te^{135} \\ 2 \text{ m.}} \arrow[r] & \substack{I^{135} \\ 6.68 \text{ hr.}} \arrow[ur] & & \substack{Cs^{135} \\ 2.1\text{x}10^6 \\ \text{yr.}} \arrow[r] & \substack{Ba^{135} \\ \text{stable}} \\
 & & \substack{Xe^{135} \\ 9.13 \text{ hr.}} \arrow[ur] & &
\end{tikzcd}$$

Two simplifying assumptions can be made:

(i) All of the 135 mass chain starts at I^{135}. That is, the primary yield of Xe^{135} is assumed to be zero, and the short lived precursors of I^{135} are neglected.

(ii) The 15.3 minuted Xe^{135} is neglected compared with the longer lived 6.68 hour I^{135} and the 9.13 hour Xe^{135}.

Having made these assumptions it has been shown (59) (60) that R_b, the ratio of the amount of the 135 chain consumed by capture to the total fission yield for mass 135, is given by

$$R_b = \frac{f\sigma_c}{t}\left[\frac{t}{K} + \frac{e^{-Kt}-1}{K^2} + \frac{e^{-\lambda_1 t}-1}{\lambda_1(K-\lambda_1)} - \frac{e^{-Kt}-1}{K(K-\lambda_1)}\right] \text{........ (1}$$

Where $K \equiv (\lambda_2 + f\sigma_c)$

and f is the thermal neutron flux;

σ_c is the neutron capture cross-section of Xe^{135};

t is the time of irradiation;

λ_1 is the decay constant of I^{135} (0.1037 hr.$^{-1}$);

λ_2 is the decay constant of Xe^{135} (0.0759 hr.$^{-1}$).

For the sample under consideration at present, namely the BF_3-monitored uranium, it was found (from pile data) that the irradiation during the period stated in Table IV (36 days) was not continuous, but consisted of five periods ranging from 70 hours to 140 hours. Fortunately, however, the time between periods was long enough to permit 99% or more of the Xe^{135} formed during the latest irradiation period to decay before irradiation was resumed. Hence, by assuming complete decay of Xe^{135} between periods, and by treating each period as an independent irradiation, only a very small error (less than 1%) was introduced. The flux during all irradiation periods was assumed to be constant and to be given by dividing the total (actual) operating time into the ft value obtained from the BF_3 data (Appendix A). Thus with

$$ft = \frac{0.0286}{\sigma_B} \quad \text{(Appendix A, equation 1)}$$

and

$$t = 650 \text{ hours (operating time)},$$

$$f = \frac{4.40 \times 10^{-5}}{\sigma_B}$$

Taking the cross section of natural boron to be 755 barns (93) (94) and the abundance of B^{10} to be 18.84%, then

$$_B = \frac{755}{.1884} = 4.007 \times 10^3 \text{ barns}$$

and $f = \dfrac{4.40 \times 10^{-5}}{4.01 \times 10^{-21}} = \underline{1.098 \times 10^{16}}$ neutrons/cm.^{2}/hr.

Table XXXIII gives a few values of R_b obtained for the above value of the flux, f, and arbitrarily chosen values for $_c$ using equation 1.

TABLE XXXIII

Calculated values of R_b for various values of σ_c

R_b	σ_c (x 10^6 barns)
0.250	3.0
0.277	3.5
0.323	4.0

The value of R_b obtained experimentally for the BF_3-monitored uranium sample was $\dfrac{0.972 - 0.715}{0.972} = 0.264$, since $(135/133)_{obs.} = 0.715$ (Table IX) and $(135/133)_{fiss.} = 0.972$.

This corresponds to

$$\sigma_c = \underline{3.3 \times 10^6} \text{ barns}$$

The probable error on this result is ± 0.2 x 10^6 barns due mainly to the uncertainty in the flux measurement.

C. Half-lives and Cross-sections of Rare Earth Isotopes

(a) Half-life of Pm^{147}.

In the decay chain of mass 147, Pm^{147} decays to stable Sm^{147} with a half-life that has been reported as 2.26 years (62) and 2.6 years (85).

Inghram (62) obtained the value 2.26 years by assuming a smooth fission yield curve from masses 148 to 152 and by making use of the following equations:

$$N_{147} = \frac{N_u \sigma_f Y_{147} F}{\lambda_{147}} \left[\lambda_{147} t_1 - \exp(-\lambda_{147}(t_2 - t_1)) \exp(-\lambda_{147} t_2)\right] \ldots($$

$$N_{149} = \frac{N_u \sigma_f Y_{149} F}{149^F} (1 - \exp(-\sigma_{149} F t_1)) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2$$

$$N_{150} = \frac{N_u \sigma_f Y_{149} F}{149^F} (\sigma_{149} F t_1 - 1 + \exp(-\sigma_{149} F t_1)) \ldots\ldots (3$$

Where N_{147}, N_{149}, N_{150},	are the numbers of atoms of the corresponding samarium isotopes after a calendar time t_2;
t_1	is the time of neutron irradiation;
N_u	is the number of uranium atoms;
σ_f	is the fission cross-section for uranium;
Y_{149}	is the fractional yield of the 149 mass chain;
F	is the thermal neutron flux;
σ_{149}	is the capture cross-section of Sm^{149};
λ_{147}	is the decay constant of Pm^{147}.

In the present case, it is not necessary to assume a smooth curve as Inghram (62) did, since values of N_{147}/N_{149} and N_{149}/N_{150} are available for two samples (A and B) whose cooling times were quite different. However, it is necessary to assume that the fission ratio of mass 147 to mass 149 is the same for both samples. This is likely a valid assumption since the neodymium isotope ratios for the two samples are identical within experimental error (Table XIV).

To make the calculation, it is convenient to express N_{147} in terms of $(N_{149}+N_{150})$ since the latter sum is the actual number of atoms of Sm^{149} that would have been observed had there been no capture. Hence, we have the following equation:

$$\frac{N_{147}}{N_{149}\ N_{150}} = \frac{Y_{147}}{Y_{149}} \cdot \frac{1}{{}_{147}t_1} \left[\lambda_{147}t_1 - \exp(-\lambda_{147}(t_2 - t_1)) + \exp(-\lambda_{147}t_2) \right] \cdot\cdot($$

$$= R_{147}, \text{ say.}$$

For each sample (A and B), R_{147} is known (Table XVIII). The only unknowns are, therefore, Y_{147}/Y_{149} and λ_{147}. For further simplification, we divide the equation for R_{147} (Sample B) by the equation for R_{147} (Sample A); thus cancelling Y_{147}/Y_{149} and obtaining an equation in λ_{147} alone as follows:

For sample A: R_{147} = 1.864 (Table XVIII)

t_1 = 18 days

t_2 = 2950 days

For sample B: $R_{147} = 1.025$

$t_1 = 36$ days

$t_2 = 910$ days

Hence,

$$\frac{1.025}{1.864} = \frac{18}{36}\left[\frac{\lambda_{147}(36) - \exp(-\lambda_{147}(874)) + \exp(-\lambda_{147}(910))}{\lambda_{147}(18) - \exp(-\lambda_{147}(2932)) + \exp(-\lambda_{147}(2950))}\right] \quad \ldots(5$$

Whence

$$\lambda_{147} = 0.000753 \text{ day}^{-1}$$

This corresponds to a half-life of 2.52 years. The probable error on this result is estimated to be ± 0.09 year. This includes the error based on the standard deviations of the mass spectrometric data used (Table XVIII).

(b) The Neutron Capture Cross-Section of Sm^{149}

The equations relating the observed yields of Sm^{149} and Sm^{150} to the actual amount of mass 149 produced in fission have already been given (equations 2 and 3 above). By dividing equation 2 by equation 3 we get:

$$\frac{N_{149}}{N_{150}} = \frac{1 - \exp(-\sigma_{149}Ft_1)}{\sigma_{149}Ft - 1 + \exp(-\sigma_{149}Ft_1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (6$$

For Sample B, the Sm^{149}/Sm^{150} ratio was found to be 3.92 ± 0.006 (Table XVIII). Also Ft_1 was evaluated from the BF_3 data as $(7.14 \pm 0.25) \times 10^{18}$ neutrons. Substitution of these values in equation 6 gives a value for σ_{149} equal to 66,200 ± 2,500 barns.

(c) The Neutron Capture Cross-Section of Sm^{151} and the Half-life

of Sm^{151}.

The yield at Sm^{151} is affected by neutron capture in this isotope as well as decay after irradiation. The capture also affects the yield of Sm^{152}. Hence, to evaluate the fission yields at masses 151 and 152, the following equations have to be considered (62):

$$N_{151} = \frac{N_u \sigma_f Y_{151} F}{\lambda_{151} + \sigma_{151} F} \left[1 - \exp(-\lambda_{151} + \sigma_{151} F) t_1 \right] \exp(-\lambda_{151}(t_2 - t_1) \quad \ldots (7$$

$$N_{152} = N_u \sigma_f Y_{152} F t_1 + \frac{N_u \sigma_f Y_{151} \sigma_{151} F^2}{(\lambda_{151} + \sigma_{151} F)^2} \left[(\lambda_{151} + \sigma_{151} F) t_1 - 1 \right.$$

$$\left. \exp(-\lambda_{151} + \sigma_{151} F) t_1 \right] \quad \ldots\ldots\ldots\ldots (8$$

where the symbols convey the same meaning as before.

If we express N_{151} and N_{152} in terms of $(N_{149} + N_{150})$ then (using equations 2, 3, 7, and 8) we have

$$\frac{N_{151}}{N_{149} + N_{150}} = \frac{Y_{151}}{Y_{149}} \cdot \frac{1}{(\lambda_{151} + \sigma_{151} F) t_1} \left[1 - \exp(-\lambda_{151} + \sigma_{151} F) t_1 \exp(-\lambda_{151}(t_2 - t_1) \right] \quad \ldots\ldots\ldots (9$$

$$= R_{151}, \text{ say.}$$

$$\frac{N_{152}}{N_{149} + N_{150}} = \frac{Y_{152}}{Y_{149}} + \frac{Y_{151}}{Y_{149}} \cdot \frac{\sigma_{151} F t_1}{(\lambda_{151} \quad 151 F)^2 t_1^2} \left[(\lambda_{151} + \sigma_{151} F) t_1 - 1 \right.$$

$$\left. \exp-(\lambda_{151} + \sigma_{151} F) t_1 \right] \quad \ldots\ldots\ldots\ldots (10$$

$$= R_{152}, \text{ say.}$$

It is assumed that Y_{151}/Y_{149} and Y_{152}/Y_{149} are the same for Samples A and B. In addition for Sample A it is assumed that the neutron capture in Sm^{151} was negligible (less than 1%) since the flux was only 6×10^{11} neutrons/cm.^{2}/sec. Therefore, the $N_{151}/(N_{149}+N_{150})$ ratio for this sample is considered to be the fission ratio uncorrected for decay in Sm^{151}. Thus for Sample A, equations 9 and 10 can be simplified to the following forms:

$$R_{151}\ (A) = \frac{Y_{151}}{Y_{149}} \cdot \frac{1}{\lambda_{151} t_1} \left[1 - \exp(-\lambda_{151} t_1) \right] \ldots\ldots (11$$

$$R_{152}\ (A) = \frac{Y_{152}}{Y_{149}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12$$

Hence, by substituting Y_{151}/Y_{149} and Y_{152}/Y_{149} in equations 9 and 10 for Sample B, only three parameters remain to be evaluated, namely F, σ_{151}, and λ_{151}. However, F has been determined for Sample B from the BF_3 data. Consequently only two unknowns σ_{151} and λ_{151} remain. Since there are also two equations, these can be evaluated.

Using the appropriate data in Table XVIII, and solving equations 9 and 10 after substituting $Ft_1 = 7.14 \times 10^{18}$ neutrons (from BF_3 data), the capture cross-section of Sm^{151} was calculated to be 15,000 ± 6,000 barns, and the half-life of Sm^{151} was found to be 90 years.