THE STABLE CADMIUM ISOTOPES FROM THE FISSION OF ^{233}U AND ^{235}U

MASS SPECTROMETRIC STUDIES
OF THE
STABLE CADMIUM ISOTOPES IN THE
THERMAL-NEUTRON FISSION OF ^{233}U AND ^{235}U

By

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A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Master of Science

McMaster University

May, 1971

MASTER OF SCIENCE (1971)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario.

TITLE: Mass Spectrometric Studies of the Stable Cadmium Isotopes in the Thermal-Neutron Fission of ^{233}U and ^{235}U.

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NUMBER OF PAGES: vii, 77

SCOPE AND CONTENTS:

An attempt was made to measure the yields of the stable cadmium isotopes produced in the thermal-neutron fission of ^{233}U and ^{235}U using a solid-source mass spectrometer. The results for ^{235}U fission indicate that there is structure in the mass-yield curve for the region studied which takes the form of a depression around masses 112-114. The origin of this structure is discussed in terms of the various mechanisms which have been proposed to explain the nature of the mass distribution in the symmetric region.

The ^{233}U study was unsuccessful because of the experimental difficulties encountered, primarily the interference from terrestrial cadmium and the low recovery of the fission products.

ACKNOWLEDGEMENTS

I am sincerely grateful to my Research Advisor, Dr. R. H. Tomlinson, for his continual interest, guidance and encouragement throughout the course of this work. I wish to thank Dr. W. B. Clarke for his helpful suggestions, and Dr. O. E. Hileman, Jr. -- both of whom served on my supervisory committee.

The Chalk River sample was provided by Dr. R. W. Durham.

I also wish to thank Dr. K. S. Thind for his help with the diagrams and for providing his calculations on the yield curve in the symmetric region.

The author is indebted to the Canadian International Development Agency for their financial support.

And most of all, to Janine, who alone knows why.

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CHAPTER 1

INTRODUCTION

A. Historical Notes

Shortly after the discovery of the neutron in 1932 Fermi and his co-workers(1, 2) in Rome attempted to produce transuranic elements by irradiating uranium with neutrons. It was expected that capture of one or more neutrons by uranium nuclei would result in the formation of beta-unstable isotopes. Subsequent beta-minus decay would give nuclei with atomic numbers higher than uranium. Alternately production of an alpha-unstable nucleus could occur and emission of an alpha-particle could lead to radioisotopes with a nuclear charge of less than 92. Fermi's experiments resulted in the formation of a 13-minute activity which was assigned the atomic number 93 on the basis of its radiochemical properties. This activity could be separated chemically from elements 82 to 92 so it was concluded that it was due to a radioisotope of element 93. In addition several other activities were produced and identified as transuranic elements; four were designated as radium isotopes because they precipitated with barium compounds which were normally used as carriers of radium.

In 1939 Curie and Savitch(3) attempted to investigate the properties of these 'radium' isotopes. They found that it was extremely difficult to separate these isotopes from the barium carrier. Working along similar lines Hahn and Strassmann(4) added some radium to a solution of the barium carrier and the radio-isotopes of interest with the intention of separating the 'radium' isotopes from the barium carrier by fractional crystallization of the radium and barium salts. The 'radium' isotopes were found to be concentrated preferentially in the barium and were identified positively as radio-isotopes of barium. In a subsequent experiment of Hahn and Strassmann(5) they identified the daughter activities, thought to be isotopes of actinium, as isotopes of lanthanum. These findings provided conclusive evidence that the uranium nuclei were breaking up to form two medium weight fragments, and Meitner and Frisch(6) gave the name nuclear fission to this phenomenon.

Meitner and Frisch(6) estimated that about 200 MeV would be released per fission event, and this large energy release was confirmed by Frisch(7) and independently by Joliot(8). It was also found that on the average between 2 and 3 neutrons were emitted per fissioning nucleus from the neutron-rich fragments(9,10). Roberts et al(11) determined that a small fraction of these neutrons had relatively long half-lives ranging up to one minute. Bohr and Wheeler(12) subsequently showed that these could be attributed to certain fission product isotopes (delayed-neutron emitters) which were formed in nuclear states with excitation energies greater than the neutron binding energy from their precursors by beta-decay.

These findings indicated that a self-sustaining nuclear fission reaction releasing large amounts of energy was feasible. The neutrons emitted in the fission of a nucleus could be used to induce fission in other nuclei, and in this way a chain reaction could be achieved. The first controlled nuclear fission reaction was achieved by Fermi and co-workers in 1942 and this has resulted in the operation of nuclear reactors which utilize the large energy release to generate power. The development of the fission bomb followed in 1945.

During the past twenty one years the fission process has been the subject of much experimental and theoretical study. A great deal of experimental data has been compiled on the mass and charge distributions in the fission of many nuclides, the kinetic energies of the fission fragments and other observable quantities of interest. The theoretician has thus been faced with many features of the fission process which must be adequately explained by any fission theory - for example the preferential division of the nucleus into two asymmetric fragments in low energy fission. However the task of explaining the major features of fission and correlating the experimental data has proved to be a complex and difficult problem and no generally acceptable theory of fission has yet been developed.

B. The Fission Process

Nuclear fission is the term used to describe the phenomenon in which a heavy nucleus divides into two or more fragments of comparable mass. The most commonly observed type of fission is binary fission where two medium sized fragments are formed. In addition ternary fission into two fragments plus an alpha particle is fairly common, this occurring about once per 400 binary fission events. Ternary fission into three nearly-equal fragments, or fission into two medium fragments plus a light particle such as a ^{3}H or ^{7}Be nucleus is also possible but experimentally these have been shown to be very improbable.

Theoretically any nucleus whose mass exceeds the combined masses of the primary fragments (i.e. before neutron emission) can undergo fission. However the fission threshold energy increases rapidly for nuclides with atomic number less than about 88 and it requires large excitation energies to induce fission in these nuclides. For elements with higher atomic numbers the fission threshold decreases and in many cases spontaneous fission becomes very probable. Fission has been induced in nuclei with atomic numbers greater than 82 (Pb), in rhenium (atomic number 75) and in gold (atomic number 79), and in nuclei with masses greater than about 185. A variety of bombarding particles have been used to supply the necessary excitation energy - protons, photons, neutrons, alpha particles, etc.

The products of the fission of a nucleus such as uranium range from about zinc (mass 67, charge 30) to dysprosium (mass 164, charge 66). This covers a mass range of about 100 and a charge range of about 30 units. Over 400 nuclides have been identified as direct or indirect products of fission.

These features of the fission process indicate that fission is an extremely complex nuclear reaction.

The fission process can be depicted as in Figure 1. The steps shown are not necessarily separate identifiable stages of a fission reaction but are chosen for convenience in giving an overall picture of the reaction.

The nucleus is first excited through a suitable nuclear reaction such as neutron capture, or by photon absorption. It can then de-excite through neutron emission, gamma ray emission or fission. At low excitation the particular mode of de-excitation depends primarily on the fissionability of the nucleus. In the case of highly fissile nuclides such as ^{235}U or ^{239}Pu, fission is the primary reaction and neutron emission becomes more competitive only with high excitation energy. For nuclides of low fissionability gamma emission is the only mode of de-excitation possible until the nucleus is excited above the fission threshold when neutron emission and fission become increasingly probable. Under these conditions successive neutron emission may occur if energetically possible and may result in the formation of several nuclear species with sufficient energy for fission. Thus a single nuclear species with large excitation energies can give fission products which are the result of first-chance fission, second-chance fission following emission of a single neutron, and successive chance fission.

The fragments formed at the instant of fission are termed the primary fission fragments. These fragments are neutron-rich and they possess about 25 MeV of excitation energy between them.

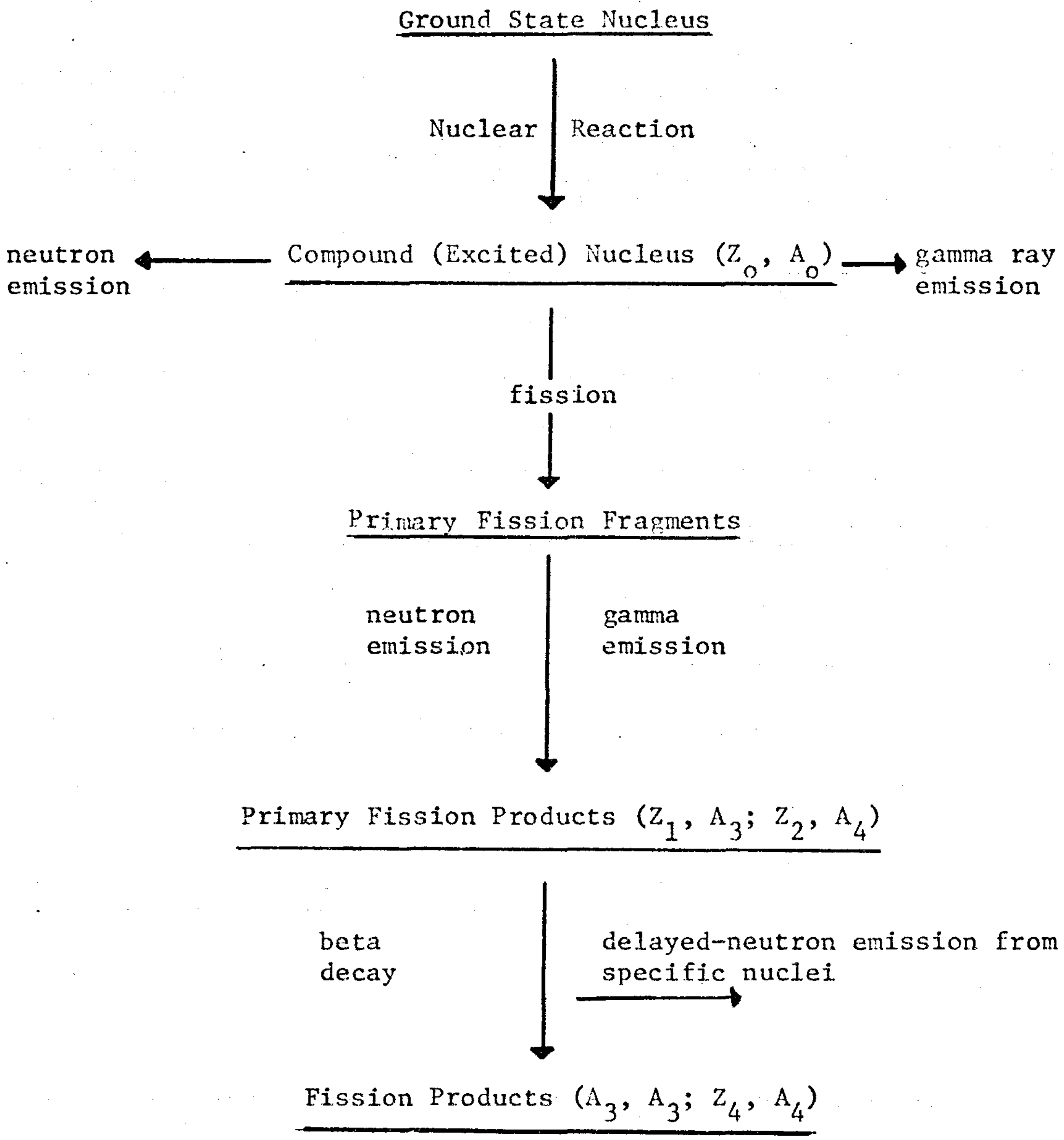

Figure 1 Stages of a Fission Reaction

Consequently they are unstable to neutron emission and have extremely short life-times of the order of 10^{-15} to 10^{-18} sec.

The primary fission fragments de-excite by emitting neutrons and gamma rays to produce the primary fission products. These fission products are in their ground states and are beta-unstable. These decay with half-lives ranging from about 10^{-3} sec to several days. Occasionally β^- emission leaves the resulting nucleus with excitation in excess of the neutron binding energy and delayed-neutron emission results. Eventually a nuclide which is stable to beta decay is produced. Figure 2 shows a typical beta-decay chain.

The primary and secondary fission products are the nuclides studied by radiochemistry and mass spectrometry. These generally have half-lives which are long enough to enable study by one or both of these methods.

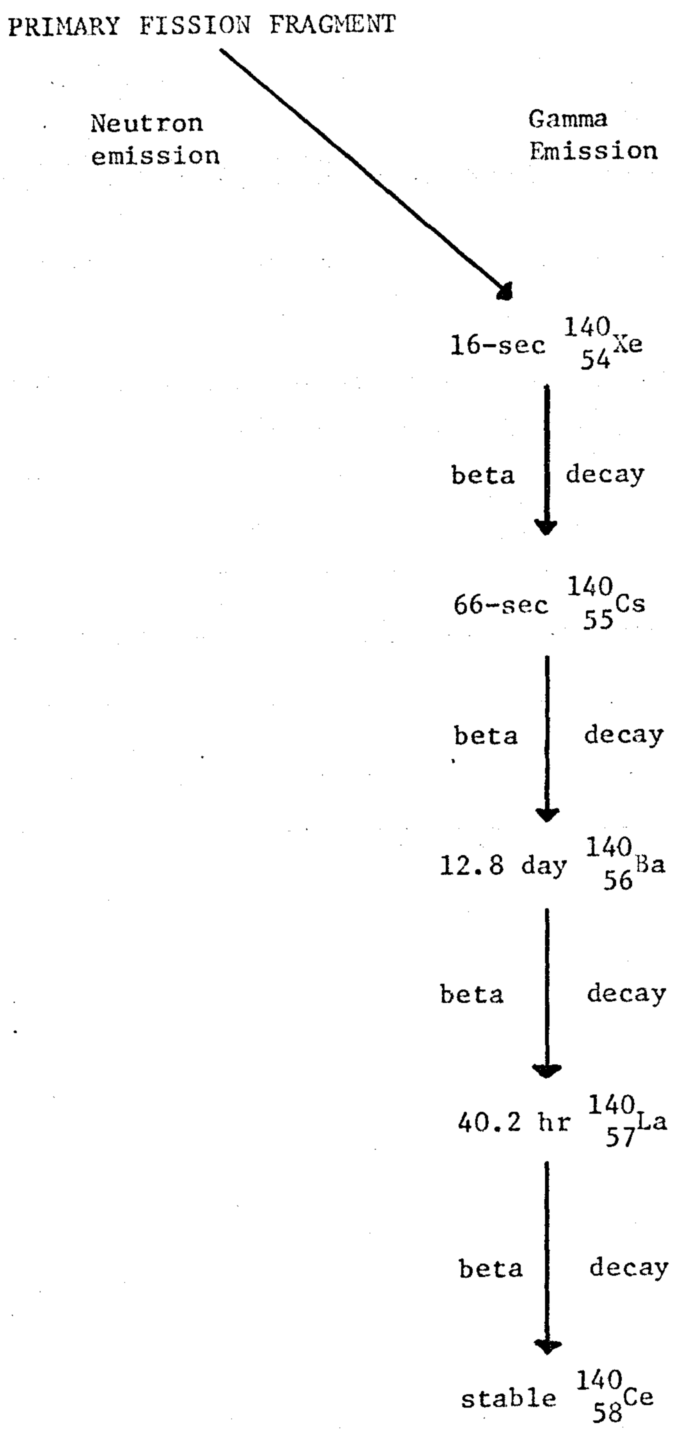

Figure 2 Beta Decay Chain for Mass 140

CHAPTER 2

MASS YIELD MEASUREMENTS

A. Experimental Techniques

There are two main techniques which have been used to measure the yields of the various fission products.

The radiochemical method involves the isolation of a radio-isotope from other interfering activities and the determination of its yield by counting techniques. The method is limited to active isotopes with half-lives long enough to allow the separation and radioactive counting of the isotope of interest. This technique can be used to measure the yields of isotopes with half-lives of the order of minutes. Using various rapid physical and chemical separation techniques isotopes with half-lives of a few seconds can be studied. For example, Weiss and Reichert(13) have determined the yield of ^{115}Pd which has a half-life of 40 ± 4 sec; Weiss and Ballou (14) have studied ^{121}Cd with a 12.8 ± 0.4 sec.

On the other hand the mass spectrometric method requires stable or fairly long-lived isotopes with half-lives of the order of days or several hours in cases where the sample can be prepared for analysis within this time. Farrar(15) has studied ^{139}Ba-half-life of 83.2 min -- using a solid-source mass spectrometer; Clarke(16) has studied ^{138}Xe-half-life of 14.0 min. -- with a gas source mass spectrometer. The elements that can be analysed depend on the sensitivity of the instrument to the element of interest. The major advantage of this technique is that one can study stable isotopes at the convenience of the experimenter. The mass spectrometer primarily gives the yields of the various isotopes of the same element relative to one another. To obtain absolute yields a variety of "tricks" must be used. Farrar, Fickel and Tomlinson(17, 18) determined many yields for the high-yield fission products and they were able to normalize the yields of the entire fission product mass range to give a total yield of 200% with very little error. The mass spectrometer is particularly suited for the study of fine structure in the mass yield curve because of the high precision with which it is possible to measure the relative yields of isotopes of a given element.

The two techniques are complementary. The yields of the shorter-lived radio-isotopes that occur earlier in the beta-decay chain can be determined by radiochemistry while the mass spectrometer can be used in the measurement of the yields of the longer-lived isotopes and especially the yields of the stable end products of the different mass chains.

A third technique using high-resolution germanium detectors has been developed in recent years. Gordon, Harvey and Nakahara(19) have used this method to determine the mass distribution for ^{233}U. Gorman(20) has used this technique in conjunction with mass spectrometry to measure the yields from the 14 MeV neutron-induced fission of ^{238}U. Also Dange et al(21) have measured ^{239}Pu yields using this technique. These workers employ a 'comparison method' with the ^{235}U yields as standard. With this method one has to assume a set of yields, normally ^{235}U since these are the most accurately known yields, and the errors associated with the assumed yields are propagated along with the errors in the gamma ray counting measurements. The use of high resolution germanium detectors has the advantage of not requiring a time-consuming chemical or physical separation of the various elements with their inherent losses as in the radiometric or mass spectrometric measurements. In addition it offers the hope that with refined techniques the detector method can be used to give direct fission yield data. However this will involve a knowledge of branching ratios for the various gamma lines, detector efficiency and other parameters.

B. Mass Yield Data

Since the discovery of fission in 1939 a great deal of data has been accumulated on the yields of the many isotopes produced in the fission of a variety of nuclides. The data is being constantly revised and compiled as better and more reliable yields are obtained. Several reviews on the mass yields of many fissile nuclides are available(22, 23).

The earliest measurements were made by radiometric techniques and the mass yield curves obtained showed that the most probable fragments formed in the low energy neutron-induced fission of ^{235}U were of unequal size with mass numbers of about 95 and 140. This two-humped curve is the most striking feature

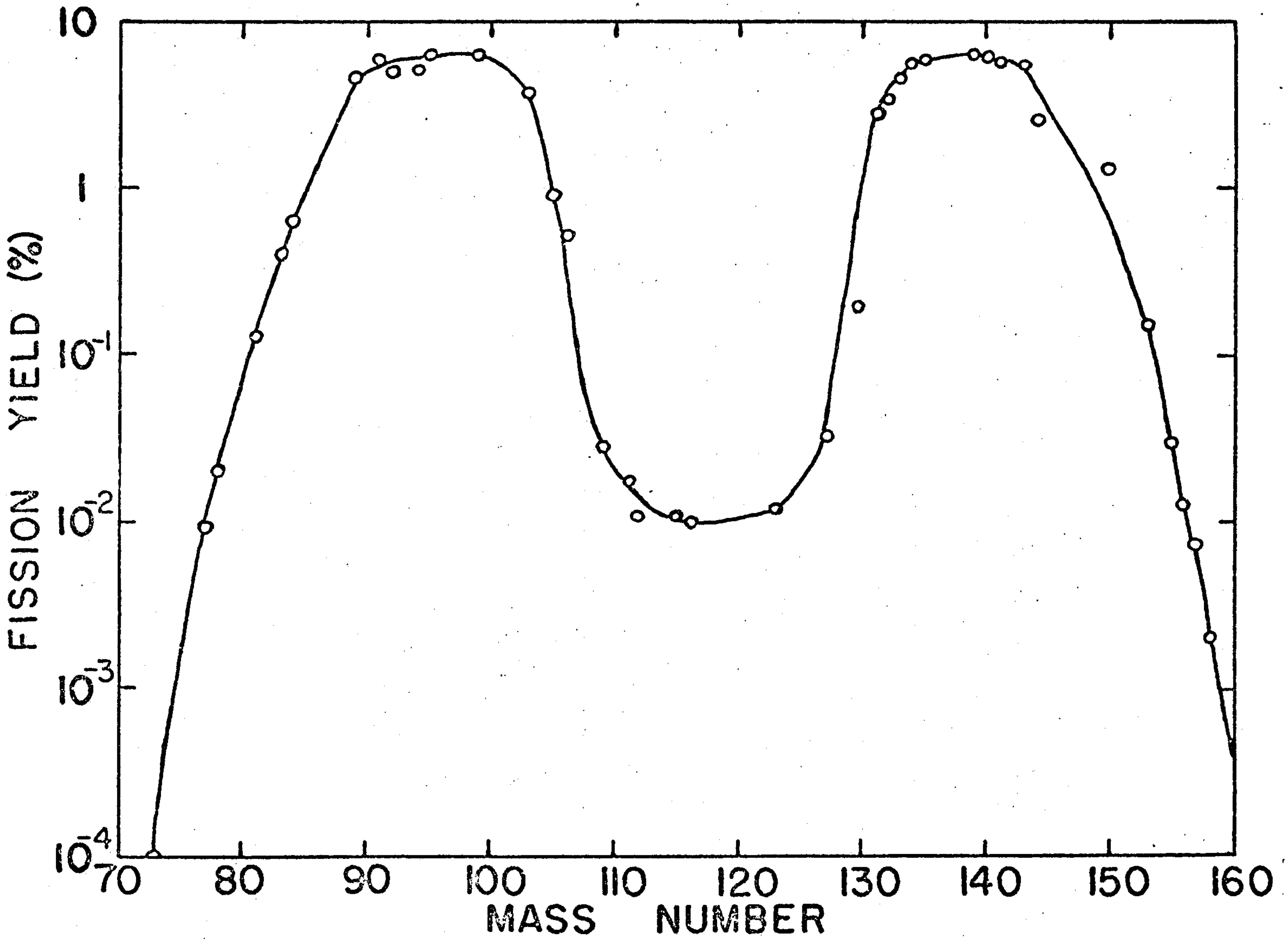

Fig. 3 Early radiochemical data(49) on the cumulative yields from the thermal neutron fission of ^{235}U.

of the mass division, and any acceptable model or theory of fission must explain the division into two asymmetric fragments. These early mass yield curves were drawn as smooth curves because of the low accuracy (typically 10-20%) of the yields. Figure 3 shows an early radiochemical mass-yield curve for ^{235}U.

The first application of the mass spectrometer to fission yield determinations was by Thode and Graham in 1947(24). They measured the yields of the krypton and Xenon fission product isotopes and they found that the yields of ^{133}Xe and ^{134}Xe were 20-30% higher than would be expected from a smooth mass-yield curve. This was conclusive evidence of the deviation from a smooth curve and established the existence of 'fine structure' in the mass curve. This 'fine structure' has since been explained in terms of a variation in neutron yield with mass(15, 17, 25), and to a small extent in the preferred formation of certain isotopes in fission because of increased stability in their nuclear structure(26, 27).

The mass spectrometric technique was used by Fickel, Farrar and Tomlinson(18) to re-determine the mass yields for ^{235}U. The result of their studies was a new mass yield curve for ^{235}U fission by thermal neutrons which eliminated many of the errors in the radiometric measurements by interrelating the yields of various mass chains with one another. This was achieved by relating the yields of the isotopes of neighboring pairs of elements by means of a pair of isobars. For example the yield of 285-day $^{144}_{58}$Ce was determined with respect to the other cerium isotopes. The yield of $^{144}_{60}$Nd was then measured relative to the other neodymium isotopes. In this way the yields of the cerium and neodymium isotopes were

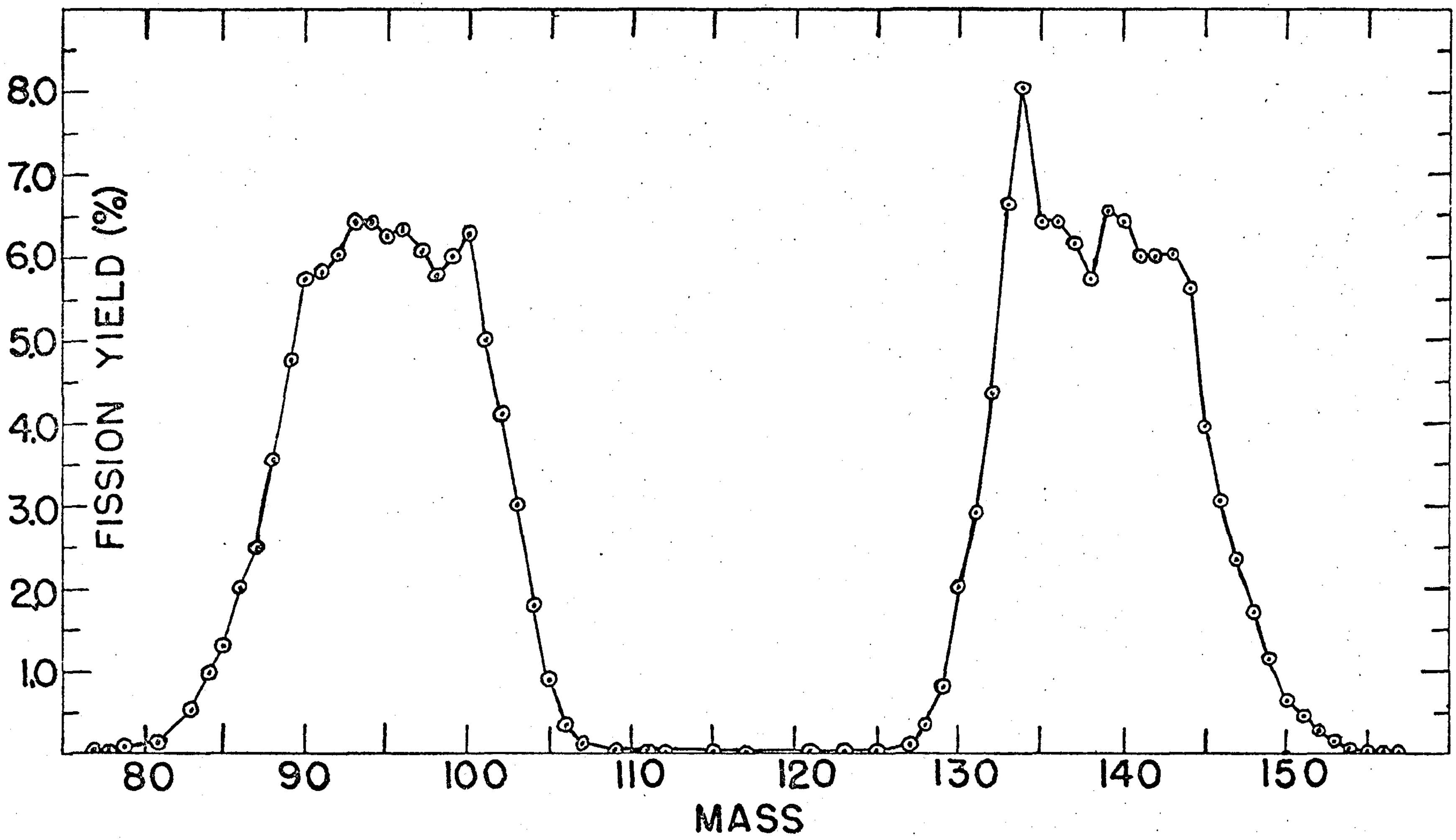

Fig 4 Mass spectrometric data(15) on the cumulative yields from the thermal neutron fission of ^{235}U.

intercalibrated. The resulting mass-yield curve was of high precision and accuracy and it remains the best known of the mass yield curves. Figure 4 shows the mass-yield curve for ^{235}U from mass spectrometric measurements.

In spite of the large amount of fission yield data available there are only a few isolated yield measurements in the mass region 105-125. This is the region of 'symmetric' mass division and in the low energy fission of most nuclides the yields are extremely low and are of the order of 0.01%. The shape of the mass yield curve for this region is not very well known because of the few yields available, and a smooth curve is normally drawn through this region to connect the regions where asymmetric mass division occurs. The scarcity of accurate yields in the symmetric or 'valley' region is due primarily to the low yields within this region and the experimental difficulties involved in these determinations. Radiochemical measurements are limited by the absence of suitable radioisotopes for study. On the other hand mass spectrometric measurements are hampered by the low sensitivity of the instrument to the elements in the valley region which would require relatively large samples. The first known attempt to measure yields in the symmetric region by mass spectrometry was by deLaeter in 1969(28) and his work was confined to the stable tin isotopes in the fission of ^{233}U with thermal and fast neutrons.

The study of ^{232}Th by Turkevich and Niday(29) indicated the possible existence of a peak in the valley region. Iyer et al(30) and Ganapathy and Kuroda(31) have also studied the fission of ^{232}Th and their data support that of Turkevich and Niday. These measurements were all obtained by radiometric methods and seem to provide conclusive proof of the presence of a small peak in the symmetric region giving a triple-peaked mass distribution.

Thind and Tomlinson(32) have suggested that this small peak may not necessarily be a true peak that would be present in the primary mass distribution i.e. before neutron emission, but could be due to perturbations in the mass yields as a result of neutron emission. They have shown by an argument similar to that used in explaining the fine structure observed by Thode and Graham that based on a smooth primary mass distribution in the symmetric region for ^{233}U and ^{235}U there could be a form of 'negative fine structure' arising from neutron emission by the fragments. They point out that the peak seen by Iyer et al may actually be the result of this 'negative fine structure', and may be a feature of the symmetric region for ^{233}U and ^{235}U. Their calculations were based on arbitrary primary mass distributions using neutron yield data with possible large errors but the existence of 'negative fine structure' may be possible nevertheless. Iyer et al also consider this possibility in discussing their results.

Fairhall and Jensen(33) were the first to obtain a triple-peaked mass distribution. They studied the fission of ^{226}Ra by 11 MeV protons and they found that in addition to the normal two peaks arising from asymmetric fission there was also a third peak of comparable size in the symmetric region.

No peak in the symmetric region has been reported for ^{235}U although triple-peaked mass distributions have also been obtained in a few other cases(34, 35).

C. The Two-mode Hypothesis - Symmetric vs Asymmetric Fission

The presence of a third peak in the mass distribution in the symmetric region has been interpreted by Turkevich and Niday(29) and by Fairhall(33) using a two-mode fission hypothesis. The triple-peak distribution is postulated to comprise a double-peaked distribution due to asymmetric fission and a single narrow peak due to 'symmetric' fission. The two-mode hypothesis requires that there be two alternate routes to fission proceeding through two separate saddle points. The one mode resulting in an asymmetric mass division is assumed to be independent of the excitation energy of the fissioning nucleus whereas the symmetric mode is strongly dependent on the excitation energy and may also depend on the type of nucleus undergoing fission.

The dependence of the mass distribution on the energy of the fissioning nucleus has been studied for many nuclei. The energy range studied covers the range from thermal neutron energies (0.025eV) to over 50 MeV. The main characteristic of the energy dependence of the mass distribution is that the yields in the valley region increase relative to those in the asymmetric region as the excitation energy of the fissioning nucleus is raised. This indicates that the probability of near-symmetric fission increases rapidly while the probability of asymmetric fission remains relatively constant. It is interesting to discuss the energy dependence as a function of nuclear type.

In the case of highly fissile nuclides ($Z > 90$) the mass distribution for low energy fission is the familiar double-peaked curve corresponding to predominantly asymmetric fission. As the energy of the compound nucleus is increased the peak-to-valley ratio decreases as a result of the increase in the yields in the symmetric region. When the energy of the compound nucleus lies in the range 10-40 MeV the symmetric region "fills in" and in a few cases(34, 35) a three-humped distribution is observed. At energies greater than about 40 MeV the mass distribution consists of a single broad peak.

For elements of low fissionability like Ac, Ra ($Z < 90$) near-threshold-fission results in a triple-peaked distribution. However as the energy of the compound nucleus is increased the peak in the symmetric region increases relative to the asymmetric peaks and symmetric fission becomes predominant. At very high energies the mass distribution becomes a single broad curve.

For slightly fissile nuclides like Pb or Bi the mass distribution at near-threshold energies consists of a single narrow peak ranging from about mass 80 to 125. This corresponds to near-symmetric fission. Asymmetric fission as seen in ^{235}U is non-existent and is not competitive until at very high energies.

The energy dependence of the mass distribution tends to support the two-mode hypothesis proposed by Fairhall. The yields in the symmetric region increase characteristically as the excitation energy of the compound nucleus is increased. The rationale of the two-mode hypothesis is that there are two distinct and competitive fission modes, one strongly dependent on the excitation energy of the compound nucleus and favoring symmetric-type fission while the other is relatively independent of energy and leads to asymmetric-type fission.

Fairhall and Jensen(33) obtained a triple-humped distribution when ^{226}Ra was bombarded with 11 MeV protons to produce the compound nucleus $^{227}_{89}$Ac. However, they did not obtain a triple-peaked curve in the fission of ^{226}Ra by 20 and 30 MeV He ions in which the compound nucleus was $^{230}_{90}$Th. Fairhall suggested that the character of the mass distribution may be influenced by the nuclear type of the compound nucleus. However Cobble and coworkers(34, 35) found that the He-induced fission of ^{233}U gave a triple-peaked curve but not ^{235}U or ^{238}U. Thus it is not clear if there exists a correlation between fission mode and nuclear type.

Alternately the characteristic broadening of the mass distribution with excitation energy is also used in considerations of the two-mode hypothesis. Many workers(36) prefer a formulation of the two-mode hypothesis in which the symmetric mode produces a broad peak covering the entire mass range of the fission products. The increased probability of very asymmetric and near-symmetric fission is believed to be a reflection of the increased contribution from the symmetric mode. The basic trend towards a justification of the two-mode hypothesis by these workers has been the attempt to decompose the mass distributions for various nuclides into their supposedly component symmetric and asymmetric distributions.

The two-mode hypothesis constitutes the main attempt so far to explain the characteristic increase in the probability of symmetric fission with excitation energy. The more successful models or theories of fission are unable so far to account for this feature of the fission process and their predictions are generally not in accord with the data. For example, Fong's theory(37) predicts that the most probable fragments in low energy fission will be the most probable fragments at all excitation energies of the fissioning nucleus. To quote Fong "...at high energy, symmetric fission and asymmetric fission will have comparable probabilities. All rare modes of fission will become more probable. However the most probable modes will remain to be most probable. This means that the widths of all distribution curves will be increased while the peaks of all distribution curves remain unshifted." This indicates that asymmetric fission will always predominate over symmetric fission at all excitation energies of the compound nucleus — a prediction which is erroneous.

However although the two-mode hypothesis appears to have some success in explaining this phenomenon it is still unsatisfactory for various reasons. It is primarily an ad hoc argument and it is limited in its usefulness towards a general understanding of the fission process. For aesthetic reasons one would prefer an explanation of the energy dependence of the mass division based on a fission theory or model that would provide a unified treatment of the various fission phenomena using only a few fundamental assumptions and with no resort to ad hoc arguments.

It is not clear how the three-humped curve from the 11 MeV proton-induced fission of ^{226}Ra can be resolved into two asymmetric-type peaks and a broad "symmetric" peak ranging over the entire mass distribution. From a cursory examination of the curve this does not seem possible. It would be interesting as well to learn how the two-mode hypothesis would explain the mass curve for ^{252}Cf spontaneous fission. The two asymmetric peaks are extremely close together with the valley region almost non-existent. Fission into two near-symmetric fragments, which would be expected to proceed through the symmetric mode, is very high (1% or greater) yet there is no apparent contribution from fission through the symmetric mode.

Also the energy dependence of the mass division does not appear to be a smooth continuous function of the excitation energy of the nucleus. Studies of the resonance fission of various nuclides indicate that the peak-to-valley ratio fluctuates with the resonance energy. The fission of ^{235}U at several resonances ranging from 10 to 63 eV was studied by the Los Alamos Radiochemistry Group(38). They found that within this energy region five resonances gave an increase in symmetric fission while eleven resonances are associated with a decrease in symmetric fission. These resonances are believed to correspond to the energies of the excited nuclear states and it would appear that the nature of the excited state or fission channel determines the nature of the mass division.

It is interesting to note that studies on the angular distribution of the primary fragments indicate that the nuclear state of the fissioning nucleus may lead to a preference for a particular type of mass division. A. Bohr(39) has suggested that for low energy fission the nucleus may bind up most of its energy in potential energy of deformation and may be 'cold' at the saddle point. The nuclear states at the saddle point may therefore resemble the quantum states of the ground state nucleus. Studies of the angular distribution of the fission fragments indicated that the lowest $K = 0, 1^-$ state of the compound nucleus at the saddle point corresponding to the vibration of the nucleus into asymmetric (pear-shaped) configurations may lead exclusively to asymmetric mass division. Fairhall, Halpern and Winhold(40) found that the products of symmetric mass division are isotropic but with asymmetric mass division the distribution of the fragments is anisotropic. This seems to suggest that a nucleus in certain nuclear states and fissioning through a single saddle point may divide preferentially into either asymmetric or symmetric fragments depending on the nature and spin of the quantum state of the nucleus at the saddle point. However Vandenbosch, Unik and Huizenga(41) have concluded from their study of the $^{234}U(d,pf)$ reaction that there is no possible correlation between angular anisotropy and mass asymmetry.

It may be possible nevertheless that asymmetric mass division proceeds through the $K = 0, 1^-$ state and other related states which are present in certain nuclear species at low energies. This may explain the predominance of asymmetric fission at low energies and its possible dependence on nuclear type. Alternately symmetric mass division may proceed through the high energy quantum states, hence its dependence on the excitation energy of the compound nucleus. Certainly it appears that the answer to the question of the energy dependence of the mass division will follow from a greater understanding of the role of the nuclear states or channels at the saddle point and their influence on the various fission phenomena. Also there has been a great surge of interest in fission resulting from the work of Strutinsky(42) on the behaviour of the nucleus under extreme deformations and it may be possible to explain the energy dependence based on these considerations without resort to the two-mode hypothesis.

D. Objective of the Present Work

The principal aim of this work was to attempt to obtain some information on the cadmium fission product isotopes in the thermal neutron fission of ^{233}U and ^{235}U. It was hoped that the relative yields of the cadmium isotopes of mass 111, 112, 113, 114 and 116 could be measured. ^{115}Cd is unstable and decays to $^{115}_{49}In$. Any new data within the symmetric region would be important in filling the conspicuous lack of data on the yields in this region.

This data would be valuable for several reasons. Apart from the fact that no mass spectrometric data on the cadmium fission product isotopes exists, there is little or no comparable radiochemical data. Coupled with the results of de Laeter, this data would cover most of the symmetric region and could be very useful in elucidating the nature and shape of the mass yield curve in the symmetric region. It may be helpful in determining whether 'negative fine structure' as proposed by Thind and Tomlinson is present in the fission of ^{233}U and ^{235}U. As well it may be possible to make certain projections which could help to resolve the question of the two-mode hypothesis.

CHAPTER 3

EXPERIMENTAL

A. Mass Spectrometry

a) The Instrument

The mass spectrometer used in these analyses has already been described in detail by Agyei(43). The instrument is a 10-inch radius, ninety-degree sector solid-source mass spectrometer. The spectra were obtained by magnetic scanning of the peaks, and the ions were detected with a 14-stage Allen-type electron multiplier with a gain of about 5×10^4. The ion current was then fed to a vibrating reed electrometer which was coupled to a chart recorder.

For the purpose of these measurements it was necessary to employ an electron-impact source of the type described by Heyland(44) and de Laeter(28). Figure 5 is a diagram of the electron impact source. Essentially it uses a triple-filament button which is modified to produce an electron beam at ninety degrees to the sample beam. The electron energies were variable, and the sample filament doubled as a repeller for the ions by introducing a variable positive voltage with respect to the case. The

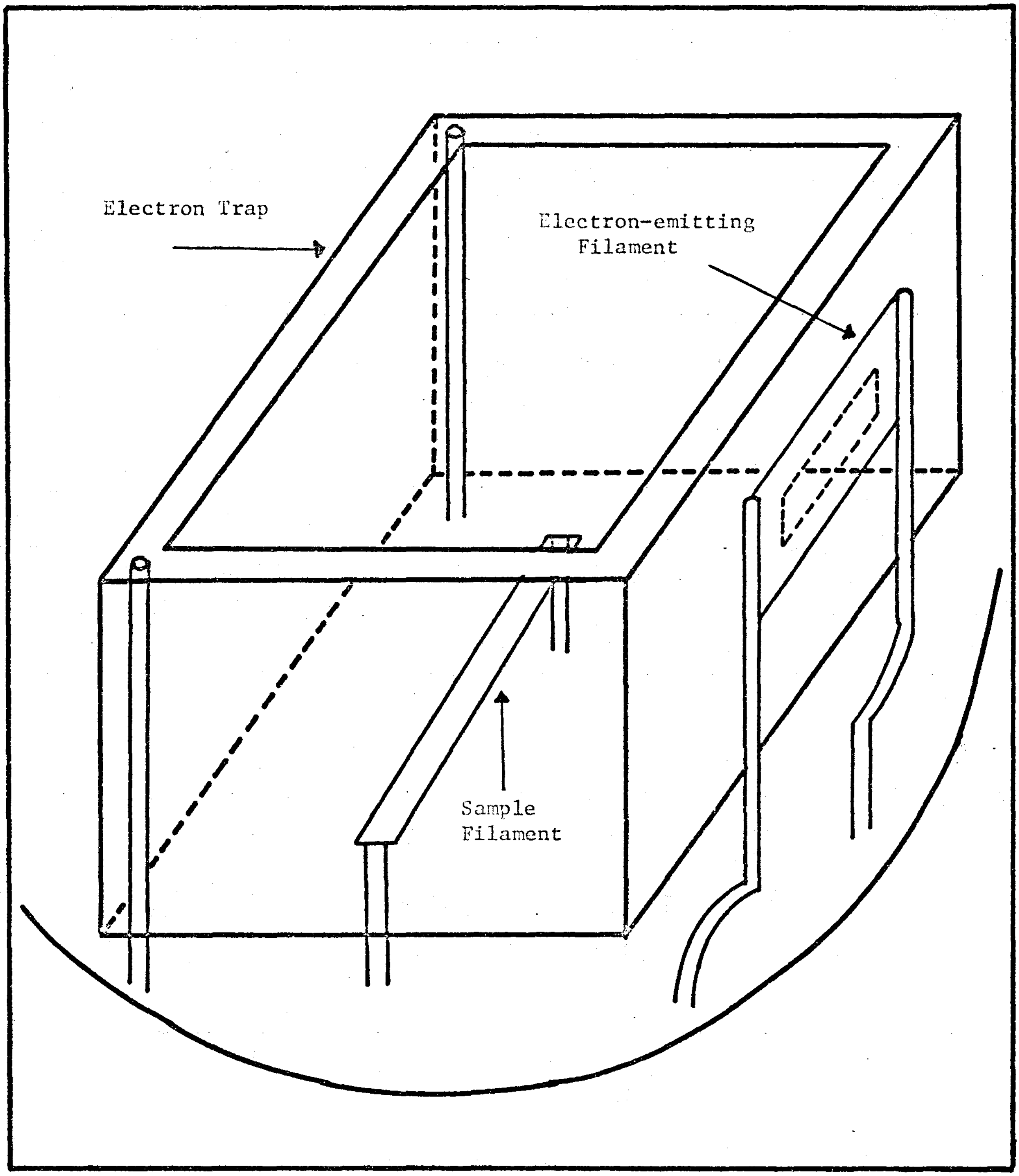

Fig 5 Electron-Impact Source

necessary bias voltages were provided by modifying the supply circuits to the source. The modified circuits are shown schematically in Figure 6.

The use of the electron-impact source resulted in the production of large beams of hydrocarbons because of the increased efficiency of the source in the production of ions. The large hydrocarbon peaks tended to obscure the cadmium peaks by overlapping them because of the insufficient resolution of the instrument. To obtain measureable cadmium spectra it was necessary to increase the resolution of the instrument from about 300 to approximately 600. This was achieved by replacing the source and collector slits with smaller ones. The source slit was reduced to 6/1000 of an inch and the collector slit to 10/1000 of an inch. The theoretical resolution of the spectrometer with these slits is given by the expression

$$\text{Resolution } R = \frac{\text{Radius of Magnet}}{\text{source-slit width} + \text{collector-slit width}} = \frac{10''}{16/1000''} \doteq 630$$

The observed resolution in the mass region 105 to 120 was found to be roughly 580. This was measured from actual spectra where the resolution is determined as follows from any two peaks in the region.

$$\text{Resolution } R = \frac{\text{Average width of peak} \times \text{Average mass of peaks}}{\text{Distance between centres of peaks}}$$

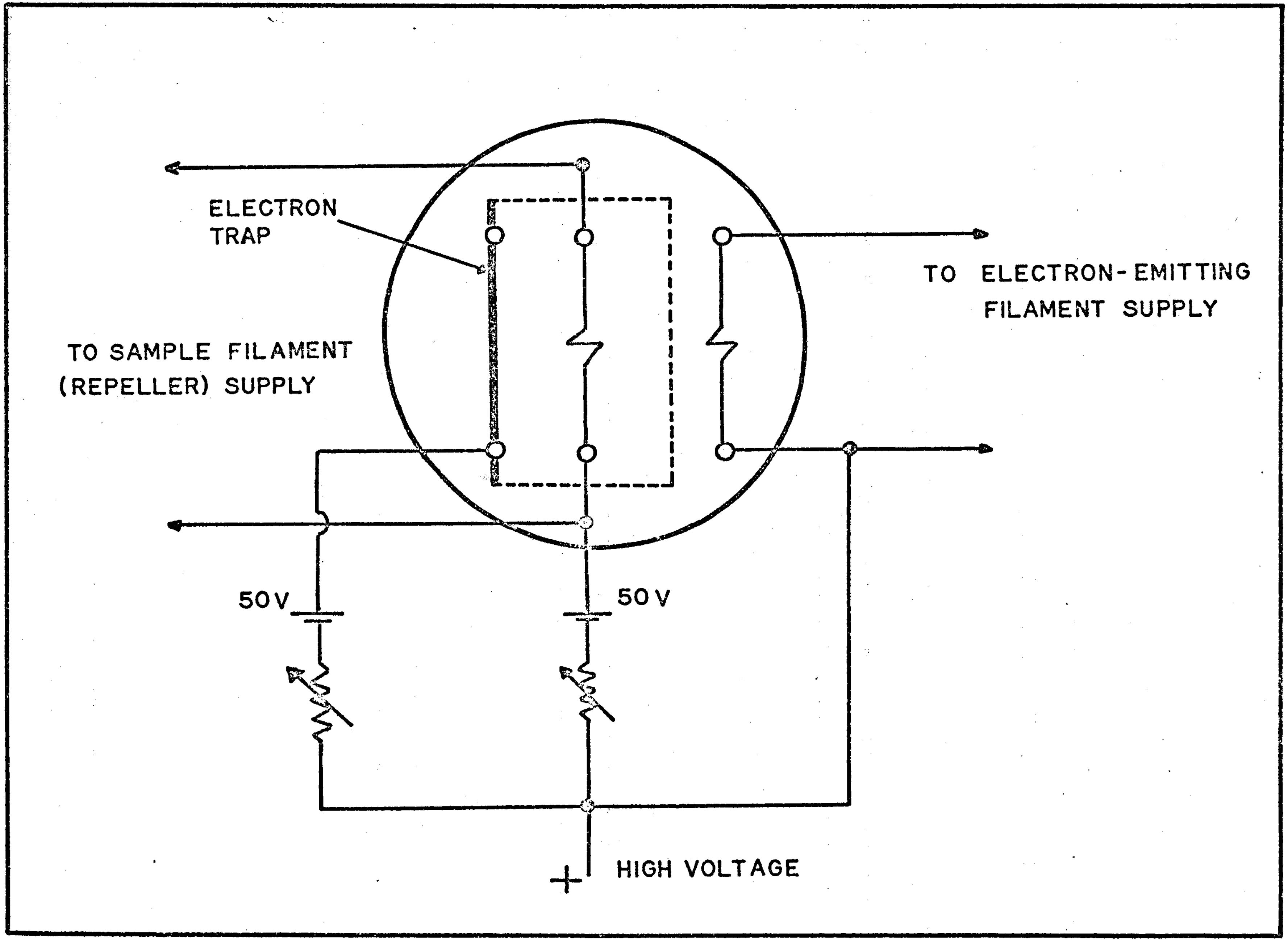

Fig 6 Modified Source Supply Circuit.

b) Preparation of the Source

The source was cleaned and heated before each sample was analysed in the mass spectrometer. The source parts were placed in an ultrasonic cleaner for about 15 minutes, washed in distilled water and alcohol, and dried with a hot-air gun. The source was then replaced in the instrument, and the sample filament and electron-emitting filament were heated by passing a current of about 4 amperes through each filament for 3 to 4 hours. The object of this procedure was to remove traces of the previous sample and to minimize 'memory' effects.

After a sample run was completed the sample filament and electron-emitting filament were heated overnight by passing a current of 4 amperes through each filament.

Occasionally replacement of the filaments was necessary. The sample filament consisted of a piece of rhenium ribbon while the electron-emitting filament was of thoriated tungsten ribbon. These filaments were welded to their supports with a spot welder.

c) Sample Loading

The sample solution was evaporated to a small drop and transferred to the sample filament using a polyethylene eyedropper. The filament was then dried by passing a small current of 0.6 to 0.8 A through it.

The source was replaced in the mass spectrometer which was then evacuated down to the operating pressure of approximately 10^{-7} torr.

d) Operating Conditions

In order to limit the hydrocarbon peaks to a tolerable level it was necessary to heat the electron-emitting filament with a current of about 3A while the mass spectrometer was being evacuated to the operating pressure. This value was obtained through experimentation and was found to be suitable enough to reduce the hydrocarbon background to reasonable levels without causing excessive loss of sample through indirect heating. Also the sample was normally run within 36 hours after insertion in the instrument before there was undue and appreciable loss of sample.

The electron energy was usually about 25 eV, this being the voltage applied to the electron collector. This value is a compromise allowing for maximum ion current and minimum hydrocarbon interference. The repeller voltage was of the order of 5 - 10 volts and was adjusted slightly before the run was started to maximize the sample signal.

About 15 minutes before measurements were recorded the electron-emitting filament current was increased to the operating value of 5.0 A. The sample filament was then turned on and slowly brought up to 0.6 A in 0.1 A steps. The repeller voltage was adjusted as stated before to maximize one of the sample peaks. The scan was then started and the spectra recorded.

The ions were accelerated through a potential of + 5000 volts. The voltage on the electron multiplier was -2500 volts. The peaks were measured on the 30 mV and 10 mV scales of the vibrating reed electrometer through a grid-leak resistor of 10^9 ohms.

e) Sensitivity of the Instrument

An attempt to analyze the cadmium samples was made initially with a conventional triple-filament source. The maximum sensitivity that was obtainable by this technique was found to be of the order of 10^{-7} g. of cadmium and there was considerable interference from the hydrocarbon background because of the low resolution of the instrument at the time. Since the estimated sample size was of the order of 5×10^{-8} g. it was necessary to employ a more efficient source. The ion-impact source used by de Laeter in a similar study of the fission product isotopes of tin was found to give a sensitivity of the order of 10^{-8} g. of cadmium. The sample size in the analyses was thus very nearly the critical amount desirable to give measurable cadmium spectra.

B. Sample Preparation

a) Purification of Uranium Samples

The samples were purified prior to irradiation by an anion-exchange procedure in order to remove any natural cadmium present. The anion-exchange columns were prepared with 200 mesh Dowex-1 anion-exchange resin, and were equilibrated with 7M HCl.

Approximately 10 mg of uranium was disolved in concentrated HNO_3 and the solution was made approximately 5M in HCl by adding concentrated HCl. This solution was then transferred to the anion-exchange column. The uranium was eluted from the column by washing with 1M HCl and collected in a teflon dish. The purified uranium

TABLE 1

Irradiation Data for the McMaster ^{233}U and ^{235}U Samples

Sample	Nuclide	Sample Size	Irradiation Time	No. of Fissions
A	^{235}U	10 mg	90 days	$\sim 10^{18}$
B	^{235}U	10 mg	90 days	$\sim 10^{18}$
C	^{235}U	10 mg	90 days	$\sim 10^{18}$
D	^{233}U	10 mg	90 days	$\sim 10^{18}$
E	^{233}U	10 mg	90 days	$\sim 10^{18}$

Thermal Neutron Flux = $(1.0 \pm 0.1) \times 10^{13}$ neutrons/cm^2/sec.

Table 2

Irradiation Data for the Chalk River Sample

Initial Composition	$^{235}U/^{238}U = 0.1115$
Final Composition	$^{235}U/^{238}U = 0.08426$
Sample Size	47.2 mg
*Integrated Flux	$\simeq 4.2 \times 10^{20}$ neutrons/cm^2

*^{239}Pu fissions $\simeq$ 0.8% of ^{235}U fissions in the sample.

*Estimated Values (Appendix B).

solution was then transferred to a quartz irradiation capsule and heated to dryness under a slow flame. Finally the uranium was converted to U_3O_8 on further strong heating. The quartz capsule was sealed and tested for leaks.

b) Irradiation of Samples

The samples were irradiated in the McMaster Nuclear Reactor in high neutron flux positions for various time intervals. A total of 5 samples were prepared; 3 of ^{235}U and 2 of ^{233}U. The irradiation data for these samples is given in Table 1.

In addition a sample of fuel rod in an HNO_3 solution was obtained from Chalk River. The sample was approximately 10% enriched in ^{235}U before irradiation. The number of fissions of ^{235}U were estimated to be 2.46×10^{18} whereas the ^{239}Pu fissions were estimated at about 0.8% of the ^{235}U fissions. The fission products therefore were thought to be essentially products of ^{235}U fission and they should be comparable to the McMaster ^{235}U fission product samples. The irradiation data for the Chalk River sample is given in Table 2.

The samples irradiated in the McMaster Reactor consisted of 93% enriched ^{235}U and essentially 100% ^{233}U.

After irradiation in the McMaster Reactor the samples were allowed to cool for at least six months to allow the radiation to decrease to workable levels.

c) Extraction of Cadmium

The samples were dissolved in concentrated HNO_3 and the resulting solution was transferred to a test-tube. The solution was then made up to about 5M in HCl and added to the anion-exchange column. The columns were prepared as outlined before. The uranium and the majority of the fission products were eluted with 1M HCl. The washings with 1M HCl were continued after the uranium was eluted so that as much of the fission products as possible could be removed.

In the case of samples A and B the cadmium fission product isotopes were eluted by washing with ion-free water. This eluting agent was also used with the Chalk River sample. In the case of the other samples the cadmium was eluted with 10 ml of an NH_3 solution of pH 8. The eluate containing the cadmium was collected in a teflon dish and evaporated to a small drop in preparation for mass spectrometric analysis.

The solution to be analysed also contained small amounts of various fission products which were not eluted with the 1M HCl. However it was felt that these impurities could be tolerated since they would not appear in the mass region of interest and interfere in the mass spectrometric analysis.

d) Purification of Reagents

The HCl solutions used in the anion-exchange separations were prepared by bubbling gaseous HCl through a large beaker of ion-free water. The saturated solution was then standardized by volumetric analysis. The solutions were made up to the required concentrations by diluting as necessary with ion-free water, and were again purified by running them through an anion-exchange column to remove any possible terrestrial cadmium.

The ion-free water used in the preparation of the reagents was obtained by running distilled water through an ion-exchange column packed with a mixed bed of cation and anion exchange resins.

The NH_3 solution was prepared by diluting concentrated NH_3 with ion-free water to the desired pH.

CHAPTER 4

RESULTS

A. Abundances of the Natural Cadmium Isotopes

Two samples of about 10^{-7} g of terrestrial cadmium were analysed for isotopes 110 - 114 and 116. Masses 106 and 108 were not included as they are not produced in fission. The abundances of the isotopes as obtained with the mass spectrometer were normalized to 97.91% which is the accepted total abundance for these isotopes. In Table 3 it can be seen that there was quite good agreement between the measured values and the accepted literature values(45). The differences can be adequately explained as statistical errors. There did not appear to be any systematic errors such as mass discrimination in the measurements. It was therefore assumed that the systematic errors were negligible or at least small in comparison with the statistical errors.

B. Chalk River Sample - ^{235}U

The Chalk River sample was divided into two roughly equal portions which were analysed in the mass spectrometer to give two sets of mass spectra of the cadmium isotopes. During run # 1

TABLE 3

Mass Spectrometric Abundances of the Natural Cadmium Isotopes

Mass Number	Run #1 Atom %	Run #2 Atom %	Weighted Average Atom %	Literature Values(45)
106	Not Measured	Not Measured	--	(1.215±0.005)%
108	Not Measured	Not Measured	--	(0.875±0.005)%
110	(12.38±0.20)%	(12.25±0.53)%	(12.36±0.19)%	(12.39±0.01) %
111	(12.68±0.18)%	(12.74±0.53)%	(12.69±0.17)%	(12.75±0.01) %
112	(24.20±0.67)%	(23.91±1.05)%	(24.11±0.56)%	(24.07±0.01) %
113	(12.35±0.33)%	(12.27±0.54)%	(12.33±0.29)%	(12.26±0.01) %
114	(28.80±0.49)%	(29.21±0.28)%	(28.91±0.45)%	(28.86±0.01) %
116	(7.49±0.29)%	(7.53±0.33)%	(7.51±0.21)%	(7.58±0.01) %
Total	97.91%	97.91%	97.91%	100.00%

19 double scans were recorded and 24 during run #2. There was a large amount of contamination due to natural cadmium but the data was considered sufficiently reliable to allow one to separate the contribution of the fission product cadmium isotopes from the contribution due to terrestrial cadmium. The results of the mass spectrometric analyses are given in Tables 4 and 5.

The fission contribution was determined for each analysis by subtracting proportionate amounts corresponding to the quantity of contamination present. The weighted average of the fission product cadmium abundances were then computed for each isotope (Table 6).

C. McMaster ^{235}U Samples

The same problem of large terrestrial cadmium contamination was encountered in the analyses of the McMaster ^{235}U samples. The amounts of cadmium observed were small and it is possible that there was substantial loss of sample in the recovery stages of the analysis. No spectra were obtained for sample B and it is therefore assumed that most of the sample was lost in the extraction process. Samples A and C showed high levels of natural cadmium which tended to obscure the contributions from the fission product isotopes. The data from the analysis of sample A was not considered reliable enough because of the extremely high contamination in the sample. Although sample C showed a large contribution of natural cadmium the data was analysed and the fission

TABLE 4

Mass Spectrometric Abundances of the Cadmium Isotopes from the Chalk River Sample

Run #1

Mass Number	110	111	112	113	114	116
Measured Relative Abundance	1.000	1.885	2.518	1.010	3.349	1.287
Terrestrial Cadmium in Sample Relative Abundance	1.000	1.029	1.943	0.989	2.329	0.612
Fission Product Cadmium in Sample	---	0.856	0.575	0.021	1.020	0.675
Fission Product Cadmium in Sample Atom %	---	(27.20±1.44)%	(18.29±1.75)%	(0.67±1.26)%	(32.40±1.47)%	(21.44±1.47)%

TABLE 5

Mass Spectrometric Abundances of the Cadmium Isotopes from the Chalk River Sample

Run #2

Mass Number	110	111	112	113	114	116
Measured Relative Abundance	1.000	1.354	2.104	1.004	2.648	0.882
Terrestrial Cadmium in Sample Relative Abundance	1.000	1.029	1.943	0.989	2.329	0.612
Fission Product Cadmium in Sample	---	0.325	0.161	0.015	0.319	0.270
Fission Product Cadmium in Sample Atom %	---	(29.84±3.21)%	(14.84±3.38)%	(1.32±2.06)%	29.27±5.03)%	(24.73±3.13)%

TABLE 6

Abundances of the Stable Fission Product Isotopes of Cadmium from the Chalk River Sample

Mass Number	111	112	113	114	116
Run #1 Atom %	(27.20±1.44)%	(18.29±1.75)%	(0.67±1.26)%	(32.40±1.47)%	(21.44±1.47)%
Run #2 Atom %	(29.84±3.21)%	(14.84±3.38)%	(1.32±2.06)%	(29.27±5.03)%	(24.73±3.13)%
Weighted Average Atom %	(27.5 ±1.3) %	(17.6 ± 1.5)%	(0.85±1.1) %	(32.1 ± 1.4)%	(22.0 ± 1.3)%

product cadmium determined.

The mass spectrometric abundances for sample A were computed from 18 double-scans whereas only 13 double-scans were obtained with sample C. (Table 7)

D. McMaster ^{233}U Samples

The two McMaster ^{233}U samples were analysed in the mass spectrometer. In the case of sample D no spectra were obtained. It is believed that most of the fission product cadmium was lost in the recovery of the fission products. The ^{233}U appeared to be fused to the quartz vial and the recovery of the fission products may have been very minimal. Losses from recoil of the fission products into the quartz may also have been a contributing factor.

In the case of sample E the amount of cadmium observed was very small and the sample decayed very quickly. Only 4 double-scans were recorded and the abundances seem to indicate that virtually all the cadmium observed was terrestrial in origin with very little contribution from the fission product cadmium. The abundances are close to the natural abundances but there are deviations that may be indicative of fission product cadmium. The 116 yield is higher than the abundance of the natural 116 isotope and this suggests that some of the mass 116 observed is due to fission product ^{116}Cd.

The abundance of mass 110 is slightly higher than the

TABLE 7

Mass Spectrometric Abundances of the Cadmium Isotopes from the McMaster ^{235}U Samples

Mass Number	110	111	112	113	114	116
Sample A Relative Abundance	1.000	1.018	1.616	1.042	2.541	0.732
Sample B Relative Abundance	---	---	---	---	---	---
Sample C Relative Abundance	1.000	1.364	2.088	1.019	2.629	1.000
Terrestrial Cadmium in Sample C Relative Abundance	1.000	1.029	1.943	0.989	2.329	0.612
Fission Product Cadmium in Sample C	---	0.335	0.145	0.030	0.300	0.388
Fission Product Cadmium in Sample C Atom %	---	(28.0±2.7)%	12.2±2.7)%	(2.5±2.1)%	(25.0±4.9)%	(32.3±3.6)%

TABLE 8

Mass Spectrometric Abundances of the Cadmium Isotopes from the McMaster ^{233}U Samples

Mass Number	Sample D	Sample E
110	-	(13.84 ± 0.09)%
111	-	(14.03 ± 0.40)%
112	-	(22.55 ± 0.18)%
113	-	(13.20 ± 0.22)%
114	-	(25.90 ± 0.58)%
116	-	(10.49 ± 0.48)%

value for natural ^{110}Cd but it appears that this discrepancy is a result of the overlap of the ^{110}Cd peak with the 'tail' of the extremely large hydrocarbon peak at mass 110. This peak is more than 10 times the size of the cadmium peak and because of the overlap between the two peaks they are poorly resolved.

The data for the ^{233}U samples was therefore considered unreliable and no attempt was made to determine the fission product contribution.

E. Correction of the ^{113}Cd and ^{114}Cd Yields for the ^{113}Cd(n,γ) ^{114}Cd Reaction

The data given in Tables 6 and 7 represents the abundances of the fission product isotopes of cadmium. The ^{113}Cd and ^{114}Cd yields are not the actual cumulative yields for mass 113 and 114 since there is substantial conversion of mass 113 into mass 114 through the ^{113}Cd(n,γ)^{114}Cd reaction. However, the sum of the 113 and 114 yields does constitute the total cumulative yields of the 113 and 114 mass chains. Ideally the actual yields of mass 113 and 114 should be determined by correcting for the loss of ^{113}Cd through the (n,γ) reaction. This is not possible to any satisfactory degree of accuracy because of the incomplete knowledge of the parameters involved. The mass 113 and 114 abundances were therefore determined by fitting the 113 and 114 abundances to a smooth mass-yield curve. The rationale for this method of correction is discussed in Chapter 5, Section A. Table

TABLE 9

Mass Spectrometric Abundances of the Stable Cadmium Fission Product Isotopes In the Chalk River and McMaster ^{235}U Samples

Mass Number	111	112	113	114	116
Chalk River Sample					
Fission Product Cadmium (Corrected for neutron capture) Atom %	(27.5 ± 1.3)%	(17.6 ± 1.5)%	(15.0 ± 1.5)%	(17.9 ± 2.0)%	(22.0 ± 1.3)%
Relative Yields	1.00 ± 0.05	0.64 ± 0.05	0.54 ± 0.06	0.65 ± 0.08	0.80 ± 0.05
McMaster ^{235}U Sample					
Fission Product Cadmium (Corrected for neutron capture) Atom %	(28.0 ± 2.7)%	(12.2 ± 2.7)%	(12.0 ± 4.2)%	(15.5 ± 5.6)%	(32.3 ± 3.6)%
Relative Yields	1.00 ± 0.10	0.44 ± 0.10	0.43 ± 0.15	0.55 ± 0.20	1.15 ± 0.13

9 gives the abundances of the fission product isotopes of cadmium and the estimated 113 and 114 yields.

CHAPTER 5

DISCUSSION

A. Correction of the ^{113}Cd and ^{114}Cd Yields

A substantial amount of fission product ^{113}Cd is transformed into ^{114}Cd through the ^{113}Cd(n,γ)^{114}Cd reaction because of the high capture cross-section (2×10^4 barns)$^{(50)}$ and large values of the integrated flux for the irradiations -- 4.2×10^{20} neutrons/cm^2 (Appendix B).

The abundances of the ^{113}Cd and ^{114}Cd isotopes after correcting for terrestrial contamination in the samples represent the amount of fission product ^{113}Cd and ^{114}Cd remaining from the (n,γ) reaction during the irradiation. The yield of ^{113}Cd must therefore be increased by an amount corresponding to the loss by neutron capture while the ^{114}Cd yield must be reduced by a similar amount.

The correction for ^{113}Cd burn-up (Appendix A) involves a knowledge of two quantities - the integrated neutron flux and the cross-section for neutron capture. The neutron flux seen by the samples has an energy distribution which depends on the characteristics of the reactor and the irradiation position of the samples. The

Chalk River sample was a portion of fuel rod and it was irradiated in a heavy-water moderated reactor. The McMaster samples were irradiated in core positions and the neutron flux was moderated with normal water. The neutron flux for these two sets of samples thus had different energy distributions.

The effective capture cross-section for the samples depends appreciably on the characteristics of the neutron energy distribution. Westcott(51) has shown that for a well-moderated neutron energy spectrum the effective cross-section for a process such as neutron capture is given by the expression

$$\hat{\sigma} = \sigma_{2200}\ (g + r\ s)$$

where $\hat{\sigma}$ = effective cross-section

σ_{2200} = thermal-neutron cross-section (2200 metres/sec)

g = g- factor

r = epithermal index

s = s-factor

For a 1/v law cross section $g = 1$ and $s = 0$. The s-factor is related to the resonance integral in the epithermal region while the g-factor is a measure of the deviation of the cross-section from the 1/v law. The effective cross-section is in reality a complex function since the g-, r-, and s-factors are dependent on the neutron temperature which must be estimated for the samples. In addition the r-factor also varies with the irradiation position in the reactor. The $\hat{\sigma}$ for cadmium is estimated roughly at 2.7×10^4 barns for the Chalk River sample and at 3.0×10^4 barns for the McMaster samples. The estimated integrated flux for the Chalk River sample is 4.2×10^{20} neutrons/cm^2 while for the McMaster samples it was about 0.3×10^{20} neutrons/cm^2.

In order to correct for neutron capture the ^{113}Cd yield must be multiplied by a factor - $\hat{\sigma}\phi t$ - which is the algebraic product of the effective capture cross-section for ^{113}Cd and the integrated flux. For the Chalk River sample the correction factor is roughly 11.3, and about 2.4 for the McMaster samples. The measured fission product ^{113}Cd abundance in the various analyses was very small and had relatively large uncertainties (Tables 6 and 7). Using this method the ^{113}Cd abundance corrected for neutron capture for the Chalk River sample is (9.6 ± 12.4) atom % while for the McMaster sample it is (6.0 ± 5.0)% assuming that there is no error in the correction factors. It is apparent that the ^{113}Cd and ^{114}Cd yields can not be determined analytically with any satisfactory degree of accuracy because of the large errors in the ^{113}Cd and ^{114}Cd yields and in the correction factors.

In addition the ^{113}Cd abundance after correction for contamination may not be the actual fission product contribution remaining from the (n,γ) reaction. In view of the large quantities of natural cadmium observed in the samples the possibility of contamination in the samples prior to irradiation can not be ruled out entirely. This makes the significance of the ^{113}Cd abundance after correction for contamination very obscure and this may account for the lower ^{113}Cd abundance obtained when the McMaster sample is corrected for neutron capture.

Since the ^{113}Cd and ^{114}Cd yields cannot be calculated analytically with any reasonable degree of accuracy it was decided to estimate these yields by fitting them to a smooth continuous curve drawn through masses 111-116 (Fig. 7). Although the ^{113}Cd fission product yields known with only about 130% precision for the Chalk River sample and about 35% for the McMaster sample, the total ^{113}Cd and ^{114}Cd fission product yields are precise to about 8% for the Chalk River sample and to about 26% for the McMaster sample.

It is important to note that regardless of whether the sample was contaminated before and after irradiation the sum of the ^{113}Cd and ^{114}Cd yields after correction for contamination is always equal to the total fission product yields of these two isotopes. Also the sum of these yields is smaller than expected if the yields from mass 111-116 were about the same for all masses in this region. The individual yields at 113 and 114 are thus depressed relative to the other masses if one assumes that the mass yield curve is a smooth function and there is structure in the mass curve which takes the form of a depression around masses 111, 112 and 113.

It should be emphasized that the distribution of the individual ^{113}Cd and ^{114}Cd yields is based on the arbitrary assumption that the mass yield curve is smooth throughout the mass range 111-116. It is probable that the 113 yield may be appreciably higher than estimated in which case the 114 yield would be very low and vice versa. These yields are not independently variable since their sum is known fairly precisely and therefore any distribution of the 113 and 114 yields will result in some form of structure in the mass-yield curve. However there is no reason to expect that the 113 and 114 yields are appreciably different since there is no evidence that the mass 113 isobars are greatly favored over the mass 114 isobars in the fission or post-fission process and vice versa.

B. Contamination by Terrestrial Cadmium

In spite of the various precautionary measures taken the analysis of the cadmium samples indicated the presence of large and varying amounts of contamination with natural cadmium. The cadmium isotope of mass 110 is not formed in appreciable quantities in fission since it is shielded in the beta-decay mass chain by $^{110}_{46}$Pd which is stable. The 110 mass chain therefore terminates at $^{110}_{46}$Pd and the only possible sources of fission product $^{110}_{48}$Cd are its independent formation in fission or from the beta decay of fission product $^{110}_{47}$Ag. The yield of $^{110}_{48}$Cd from these sources is negligible in comparison with the cumulative yields of the various mass chains in this region and would not be detectable on the mass spectrometer used in these measurements. The ^{110}Cd peak observed in the analyses was therefore taken to be an indicator of the amount of cadmium contamination from natural sources and the mass spectrometric data was adjusted accordingly to correct for this source of error.

This conclusion is supported by the observation that the abundance of mass 110 and the other masses varied from analysis to analysis. For example two runs were made from the Chalk River sample. The spectra would be expected to be identical if only fission product cadmium were present. However the different abundances of the various peaks reflect the difference in the ratio of fission product cadmium to natural cadmium. Run #1 can be seen to have relatively less natural cadmium than run #2. The different abundances are expected since the amount of fission product cadmium would not be equal in both samples and certainly the amount of contamination introduced would not be identical.

It is believed that most of the contamination occurred in the post-irradiation stages and most probably in the anion-exchange separation of the cadmium fission products. The total volume of the various reagents used in the process was about 25 ml and assuming an equal level of contamination from natural cadmium in the reagents, the presence of roughly a few parts per billion of natural cadmium would account for the amount of contamination observed in the analyses.

In addition the ratio of mass 110 to mass 113 in all the analyses was always close to that for natural cadmium. Since most of the ^{113}Cd is transformed to ^{114}Cd by neutron capture (n,γ reaction) any ^{113}Cd in excess of the anticipated amount of contamination would be due to fission product cadmium. The possibility of contamination in the sample prior to irradiation cannot be ruled out and this leads to complications in the correction procedure for the neutron capture decay of ^{113}Cd.

There is also the possibility that the 110 peak in the mass spectrum was not totally due to ^{110}Cd but to the presence of an interfering ion such as ^{110}Pd or some molecular ion. This was considered and it is believed that the mass 110 peak is due entirely to ^{110}Cd. The operating conditions for the most efficient production of cadmium ions are to a large degree unique; it is highly improbable that other ions that would interfere with the spectra in this region would be produced as efficiently under these conditions. In addition they would have to be present in all the samples in appreciable amounts to produce the observed level of interference. Certainly interference from ^{110}Pd ion is not possible. An attempt was made to study the feasibility of the mass spectrometric analysis of the palladium fission products with the same electron-impact source and it was found that it was extremely difficult to analyse Pd. The maximum sensitivity to Pd was about 10^{-6}g and the sample decayed very quickly (15-20 min.) so that it was not possible to obtain meaningful spectra. Also mixed samples of natural Cd and Pd showed no interference between the Cd and Pd peaks since the spectra for these elements were obtained under totally different operating conditions. Even if interference from Pd were possible the small fission product sample of Pd (10^{-7}g maximum) would not be detectable in the mass spectrometer because of its low sensitivity to Pd.

In addition if the peaks in a mass spectrum are a composite of the contributions from two or more elements or molecular ions the abundances of the various peaks will normally show a characteristic variation during the course of the analysis as a result of the differing rates of growth and decay of the component ion peaks. No variations other than the expected statistical fluctuations were observed in the abundances of the different masses during any of the analyses. There is no doubt that the peaks in the mass range 110-116 were due to the ions of a single element viz cadmium.

C. The Data

The results of the analyses of the Chalk River and McMaster ^{235}U samples are given in Table 9. These two sets of abundances represent the yields of the cadmium isotopes in the fission of ^{235}U. The Chalk River sample contained as well the products of ^{239}Pu fission which contributed an estimated 3.2% of the total fission product cadmium measured and it is believed that the yields obtained should reflect primarily the ^{235}U fissions. The estimated contributions from ^{235}U and ^{239}Pu fission are computed in Appendix B.

The two sets of data for the fission product isotopes of cadmium are similar although there are some apparent discrepancies. The 112 yield is appreciably lower and the 116 yield much higher in the McMaster sample. However both samples show a region of depressed yields around 112-114. The observed differences in the yields may arise from the different contamination corrections in each analysis.

In addition there are minor factors which may introduce small variations in the two sets of results. The two types of samples were not identical and they were irradiated under different conditions. The Chalk River sample consisted of ^{235}U and ^{238}U enriched to about 10% in ^{235}U while the McMaster samples were of ^{235}U and ^{238}U enriched to roughly 93% in ^{235}U. The Chalk River sample was a portion of fuel rod and it was irradiated in a primarily thermal-neutron flux (heavy-water moderated) whereas the neutrons

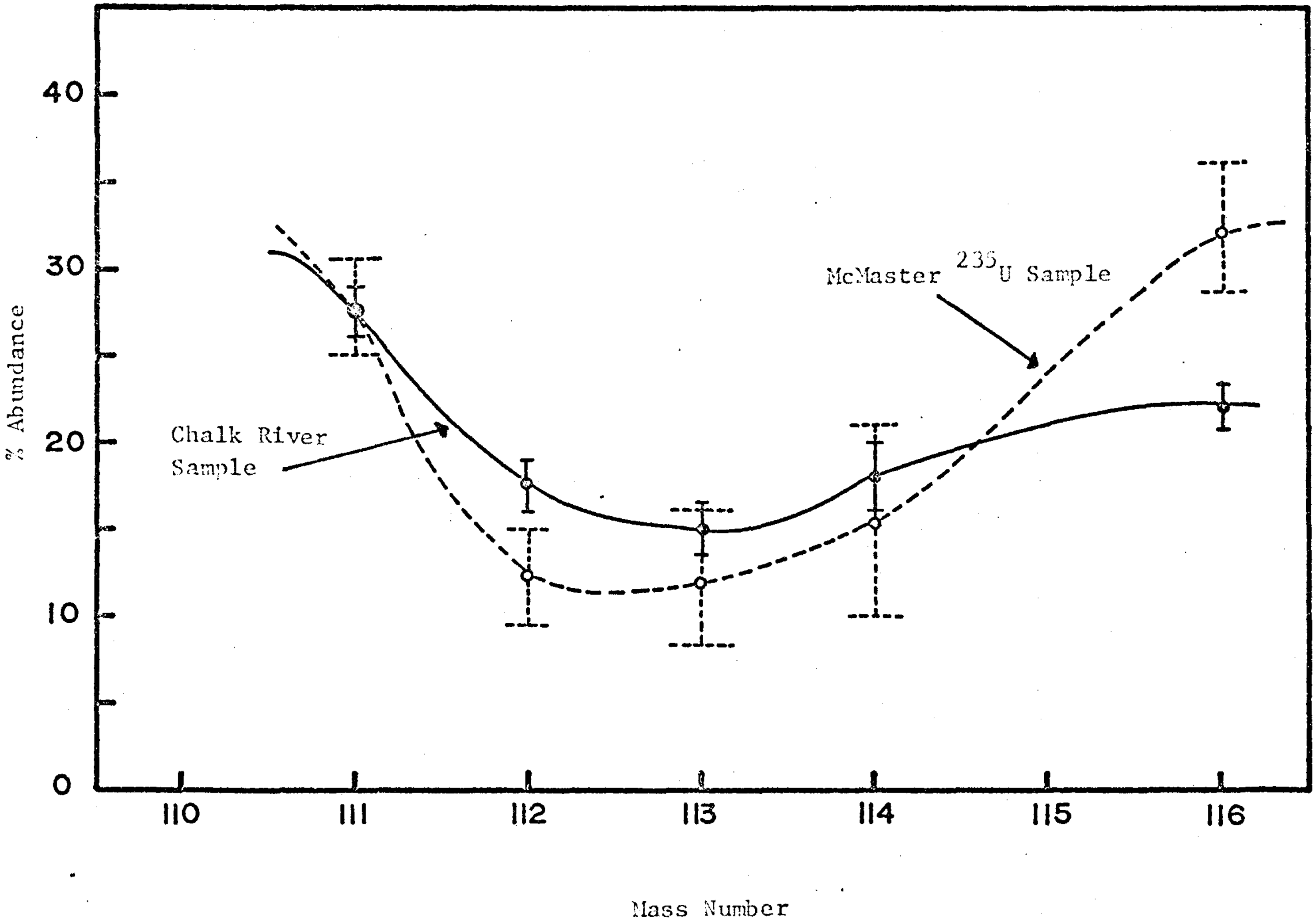

Fig. 7 Mass Yield Curve for the Stable Cadmium Isotopes from the Thermal Neutron Fission of ^{235}U.

from the McMaster reactor were moderated with normal water and there was an appreciable component of non-thermal neutrons. The Chalk River yields thus contained small perturbations from ^{239}Pu fission while there were small contributions from fission at various resonance energies in the McMaster yields.

The importance of these factors and the extent of their influence on the yields is uncertain. Also the Chalk River results represent the weighted mean of two runs of the same sample whereas the McMaster results were obtained from a single analysis. It was therefore decided that it was not justifiable to consider the two sets of data to be identical and they were treated as independent results. (Figure 7)

D. Conclusion

The results of this mass spectrometric study of the stable cadmium fission product isotopes of ^{235}U indicate that there is a depression in the mass-yield curve around masses 112 - 114. De Laeter(28) found that for ^{233}U fission there is little structure in the mass region 117 - 126 (Figure 8). If it is assumed that the mass-yield curve for ^{235}U in this region is similar to that for ^{233}U, a makeshift mass curve (Figure 9) for ^{235}U fission can be drawn for the mass region 111 to 126 by combining the data from Figures 7 and 8.

The depressed yields in the mass region 112-114 can result in two main ways. Thind and Tomlinson(32) have shown that a form of fine structure is possible as a result of the variation in

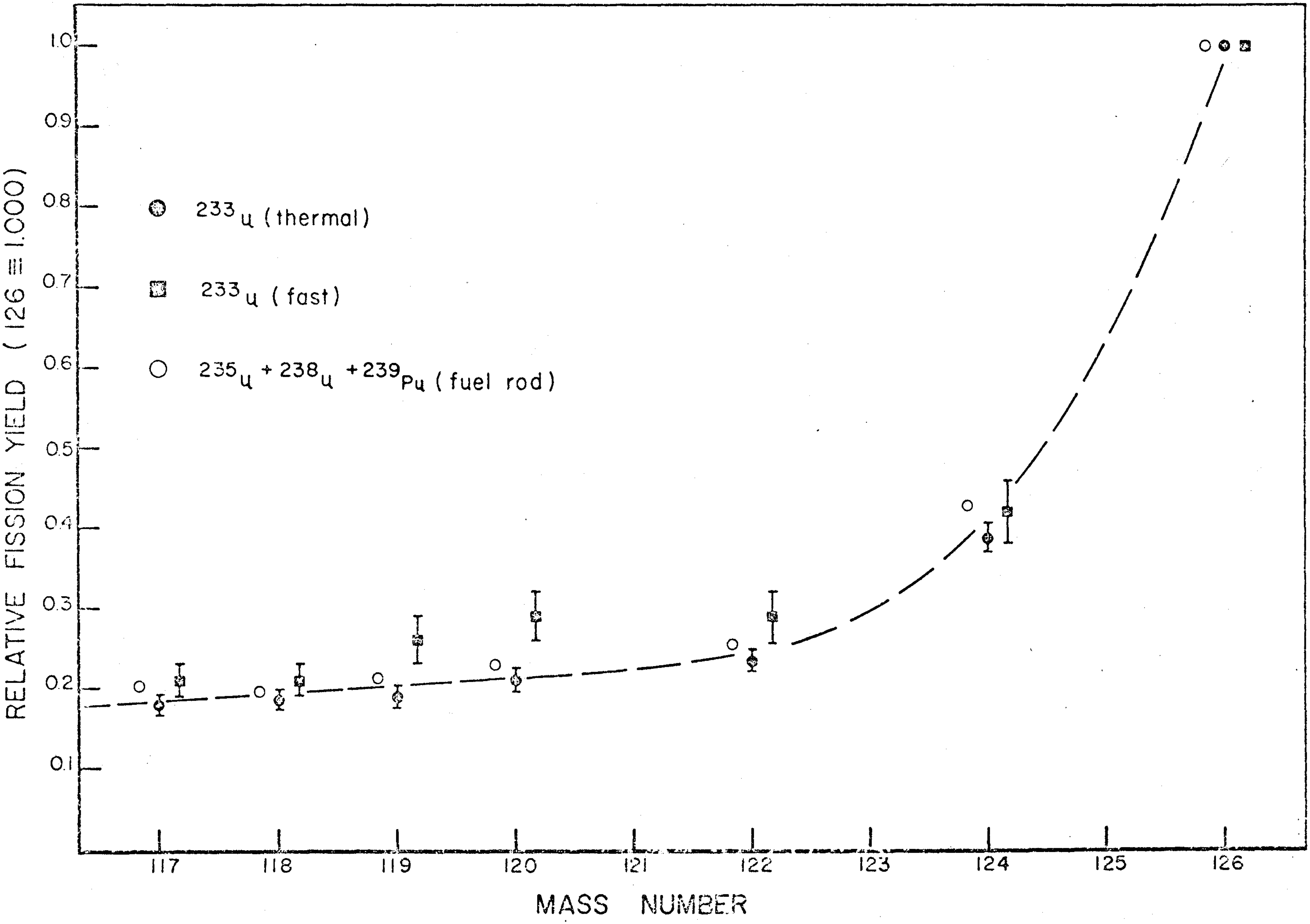

Fig 8 Mass Yield Curves for the Stable Tin Isotopes(28).

neutron yields in this region. Figure 9 can be compared with their theoretical curve (Figure 10). It is now known that their prediction of an extremely sharp depression at mass 125 is erroneous. Thind$^{(46)}$ has recalculated the yields for the symmetric region using the neutron-yield data of Apalin$^{(47)}$ and Milton and Fraser$^{(48)}$, and the results are shown in Figure 11. The pronounced depression at mass 125 no longer is predicted since this resulted from the original incorrect assumption of a curve in which the neutron yield was zero at mass 126. The observed fine structure around masses 112-114 appears to be similar to that predicted by Thind for this mass region. However the presence of structure from mass 117 - 126 is also expected and this is not apparent in de Laeter's results. The reason for this disagreement between the data of de Laeter and the prediction of Thind is not clear. It may be possible that the presence of structure is confined to a narrow region around mass 125 as in Figure 10. The yields begin to rise sharply in this region and the structure may be masked by this effect. It is an open question whether the cumulative yield curve would be a smooth continuous function with no apparent structure as reported by de Laeter in this mass region where the neutron-yield curve reverses itself. More experimental data on the mass- and neutron-yields in the symmetric region must be obtained before this question can be resolved.

The other possible explanation for the depressed yields in the 112-114 mass region would be that the observed structure is present in the primary mass distribution. This raises the question

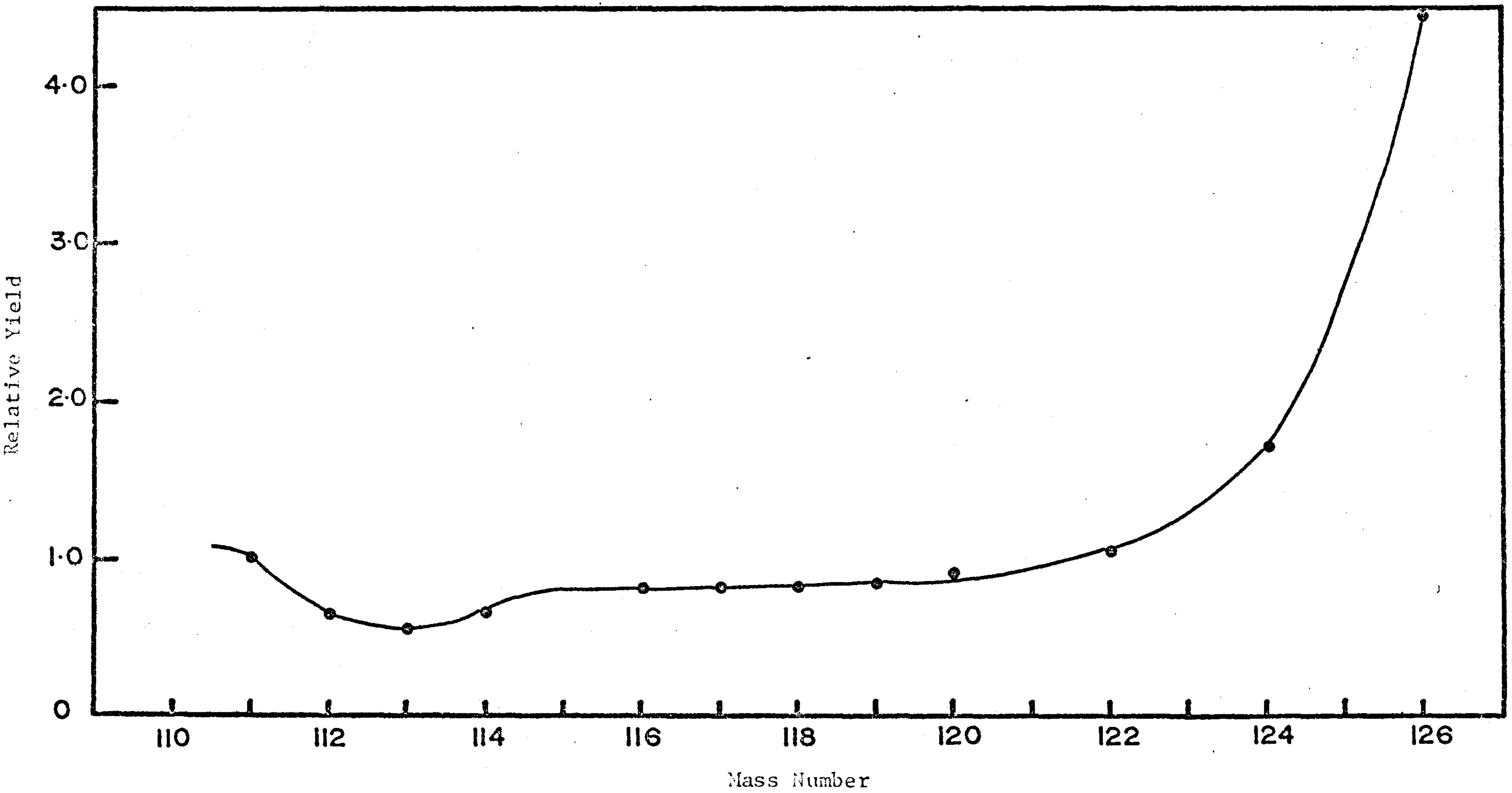

Fig. 9 Proposed Cumulative Yield Curve from Mass 111 to 126.

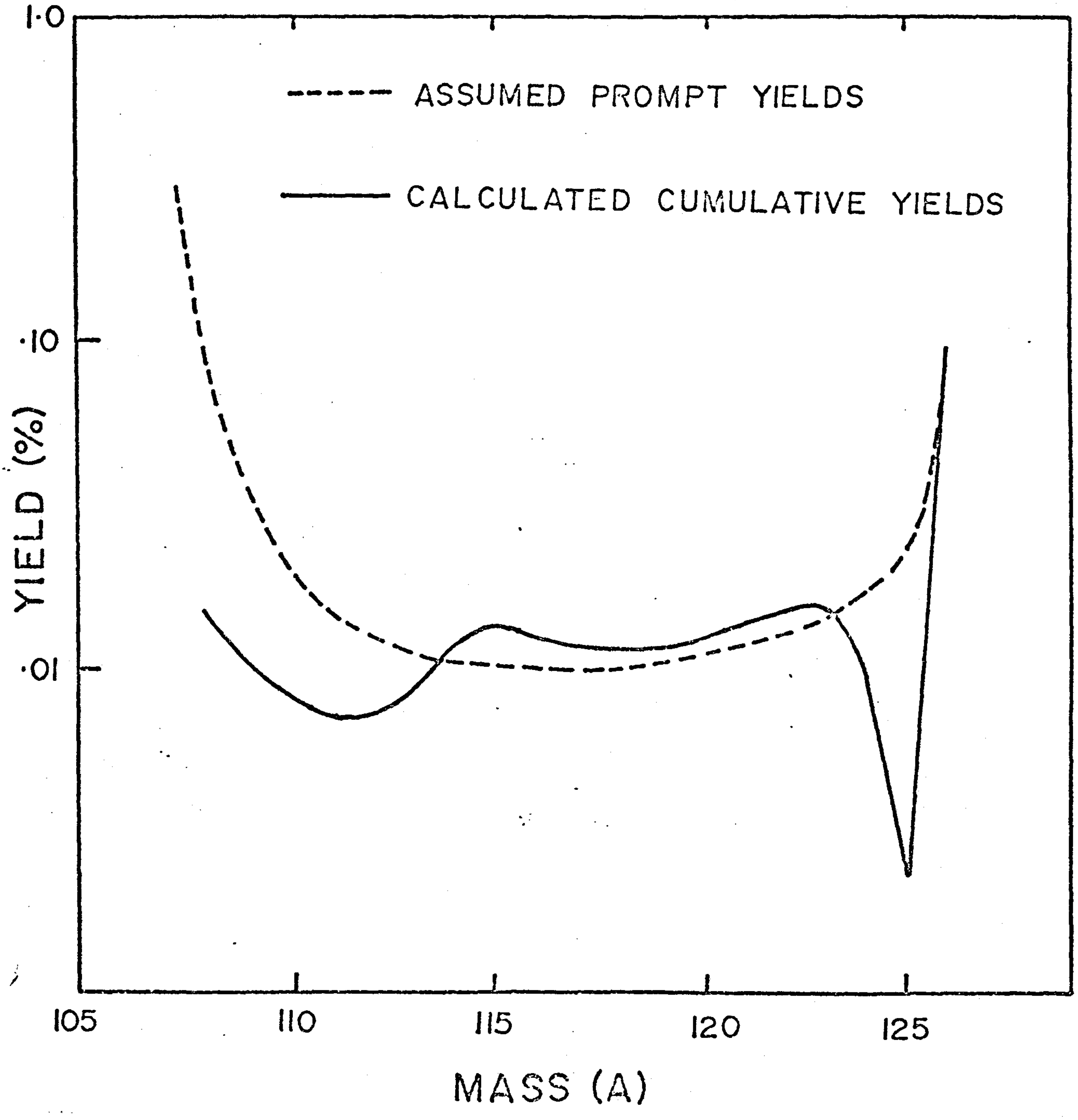

Fig 10 Theoretical Mass Yield Curve for Symmetric Region(32).

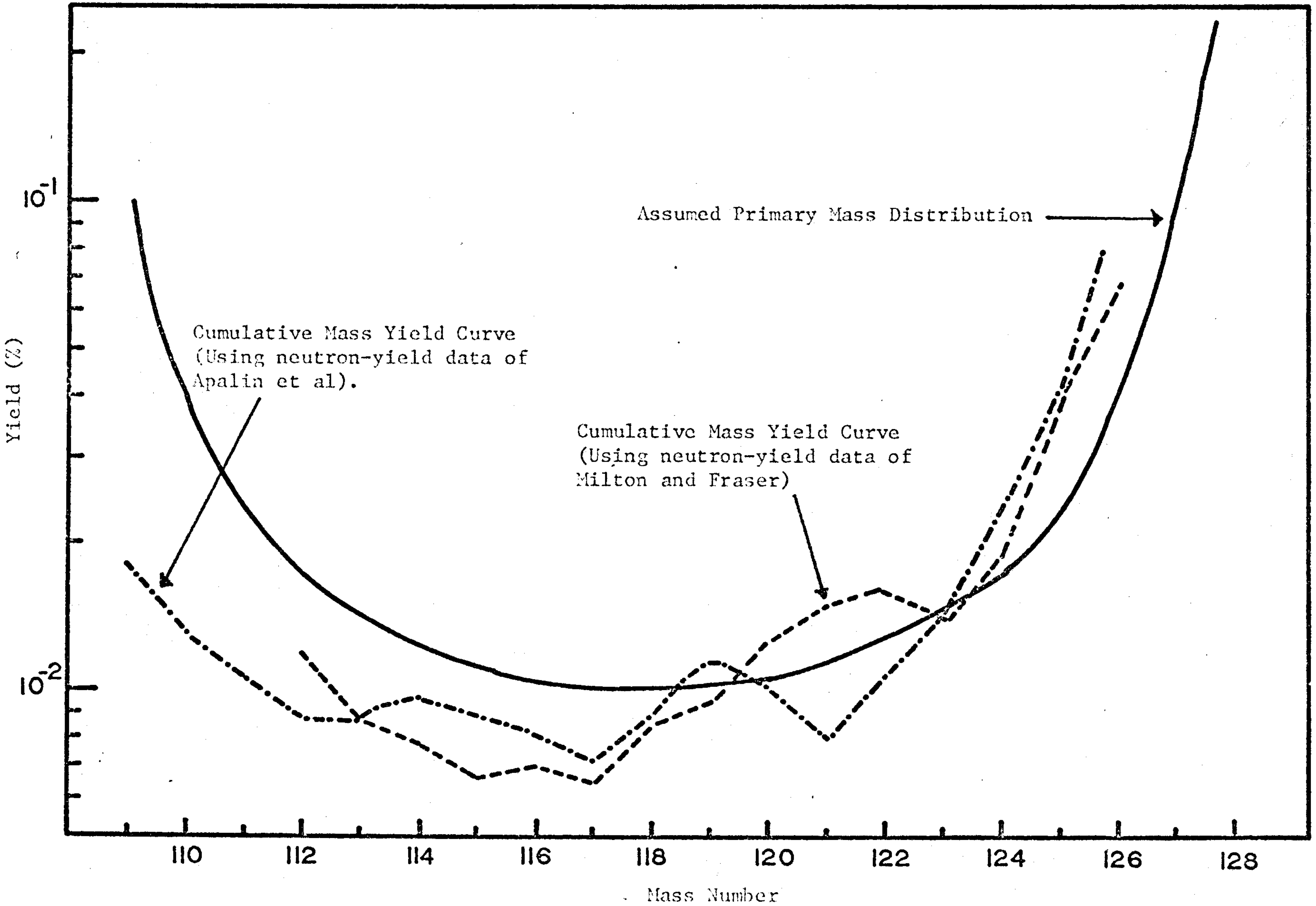

Fig. 11 Revised Theoretical Mass Yield Curve for Symmetric Region(46)

of complementary structure around mass 119-122. DeLaeter did not find any structure in this region for ^{233}U fission and this would appear to rule out the existence of structure in the primary distribution. However it may be possible that this structure is washed out fortuitously by the effects of neutron emission. One would expect the structure to be smeared out by neutron emission from the primary fragments but it is very improbable that it would be obscured entirely. Also if there are structural effects in the primary distribution one would have to rationalize the apparent lack of preference of formation of these masses.

If one assumes that the observed depression in the mass yield curve is a real phenomenon then it appears that this depression results from the variation in the neutron yields in this region. This would be the type of 'negative fine structure' proposed by Thind and Tomlinson(32). There does not seem to be a peak per se in the symmetric region and one would therefore have to dismiss the possibility of a peak resulting from a symmetric mode of fission.

It is unfortunate that the cadmium yields for ^{233}U fission were not obtained as it would have been possible to determine whether there is fine stucture in the symmetric region for ^{233}U. Certainly there is a need for further study of the yields in the valley region to elucidate the nature of the mass-yield curve in this region and to determine if there is any dependence on nuclear type. The low fission product yields, the possibility of contamination by naturally-occurring isotopes and the low sensitivity of the mass spectrometer to the elements in the symmetric region make this a very difficult task.

APPENDIX A

Correction for loss of ^{113}Cd through the (n,γ) Reaction

Rate of formation of ^{113}Cd = rate of formation in fission

- rate of neutron capture to form ^{114}Cd.

$$\frac{dN^{113}}{dt} = N^{235} \cdot \sigma_f \cdot \Phi \cdot y^{113} - N^{113}\, \sigma_c^{113}\, \Phi \qquad (1)$$

where N^{113} = no. of atoms of ^{113}Cd at any instant

N^{235} = no. of atoms of ^{235}U at any instant

σ_f = fission cross section for ^{235}U

Φ = neutron flux

y^{113} = yield of ^{113}Cd

σ_c^{113} = capture cross section for ^{113}Cd

Equation (1) can be written

$$\frac{dN^{113}}{dt} = N^{235}\lambda - N^{113}\lambda^{113} \qquad (1a)$$

where $\lambda = \sigma_f \cdot \Phi \cdot y^{113}$

and $\lambda^{113} = \sigma_c^{113} \cdot \Phi$

or

$$\frac{dN^{113}}{dt} + \lambda^{113} N^{113} = N^{235}\lambda \qquad (1b)$$

Multiply by the integrating factor $e^{\lambda^{113}t}$

$$e^{\lambda^{113}t} \cdot \frac{dN^{113}}{dt} + e^{\lambda^{113}t}\, \lambda^{113} N^{113} = N^{235}\, \lambda\, e^{\lambda^{113}t} \qquad (2)$$

$$\frac{d}{dt}\left(N^{113}\ e^{\lambda^{113}t}\right) = N^{235}\ \lambda\ e^{\lambda^{113}t} \qquad (2a)$$

Integrating

$$Ne^{113\lambda^{113}t} = N^{235}\ \frac{\lambda}{\lambda 113}\ e^{\lambda^{113}t} + \text{const.} \qquad (3)$$

When $t = 0$, $N^{113} = 0$

Therefore Const. $= -N^{235}\ \dfrac{\lambda}{\lambda^{113}}$ (4)

Substituting in Equation (3)

$$N^{113}\ e^{\lambda^{113}t} = N^{235}\ \frac{\lambda}{\lambda^{113}}\ \left(e^{\lambda^{113}t} - 1\right) \qquad (5)$$

i.e. $N^{113} = N^{235}\ \dfrac{\lambda}{\lambda 113}\ \left(1 - e^{-\lambda^{113}t}\right)$ (6)

$$N^{113} = N^{235}\ \frac{\sigma^{235}\ y^{113}}{\sigma_c^{113}}\ \frac{\phi}{\phi}\ \left(1 - e^{-\lambda^{113}t}\right) \qquad (7)$$

Assuming no neutron capture, the true number of ^{113}Cd atoms is

$$*N^{113} = N^{235}\ \sigma^{235}\ \phi\ y^{113}\ t \qquad (8)$$

Dividing Equation (7) by Equation (8)

$$\frac{N^{113}}{*N^{113}} = \frac{1}{\phi\sigma_c t}\ \left(1-e^{-\sigma_c^{113}\phi t}\right)$$

$$= \frac{1}{\Phi\sigma_c^{113}t} \qquad (9)$$

The ratio of measured 113 atoms to true number of 113 atoms is given in Equation (9).

The mass spectrometric abundance is given by

$$\%^{113} \text{ abundance} = \frac{\text{no. of 113 atoms}}{\text{total Cd atoms (111-116)}} \times 100\%$$

The % abundance is thus directly related to the number of 113 atoms (N^{113}).

APPENDIX B

Estimates of the Integrated Flux and the Number of ^{239}Pu fissions in the Chalk River Sample.

A. Initially $$\frac{\text{No. of } ^{235}\text{U atoms}}{\text{No. of } ^{238}\text{U atoms}} = \frac{^{235}\text{U}}{^{238}\text{U}} = 0.1115 \qquad (1)$$

After irradiation

$$\frac{^{235}\text{U}^*}{^{238}\text{U}^*} = 0.08426 \qquad (2)$$

Also $$^{238}\text{U}^* = {}^{238}\text{U}\ e^{-\sigma_c \phi t} \qquad (3)$$

and $$^{235}\text{U}^* = {}^{235}\text{U}\ e^{-\sigma_c \phi t} \qquad (4)$$

where σ_c = capture cross-section for ^{238}U = 2.73 barns

σ_a = absorption cross-section for ^{235}U = 668 barns

ϕt = integrated flux for the irradiation

From (3) and (4)

$$\frac{^{235}\text{U}^*}{^{238}\text{U}^*} = \frac{^{235}\text{U}}{^{238}\text{U}}\ e^{-(\sigma_a-\sigma_c)\phi t}$$

i.e. $$\frac{0.08426}{0.1115} = e^{-(\sigma_a-\sigma_c)\phi t}$$

$$(\sigma_a-\sigma_c)\phi t = \ln\left(\frac{0.1115}{0.08426}\right) = \ln(1.323) = 0.2800$$

Therefore Integrated Flux $\phi t = \dfrac{0.2800}{\sigma_a-\sigma_c} = \dfrac{0.2800}{665.3 \times 10^{-24}}$

$$= 4.2 \times 10^{20} \text{ neutrons/cm}^2$$

B. $$ {}^{235}\mathrm{U}\ \text{fission rate} = {}^{235}\mathrm{U}\ \sigma_f^{235}\ \phi \tag{1}$$

$$ {}^{239}\mathrm{Pu}\ \text{fission rate} = {}^{239}\mathrm{Pu}\ \sigma_f^{239}\ \phi \tag{2}$$

Initially there is no ${}^{239}\mathrm{Pu}$ in the sample. ${}^{239}\mathrm{Pu}$ is formed through the following process:

$$\begin{tikzcd}
{}^{238}_{92}\mathrm{U}\ (n,\gamma)\ {}^{239}_{92}\mathrm{U} \arrow[d, "\beta^-"', "(23.5\ \text{min})"] \\
{}^{239}_{93}\mathrm{Np} \arrow[d, "\beta^-"', "(2.35\ \text{day})"] \\
{}^{239}_{94}\mathrm{Pu}
\end{tikzcd}$$

The number of ${}^{239}\mathrm{Pu}$ atoms present in the sample at any time is found by solving the series of differential equations

$$\frac{d}{dt}\ {}^{238}\mathrm{U} = -{}^{238}\mathrm{U}\ \sigma_c^{238}\ \phi \tag{3}$$

$$\frac{d}{dt}\ {}^{239}\mathrm{U} = {}^{238}\mathrm{U}\ \sigma_c^{238}\ \phi - {}^{239}\mathrm{U}\ \lambda_U^{239} \tag{4}$$

$$\frac{d}{dt}\ {}^{239}\mathrm{Np} = {}^{239}\mathrm{U}\ \lambda_U^{239} - {}^{239}\mathrm{Np}\ \lambda_{Np} \tag{5}$$

$$\frac{d}{dt}\ {}^{239}\mathrm{Pu} = {}^{239}\mathrm{Np}\lambda_{Np} - {}^{239}\mathrm{Pu}\ \sigma_f^{239}\ \phi \tag{6}$$

where λ_{Np} = decay constant for ^{239}Np

λ_{U}^{239} = decay constant for ^{239}U.

For the purpose of this work we can make the approximation that the number of ^{239}Pu atoms is given by

$$^{239}\text{Pu} \simeq {}^{238}\text{U} \; \frac{\sigma_c^{238}\phi t}{2} \tag{7}$$

This would be the amount of ^{239}Pu formed in a long irradiation of time t assuming that there is no hold-up by its precursors and that there is no decay of ^{239}Pu by transmutation or fission.

Substituting Equation (7) in Equation (2)

$$^{239}\text{Pu fission rate} = \left({}^{238}\text{U} \; \frac{\sigma_c^{238}\phi t}{2}\right) \sigma_f^{239} \; \phi \tag{8}$$

The % of ^{239}Pu fissions relative to ^{235}U fissions is given by

$$\% \; \frac{^{239}\text{Pu fissions}}{^{235}\text{U fissions}} = \frac{^{239}\text{Pu fission rate}}{^{235}\text{U fission rate}} \times 100\%$$

$$'' \qquad = \frac{^{238}\text{U} \; \sigma_c^{238}\phi t \; \sigma_f^{239}\phi}{^{235}\text{U} \; \sigma_f^{235}\phi} \times \frac{100}{2} \%$$

$$'' \qquad = \frac{^{238}\text{U}}{^{235}\text{U}} \; \sigma_c^{238}\phi t \; \frac{\sigma_f^{239}}{\sigma_f^{235}} \times \frac{100}{2} \%$$

$$'' \qquad = 9.0 \times 2.73 \times 10^{-24} \times 4.2 \times 10^{20} \times 1.6 \times \frac{100}{2} \%$$

Therefore

$$\% \frac{^{239}\text{Pu fissions}}{^{235}\text{U fissions}} = 0.81\%$$

Therefore the ^{239}Pu fissions amount to ∿0.8% of the ^{235}U fissions. Assuming that the yields for the Cd isotopes in ^{239}Pu fission are of the order of 0.04% and those for ^{235}U fission are 0.01%, then the contribution of fission product Cd from ^{239}Pu in the Chalk River sample is about 3.2%.

Appendix C

Figure 12 shows a typical mass spectrum of the cadmium isotopes from run #1 of the Chalk River sample.

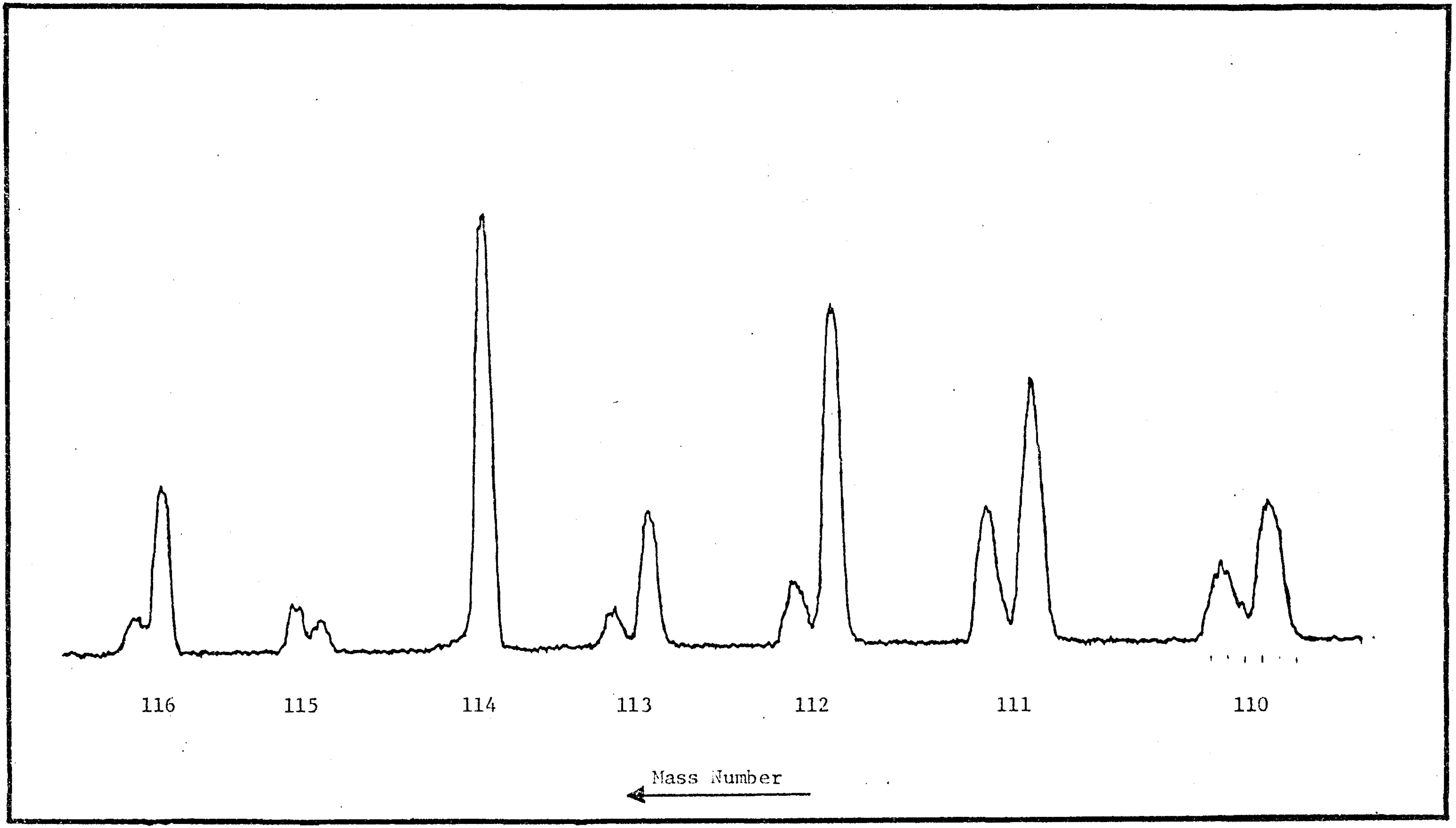

Fig 12 Mass Spectrum of Chalk River Sample. Peaks on high-mass side of cadmium peaks are due to hydrocarbons.

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