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RADIOCHEMICAL STUDIES ON THE PHOTOFISSION OF THORIUM

BY

Dale M. Hiller

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

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Dean of Graduate College

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INTRODUCTION

An important part of the study of nuclear fission is the determination by radiochemical methods of the fission yield curve, in which the nucleon number (89) (frequently called mass number) is plotted against the proportion of nuclear fissions yielding products of that particular nucleon number. The most familiar of these curves is the one for thermal neutron fission of U^{235} (85). Other curves have been determined for the thermal fission of U^{233} (36, 37, 38, 86) and Pu^{239} (85), fast neutron fission of Th^{232} (93), U^{235} (83), U^{238} (85) and Pu^{239} (85), photofission of U^{235} (83) and fission of Th^{232} by 37.5 Mev α-particles (60). All of these curves have two peaks of essentially equal height, because nearly all fission events are binary in nature, producing two major fragments (35,56,57,80,84,91,92,100) and because the most probable mode of fission at low or medium energies of excitation is asymmetrical, resulting in the formation of fragments having a mass ratio of about 1.5. Thus the typical fission yield curve is "double-humped" and is symmetrical about a nucleon number equal to half the difference between the nucleon number of the initial compound nucleus and the average number of neutrons produced per fission event.

Attempts to propose a theoretical explanation of the fission process have not met with complete success. The liquid drop model of the excited nucleus, which was proposed by Bohr and Wheeler (10) in 1939 and remains the basis of most attempts to explain fission, predicts according to the calculations of Frankel and Metropolis (23) that the nucleus will most probably split into two fragments of equal mass. Except for quite high excitation energies, this prediction is contrary to observation. Frenkel (24) has suggested that asymmetrical fission, though requiring more energy according to the liquid drop theory, takes place by means of a tunnel effect before there has been time for sufficient energy to be concentrated in the mode of oscillation leading to symmetrical fission. Swiatecki (90), on the other hand, has attempted to improve the liquid drop treatment by postulating a neutron-proton fluid which is somewhat compressible, leading to a compressibility term which predicts that asymmetrical fission actually requires less energy than symmetrical fission.

Since neither of these explanations seems wholly satisfactory, there remains a need to collect considerably more experimental information about the fission process in order that a comprehensive theory of fission eventually be established.

The ratio of the yield of the most probable mode of fission to that of the symmetrical mode varies with the nature of the compound nucleus and also varies inversely with the energy of the impinging particle, the ratio being 600 in the case of thermal neutron fission of U^{235} (85), whereas it is two in the case of fission of Th^{232} by 37.5-Mev α-particles (60). This trend is further exemplified by the fact that in two types of Bi^{209} fission, using 100-Mev bremsstrahlung (87) and using 190-Mev deutrons (33), symmetrical fission was observed to be the most probable mode. This is also true for the 90-Mev neutron fission of U^{238} (42).

In the case of those fission yield curves with "wells" of appreciable depth, the width of the peaks is of interest as an indication of the spread in the number of modes of relatively probable fission. This spread is commonly measured in terms of the width of the curve in nucleon numbers at half-height. For thermal neutron fission the reported values are 15.5 for U^{235} (85) and 16.0 for Pu^{239} (85); for pile neutron fission (effective average energy of 2.6-Mev) (93) it is 14.0 for Th^{232} (93); for 14-Mev neutron fission of U^{235} the value is 15.5 (83) and for photofission of U^{235} it is 14.0 (83).

When a heavy, naturally-occurring isotope undergoes fission, its two fragments will be highly unstable because of an excess of neutrons (4). The fragments may achieve stability either by emitting one or more neutrons or by undergoing beta-decay, and typically they do both. The spontaneous fission of U^{238} produces an average of 2.4 neutrons per fission, while that of Th^{232} yield 2.6 neutrons per fission (9). The thermal neutron fission of U^{235} yields about 2.5 ± 0.1 neutrons per fission.

It has been shown in the case of thermal neutron fission of U^{235} that the neutrons are emitted from the fission fragments rather than from the parent compound nucleus (18, 101). The same thing is probably true in the case of spontaneous fission. In general, it seems likely that each neutron-excessive fission fragment emits an average of slightly more than one neutron. When the compound nucleus is highly excited, some neutrons are "boiled off" before fission occurs. Each neutron lost in this way reduces the excitation of the compound nucleus by 6-10 Mev, some of the energy being in the form of binding energy and some in the form of kinetic energy (25).

The fission process thus appears to take place in the following steps: (1) formation of the compound nucleus by absorption of energy, a particle or both, (2) "boil-off" of neutrons if the level of excitation is sufficiently high, (3) fission into two fragments, (4) emission of neutrons by fragments if they are highly neutron-excessive and (5) stabilization of fission products by beta-decay. This process may be complicated by the formation of spallation products (70,71,79,88) or by triple fission (35,56,57,80,84,91,92, 100), but the variations in the fission yield curve caused by these processes at low or medium excitation energies is too small to be detected by ordinary radiochemical methods.

In order to understand the fission process, it is necessary to identify the compound nucleus which actually undergoes fission. Its charge may be taken as equal to that of the original compound nucleus. Its nucleon number may be found by doubling the value (not always expressed in whole numbers) of the nucleon number about which the fission yield curve is symmetrical and adding to it the 2-2.5 neutrons which are usually emitted after fission.

In the case of low-energy fission, such as spontaneous fission and thermal neutron fission, the two primary fission products formed in a specific fission event tend to be equally neutron-excessive, that is, the most probable charges of the two primary fission products are equally smaller than those corresponding to the most stable nuclei for their respective nucleon numbers (30). On the other hand, in the case of high-energy fission, the fissioning nucleus, still highly excited even after emitting one or more neutrons, seems to divide into two particles having the same neutron-proton ratio. In the latter case, the heavy primary fission products have been observed to be less neutron-excessive, often being stable or even neutron-deficient (33,70,71,79).

If a radiochemical determination of the yield curve for a particular type of fission shows that the yields of heavy neutron-excessive isotopes are smaller than the reflected values from the light side of the curve, it indicates that several neutrons are being emitted from the compound nucleus before fission occurs.

Of the various types of fission processes, photofission is of especial interest because the nucleus is excited not by the absorption of one or more additional nucleons but by the absorption of electro-magnetic radiation, a process which will hereafter be called photoexcitation. Thus it is possible to study the fission of excited nuclei such as Bi^{209}, Th^{232} and U^{238} which, in their ground states, are already relatively familiar and which may be studied further with relative ease.

Photofission was first observed in 1940 by Haxby and co-workers (39), who irradiated uranium and thorium with 6.3-Mev photons and detected the fission fragments with ionization chambers. Their results were subsequently confirmed by a group of Japanese workers (2). Previous unsuccessful attempts to observe photofission (40,77) were apparently the result of insufficient irradiation intensities.

Shortly thereafter, Langer and Stephens (47) showed that the strontium and barium activities resulting from the photofission of uranium and thorium were identical with those produced by neutron fission, thus establishing the phenomenon as a true fission process.

With the development of the Manhattan Project, the investigation of photofission was largely postponed, although Koch (44) made preliminary determinations of several photofission thresholds, which were later revised (45) due to new methods of betatron calibration. The final values reported were 5.08 ± 0.15 Mev for U^{238} and 5.40 ± 0.22 Mev for Th^{232}. These values are of particular interest because they lie below the thresholds of the respective photoneutron reactions, reported as 5.9 Mev for U^{238} (1) and variously as 6.0 ± 0.15 Mev (73) and as 6.35 ± 0.04 Mev (51) for Th^{232}.

In 1947, Baldwin and Klaiber (6) reported that the photofission cross-sections of U^{238} and Th^{232} both diminished to very low values at photon energies above 30 Mev, after passing through resonance peaks at 15-16 Mev for U^{238} and at 17-18 Mev for Th^{232}. They surmised that competition from other reactions diminished the photofission cross-section above 30 Mev, and also reported that the uranium cross-section was double the value of the thorium cross-section at corresponding energies.

McElhinney and Ogle (54,72) subsequently reported essential agreement as to the locations of the U^{238} and Th^{232} photofission resonance peaks, but claimed that at comparable energies, the ratio of photofission cross-sections for Th^{232}/U^{238} equals 0.257 ± 0.010, with a possible additional systematic error of 10-15 per cent. The discrepancy between these reported ratios of cross-section can be partially but not entirely explained, and has not yet been resolved.

Recently Anderson and Duffield (1) have reported that both the photofission cross-section for U^{238} and the total photo-neutron yield have peaks at 15 Mev and become quite low by the time a photon energy of 23 Mev is reached. They also reported a value of 5.2 ± 0.1 Mev for the U^{238} photofission threshold, in essential agreement with Koch and coworkers. A sharp break in the photofission cross-section curve was noted at 5.9 Mev, the threshold of the (γ,n) reaction.

The above data serve to establish that photofission may be expected to resemble "low-energy" fission rather closely, resulting as it does from excitations only a few Mev higher than those occurring in thermal neutron fission.

Photofission commonly produces only two fission fragments of comparable mass. Ternary photofission has been shown to exist for both uranium and thorium (35,91,92), an α-particle being emitted along with the two major fission fragments.

However, in both instances binary photofission occurs about 500 times as frequently as does ternary photofission, so that the latter may be safely neglected in determining the photofission yield curve.

Photoexcitation, of course, gives rise to many other reactions besides photofission, the (γ,n) process being particularly noteworthy. Elastic scattering, however, has been shown to be quite rare (19,26). The photo-nuclear process is believed to occur by the following steps: (1) absorption of photons by single nucleons (16,49,50,53,81), mostly in the resonant region from 10-30 Mev (5,22,1), (2) interaction of the individual nucleon with its neighbors to form an excited nucleus and (3) break-up of the excited nucleus in the manner predicted by the statistical model.

It seems likely that a few nucleons are ejected from their nuclei immediately after absorbing a photon (16,53), without reacting with neighboring nucleons. This is consistent with the observation that proton emission is more frequent than the statistical model would predict for heavy elements (41) and also helps to explain the anisotropic emission of protons and neutrons which has been observed in numerous instances (43,99). However, these reactions are so infrequent that they do not contribute appreciably to the total cross-section.

In the case of nuclei heavy enough to undergo photofission, the coulomb barrier is so high that very few protons can be emitted by the excited nucleus. Thus the two factors which limit the photofission cross-section are the over-all absorption cross-section and the competition offered by the (γ,n) and (γ,2n) processes.

Goward and co-workers (34) have measured the fission and neutron yields of uranium irradiated with the 23-Mev bremsstrahlung from the Harwell synchrotron. They reported that 10.5 ± 2 neutrons were emitted for each photofission event, and also that the average energy of the neutrons was 1.8 ± 0.5 Mev. Price and Kerst (74) reported that, under irradiation by 22-Mev bremsstrahlung from the University of Illinois betatron, U^{238} emitted 1.76 times as many neutrons as it would be expected to emit if photofission were not occurring, and that Th^{232} emitted 1.36 times as many. Since the irradiating beam had nearly the same maximum energy in both cases, the assumptions that the energy spectra of the two beams were similar and that the neutron measurements were accurate in both cases permit the use of the data from the above-mentioned experiments to estimate the average number of neutrons formed in each fission event.

Eyges (22) has shown that in heavy elements the (γ,2n) cross-section is appreciably smaller than the (γ,n) cross-section. Thus, as a first approximation, it may be assumed that the total cross-section of U^{238} under photon irradiation is made up of the cross-sections for the (γ, n) and

(γ,f) processes, and that the cross-section for total number of photonuclear reaction events, being essentially equivalent to the absorption cross-section, corresponds to the extrapolated value of the (γ,n) curve of Price and Kerst.

Setting R = neutrons per event = 1.76

$$\text{total events/fission events} = 10.5/R = 10.5/1.76$$

$$= 6.0$$

$$= \frac{\sigma_{\gamma,n} + \sigma_{\gamma,f}}{\sigma_{\gamma,f}} = \frac{\sigma_{\gamma,n}}{\sigma_{\gamma,f}} + 1$$

$$\frac{\sigma_{\gamma,n}}{\sigma_{\gamma,f}} = 5.0$$

$$\text{Neutrons/fission event} = 10.5 = \mu + \frac{\sigma_{\gamma,n}}{\sigma_{\gamma,f}} = \mu + 5.0$$

μ = 5.5, neutrons resulting from one photofission event in U^{238}

If the same value of μ is assumed in the case of Th^{232}, it leads to the prediction that 17 neutrons are formed per photofission event, under the above experimental conditions.

One must now recall the previously-mentioned information which has been reported on the photofission, (γ,n) and $(\gamma,2n)$ thresholds and the variation of their cross-sections with energy, as well as the degree of excitation required to boil off neutrons before fission, the resonance absorption curve for photoexcitation and the neutron yield of spontaneous fission. In view of these facts, a value of 5.5

for μ is quite surprising, being indeed about twice as large as would be anticipated.

The results of the present investigation of the photofission yield curve of Th^{232}, originally undertaken out of general interest in the characteristics of photofission, should also cast some light upon the question raised in the preceding paragraph and may help to resolve the apparent discrepancies.

INVESTIGATION

Objectives

The principle objective of this investigation was the determination of the fission yield curve of Th^{232} under irradiation by 69-Mev bremstrahlung from the Iowa State College synchrotron.

A further objective was the correlation of the abovementioned photofission yield curve with any other data available at the conclusion of the investigation in order to establish a more comprehensive picture of the general photofission process.

Hypotheses

Assumptions about competing fission processes

Since pure thorium was irradiated, it was assumed that the only possible alternative fission process which might be taking place was the fast neutron fission of Th^{232}. Trial calculations were therefore carried out, making the least favorable assumptions which seemed possible, to determine the probability, "P", that the neutrons associated with one photofission event escape from the sample without causing fission.

For these calculations, it was assumed firstly that 17 neutrons were emitted per fission event (See Introduction), assuming that each fission event produced 5.5 neutrons, which is the highest value reported to date. Secondly, it was assumed that the neutrons from (γ, n) or (γ, f) processes are emitted isotropically. If there is any deviation from this, the neutrons will tend to be emitted at right angles to the beam (43,99), which will make neutron fission less probable. Thirdly, an average (n, f) cross-section of 0.2 barns was assumed for neutrons emitted during irradiation. Lastly, since scattering tends to reflect more neutrons out of the sample than back into it, scattering effects were ignored.

All samples were in the form of right cylinders with a radius of 0.4 centimeters. Samples ranged in weight and length from 13 grams and four centimeters to 20 grams and ten centimeters. For each of these two extremes in sample dimensions, calculations were made assuming (a) a point neutron source at one end of the cylinder and (b) a point neutron source at the center. Results were as follows:

For the 13 gram, four centimeter sample,

$P_{end} = 0.983$

$P_{center} = 0.966$

For the 20 gram, ten centimeter sample,

$P_{end} = 0.988$

$$P_{center} = 0.961$$

Thus the assumption that the fission products isolated in this work may be attributed, within the limits of experimental error, entirely to the photofission process seems to be well justified.

Assumptions about nuclear data

The National Bureau of Standards handbook, "Nuclear Data," NBS Circular 499, with its supplements 1 and 2, (96, 97,98), was accepted as the final authority on matters of nuclear half-lives, decay schemes and mass assignments, whenever there were conflicting reports in the literature. Data appearing in the supplements were assumed to supersede those in the original circular. The data on "most stable charge" for given nucleon numbers given by Glendenin, Coryell and Edwards (30) was used.

Assumptions about the nature of the fission process

It was assumed that the actual compound nucleus undergoing fission was Th^{232}, and that the primary fission fragments were formed with equal charge displacement (29,30).

Following the line of reasoning outlined in the introduction, it was assumed that 5.5 neutrons are emitted in each photofission event. Then, assuming the postulate of equal charge displacement, the expression for the most probable charge produced in a given fission product nucleon number chain is:

$$Z_P = Z_A - \frac{Z_A + Z_{(226.5-A)} - 90}{2},$$

where Z_A and $Z_{(226.5-A)}$ are the most stable charges of the given nucleon number and the complementary fission nucleon number respectively. The independent chain yields of various isotopes may then be determined by the method of Glendenin, Coryell and Edwards (30).

These assumptions led to the minimum value for $Z_A - Z_P$ which could reasonably be expected. Thus it was believed that any isotope which was calculated to contain the total chain yield for its nucleon number on the basis of the above assumptions did in fact contain the total chain yield whatever the actual conditions may have been.

It was further assumed that in photofission of Th^{232}, an insignificant amount of triple fission occurred (91).

The chemical assumptions

It was assumed that the chemical procedures which were followed resulted in complete exchange between the inactive carriers which were added to the matrix solution and the trace quantities of the corresponding radioactive isotopes which were present as a result of photofission.

Strontium, cadmium, ruthenium and cerium were determined by gravimetric methods in forms which are not ordinarily used. The per cent of recovery, however, was assumed to be accurate because in all cases the carrier solution was standardized by precipitation and weighing in the same form used for the determination of the radioactive sample.

Assumptions about counting data corrections

In order to compare the absolute disintegration rates of samples containing different radioactive isotopes, it was necessary to attempt to correct the raw counting data for absorption in the counter window, air and the cellophane covering, for self-scattering and back-scattering, for fore-scattering (scattering of radiation into the counter by the sample cover and by air), and for the geometry factor of the sample in a given counter.

For purposes of comparing samples, the assumption was made that the geometry factor for any given counting set-up was the same for all samples, no matter what type or energy of radiation was being emitted. Thus, in comparing samples, the geometry factor cancelled out. This was probably not an entirely accurate assumption, but it was the best possible one short of experimentally determining the geometry factors for each type of radiation measured, which would have been impractical, particularly since some of the samples contained several active isotopes which would have been impossible to isolate from each other.

Empirical corrections for air, window and sample cover absorption and for forescattering were taken from the work of Zumwalt (102). Other empirical corrections for self-scattering and back scattering were taken from the data of Engelkemeir et al. (20). In both cases, it was frequently necessary to interpolate between the published experimental results on the assumption that the variation in these corrections was a function of energy alone. This was an admittedly hazardous assumption, but under the circumstances was the only possible choice.

Summation

Among the experimental assumptions, the two most likely to lead to large errors are (1) the assumption that complete exchange occurs and (2) the assumption that the corrections to the sample counting rates actually serve to give accurate comparisons of absolute disintegration rates. Under the experimental conditions used, neither one of these assumptions is subject to a direct check. Indirectly, they may be assumed to be roughly correct if they lead to consistent results. Total error, however, may still be as much as ± 20 per cent in individual cases.

Limitations

The chief limitation on the present work was imposed by the relatively low intensity of the beam of the Iowa State College synchrotron. Rough measurements showed that the half-thickness of thorium was approximately 13 grams per square centimeter. Since the target had a cross-sectional area of about 0.5 square centimeters, and since it was necessary to irradiate at least two and sometimes three half-thicknesses of thorium, the targets weighed from 13 grams to 20 grams. When these targets were split into four aliquots, making possible two separations, each in duplicate, the initial counting rates of the resulting samples ranged from a few hundred to several thousand counts per minute with no absorbers. This general level of activity permitted the study of decay curves, but did not permit the determination of absorption curves. Thus the activities present were identified only by their half-lives.

When powdered thorium was irradiated, aliquots were weighed out and then dissolved; when pellets were irradiated, the entire target was dissolved and aliquots were then pipetted. In either case, the minimum time for dissolving was two hours, and in some cases it took as long as six hours. When the time for radiochemical separation was added to the "dissolving time," it meant a minimum of four hours elapsed time between the end of irradiation and the beginning of the counting of the sample. Thus it was not possible to determine the yield of any fission isotope with a half-life shorter than two hours. On the other hand, the yield of fission isotopes with half-lives longer than two months was too low to make it practical to attempt to measure them without carrying out inordinately long irradiations.

Using the assumption that 5.5 neutrons were given off per fission event, the difference between the most probable charge and the most stable charge for a given nucleon number was appreciably smaller than it is for neutron fission of U^{235}. This limited the number of isotopes which could be regarded as representing substantially the entire fission yield for their respective nucleon numbers, thus placing a further limitation on the number of isotopes for which chemical determinations would produce useful data. In all but one case, it was impractical to attempt to analyze for various isotopes of the same nucleon number which had independent yields.

The aliquots from which the counting samples were prepared usually contained from 3.5 grams to 5 grams of thorium in acid solution. The high concentration of thorium salts and generally high ionic strength of the matrix solutions placed limitations on the practical methods of separation which will be discussed in more detail under the section on chemical procedure.

METHOD OF PROCEDURE

Irradiation

The typical sample consisted of from 13 grams to 20 grams of thorium metal prepared by the Metallurgy Group of the Ames Laboratory of the United States Atomic Energy Commission. The thorium was either in the form of powder or in the form of pellets weighing about 1.67 grams apiece. In either case, the sample was packed into a pyrex glass tube with an inside diameter of approximately eight millimeters and an outside diameter of about ten millimeters, varying in length from four centimeters (eight pellets) to ten centimeters (20 grams powder).

The irradiations were carried out in the 69-Mev beam of the Iowa State College synchrotron and were all of four to five hours duration. The sample was placed longitudinally in the beam, just far enough away from the outside of the donut so that there was no contact between holder and donut, resulting in a distance of 9.5 inches from the 0.005 inch tungsten target. (See Figure 1.). A roentgen-meter, which consisted of a Victoreen thimble chamber inclosed in a 1/8 inch lead cylinder fitted with a 1/8 inch base, placed one meter from the target, measured the intensity of the beam to be from 100 to 150 roentgens per minute. Variation of intensity during individual irradiations, however, was

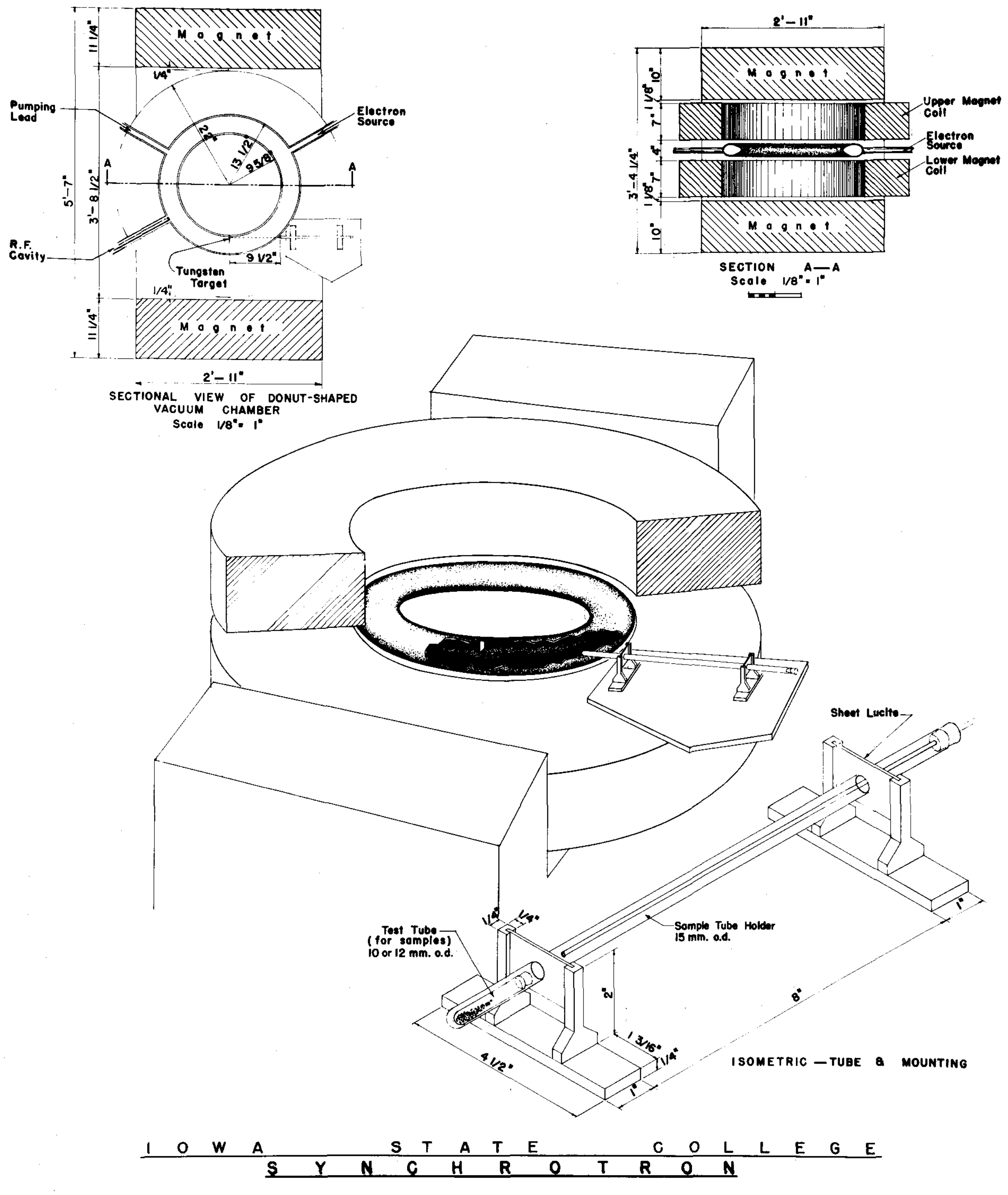

Figure 1. Iowa State College Synchrotron

usually not more than 20 per cent.

The results herein reported were obtained from fifteen irradiations carried out over a period of a year and a half.

General Radiochemical Procedure

The freshly-irradiated thorium pellets were dissolved in hydrochloric acid, a small amount of fluosilicate ion being added as catalyst to aid in dissolving small quantities of thorium carbide and thorium oxide, and aliquots were taken for the determination of the various fission products. When powdered metal was irradiated, the target material was transferred to a dry Erlenmeyer flask and mixed thoroughly, after which samples were weighed out and dissolved separately in hydrochloric or nitric acid plus fluosilicate catalyst. Determinations were made in duplicate for each element. In only two cases (strontium-barium and iodine-molybdenum) were analyses made for more than one element on the same aliquot.

The fission products were isolated by adding a known amount of inactive carrier of the element being separated, promoting exchange between the carrier and the trace quantities of the corresponding fission products, and then purifying the element from thorium, the decay products of thorium and the other fission products. The sample was finally precipitated, filtered on a disk of filter paper using the apparatus shown in Figure 2 so as to have a uniform deposit

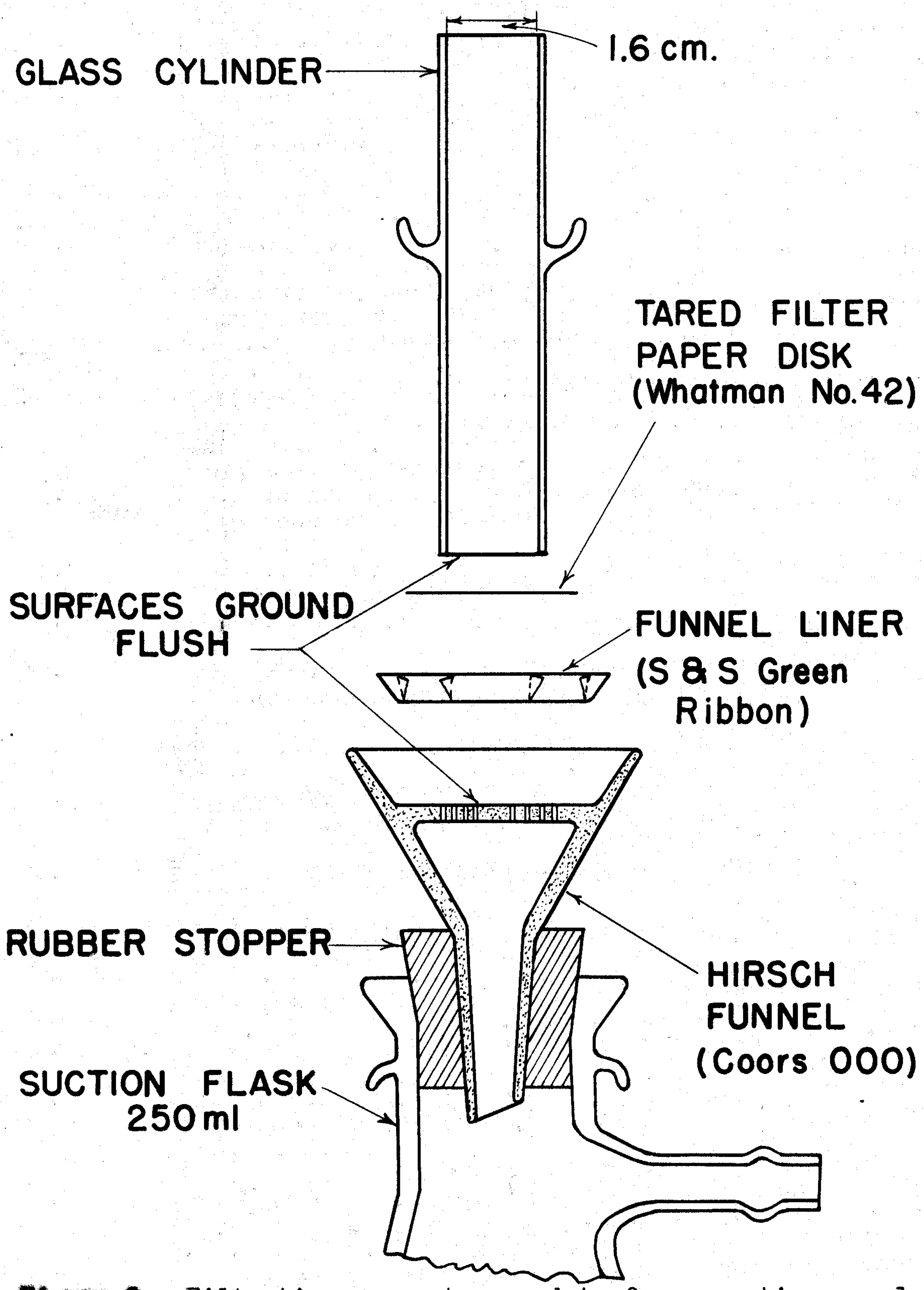

Figure 2. Filtration apparatus used to form counting samples.

with an area of two square centimeters, weighed and mounted for counting. Mounting consisted of placing the filter paper disk on cardboard, covering the sample with cellophane weighing 3.25 milligrams/square centimeters, and fastening the cardboard to a standard aluminum plate which was placed in a Lucite rack beneath a thin mica end-window Geiger-Müller counter tube as shown in Figure 3. Decay curves were taken on all samples. If possible, short aluminum absorption curves were taken to facilitate estimation of the absolute counting rates.

The radiochemical procedures used were largely adapted from those reported by the Plutonium Project (15) and those subsequently reported from the Radiation Laboratory at Berkeley (55), especially those of Newton. Modifications were chiefly necessitated by the presence of a very large amount of thorium (3.5-5.0 g) in each of the aliquots, resulting in thorium-to-carrier ratios of several hundred and in unusually high ionic strengths, as well as in the presence of significant amounts of thorium decay products, particularly Ra^{224}, Pb^{212} and Bi^{212}. The large amount of thorium present also made it impractical to raise the pH of the matrix solution above three.

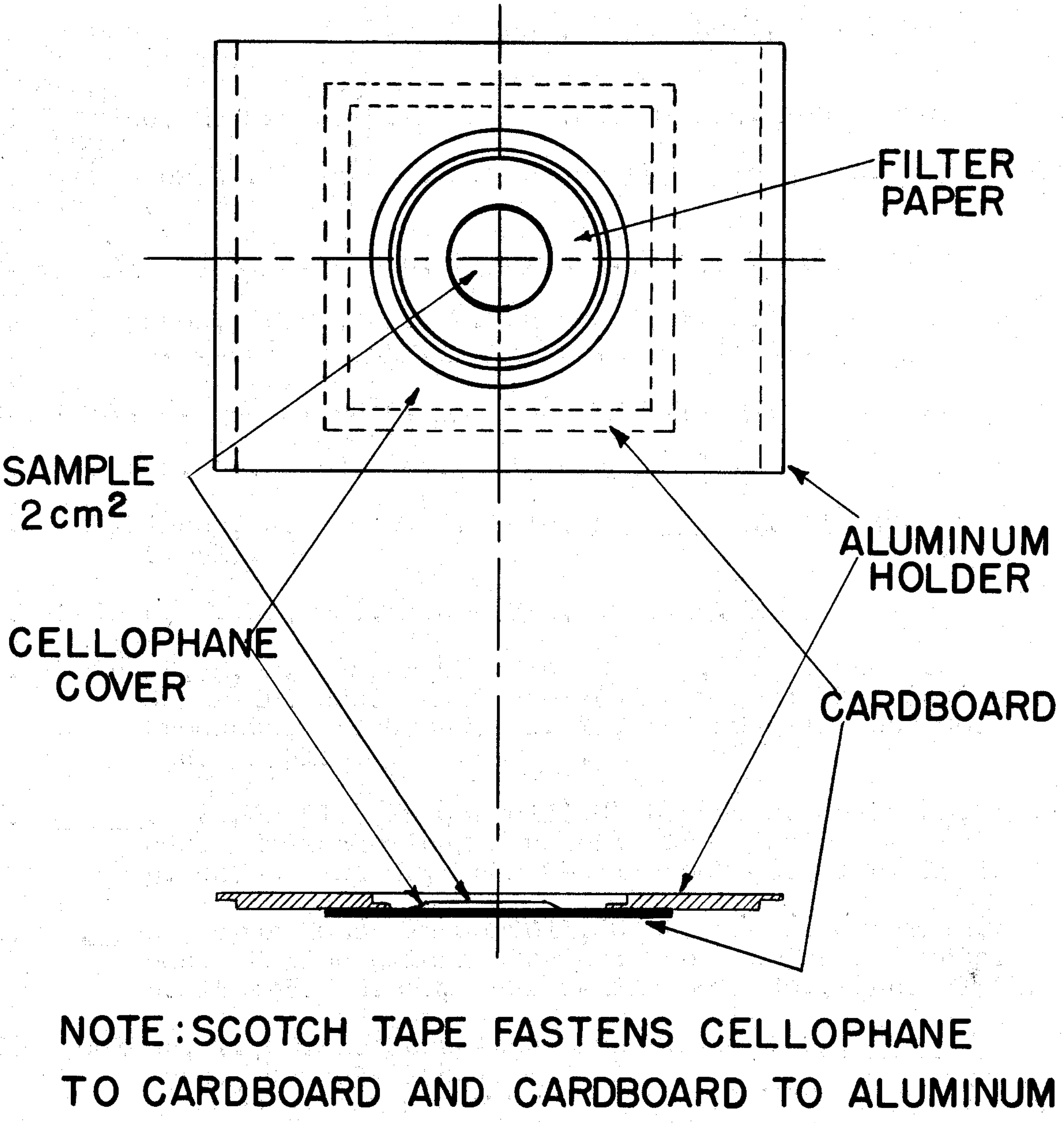

Figure 3. Standard method of sample mounting.

Chemical Procedure

Thorium

The general chemical properties of thorium have been very well described by Sidgwick (82), by Moeller, Schweitzer and Starr (59), and by Rodden and Warf (78). It is sufficient to mention here that the electronegativity of the metal resembles that of magnesium, that its hydroxide is insoluble and rather strongly basic, and that its salts are weakly hydrolyzed in aqueous solution, tending to give oxygen-bearing cationic polymers (17,46).

However, certain points with direct bearing on the present work will be described in the following paragraphs.

Preparation of target material. Thorium powder was prepared by converting turnings of thorium metal to ThH_4, followed by thermal decomposition of the hydride, according to the method of Chiotti and Rogers (13).

Pellets were formed by swaging a bar of massive thorium metal into a rod eight millimeters in diameter, then sawing this into pellets with a thickness of 3-3.5 millimeters, the edges of which were rounded and smoothed with a file so that they fit snugly into the target tube.

Speed of dissolving. A series of experiments were performed to test the relative rates at which thorium was dissolved by various acids. In all cases, a small amount of sodium fluosilicate was added to the solution as a catalyst.

Hot excess HCl acted quite rapidly, dissolving three pellets in less than an hour. Hot 6N $HClO_4$ dissolved three pellets in about ten hours. Hot 6N HNO_3 dissolved three pellets in about 24 hours, but dissolved five grams powdered thorium in less than five hours, the powder being added slowly to prevent the reaction from becoming too violent. H_2SO_4 and H_3PO_4 in various concentrations had little if any effect.

It is of interest to note that a warm mixture of ten milliliters 85 per cent H_3PO_4, five milliliters HNO_3 and ten milliliters H_2O dissolved 3.5 grams of thorium turnings in less than two hours.

A mixture of 6N acid, with molar proportions of three parts HCl to one part $HClO_4$, acted as rapidly as pure HCl. If the ratio was lowered below 3:1, the initial rate of solution was that which occurred with pure HCl. However, when the molar concentration of dissolved thorium reached one-third that of the initial concentration of HCl, the remaining thorium dissolved at a rate typical of pure $HClO_4$, behaving as if there were no chloride ion remaining in the solution. This effect was shown to be reproducible, and seems to indicate that when thorium metal dissolves in HCl, each atom of thorium acts to effectively remove an average of three chloride ions from solution. It also points to the possibility that the formation of one or more of the chloride complexes of thorium, such as $ThCl^{+3}$ or $ThCl_3^{+}$(46,94), is an important factor in the kinetics of the unique rapidity with which HCl dissolves thorium metal.

Solubility of alkali in thorium-HCl solution. 86 milli-equivalents (5g) of thorium were dissolved in 117 milli-equivalents of HCl with a little fluosilicate present; then the clear solution was diluted to 30 milliliters and heated to near boiling. Aqueous alkali was added in small increments with stirring, up to a total volume of 40 milliliters. $Th(OH)_4$ precipitated locally but redissolved with stirring. Solutions prepared as described above absorbed 100 milli-equivalents of KOH and over 100 milli-equivalents of NH_4OH without giving a permanent precipitate. The final solution had a pH of three.

This behavior may be attributed either to the presence of $ThCl^{+3}$ (17) or to the presence of various soluble oxygen-containing ions such as ThO^{+2} and Th_2O^{+6} (46), or to a combination of both.

Bromine (2.4 hr Br^{83})*

While the thorium was being dissolved in HCl, the reaction flask was fitted with a reflux condenser and the H_2 given off was passed through an alkali trap, the contents of

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*All chemical separation procedures are described in detail in the Appendix.

which were added to the matrix solution after all the thorium was dissolved. Since strongly reducing conditions prevailed during the dissolving process, it was assumed that the active bromine exchanged completely with bromide carrier. Iodide hold-back carrier was also added.

Permanganate, the oxidizing agent used by Glendenin, Edwards and Gest (31) and by Newton (61), forms a prohibitive amount of MnO_2 and fails to give a colorimetric endpoint for the oxidation of bromide to bromine in strong HCl solution. By the dropwise addition of a nitric acid solution of 2M cerium(IV) in the presence of CCl_4, it was possible to oxidize the iodide to iodine and extract it completely, then to oxidize the bromide to bromine and extract it without contamination by any chlorine, using the color of the CCl_4 layer as a visual indicator. The bromine was then put through several extraction cycles and finally precipitated as AgBr. The calculations were made assuming that 0.44 of the Br^{83} came from the 25-min Se^{83} and that the rest came from the 67-sec Se^{83}, as in thermal fission of U^{235} (3).

Strontium (9.7 hr Sr^{91} and 54 d Sr^{89})

The general method of Newton (62) was followed, involving two precipitations of barium and strontium nitrates with fuming nitric acid, followed by ferric hydroxide scavenging, removal of barium as the chromate from a buffered acetate solution and the final precipitation of strontium from ammoniacal solution as $SrC_2O_4 \cdot H_2O$. Powdered targets were dissolved directly in HNO_3, whereas aliquots of HCl solutions from pellet targets were boiled to dampness twice with HNO_3 before treatment with fuming HNO_3.

Zirconium (17 hr Zr^{97})

The method of Newton (63) was used for the attempted separation of zirconium, involving the removal of thorium as the fluoride, the separation of zirconium from other fission products as $BaZrF_6$ and its final precipitation with cupferron followed by ignition to ZrO_2 for weighing and counting. Unfortunately, the ThF_4 precipitation occludes some of the active zirconium before it can exchange with the carrier, giving results which are erratic and always much too low.

Molybdenum (67 hr Mo^{99})

A modification of the methods used by Newton (64) and by Ballou (7) was used to separate molybdenum. The samples, 6N in HCl, were extracted into ether after a Br_2 oxidation; the ether was washed and evaporated over water; the molybdenum was precipitated with α-benzoinoxime. The precipitate was then dissolved in 6N NaOH, after which the α-benzoinoxime precipitation was repeated. This precipitate was fumed with HNO_3 and $HClO_4$, scavenged with $Fe(OH)_3$ and finally precipitated, weighed and counted as $PbMoO_4$ (12).

Ruthenium (4.5 hr Ru^{105})

A modification of the method of Glendenin (28) was used to separate ruthenium. The separation was made by distilling RuO_4 from a flask containing the matrix solution, ruthenium and iodide carriers, and 0.5 grams $NaBiO_3$ into a trap containing 15 milliliters 6N NaOH plus molybdenum holdback carrier. The RuO_4 was then precipitated as RuO_2 by alcohol reduction, washed with 0.5N NaOH containing Pb holdback carrier to remove thorium decay products, dissolved in HCl and reduced with powdered magnesium to ruthenium metal, in which form it was weighed, mounted and counted.

Silver (7.5 d Ag^{111}, 3.2 hr Ag^{112}, 5.3 hr Ag^{113})

In a modification of the method of Newton (65), aliquots of the powdered thorium target were dissolved with concentrated HCl in Lusteroid tubes. Silver carrier was added, followed by dilution, which precipitated AgCl completely. The AgCl was then dissolved in NH_4OH, scavenged with $Fe(OH)_3$ and precipitated as Ag_2S. The Ag_2S was dissolved in HNO_3, made ammoniacal, scavenged with $Fe(OH)_3$, and the AgCl-Ag_2S cycle was repeated. After the second Ag_2S precipitate was dissolved, made ammoniacal and scavenged, AgCl was precipitated, weighed and counted.

Cadmium (2.83 hr Cd^{117})

Starting with 40 milliliters of chloride solution containing 3.5 grams thorium and 20 milligrams cadmium, at a pH of three, the addition of either H_2S or thioacetamide precipitated CdS at rates which ranged from rapid to indetectable and which were non-reproducible. Thus the method used by Newton (66) and by Metcalf (58) to separate cadmium from the matrix solution was not suited to the present conditions.

A new radiochemical separation of cadmium was devised, based on the method of Mahr and Ohle (52), consisting of the addition of an excess of a saturated solution of Reinecke's salt (75) to the cold matrix solution, containing a one per cent concentration of thiourea, which results in the precipitation of cadmium as an insoluble salt of the form $Cd(Th)_2[Cr(NH_3)_2(SCN)_4]_2$, where TH stands for thiourea. Reinecke's salt, $NH_4[Cr(NH_3)_2(SCN)_4]\cdot H_2O$, was synthesized in this laboratory by the method of Christensen (14-a).

After separating cadmium "Reineckate" from the matrix solution, the precipitate was dissolved in hot 1N HCl. CdS was precipitated by addition of NH_4OH and thioacetamide; then CdS was dissolved in hot 6N HCl. Lead holdback carrier was added to remove Pb^{212}; then $Cd(OH)_2$ was precipitated twice with 6N NaOH. Two scavengings with basic ferric acetate and one with basic indium acetate completed the cadmium purification. Then 1.95 hr In^{117} was permitted to grow into the cadmium and was "milked" out by precipitation of basic indium acetate, which was washed, ignited to In_2O_3, mounted and counted. The cadmium was later precipitated and weighed as the "Reineckate."

Tellurium (30 hr Te^{131} and 77.7 hr Te^{132})

In a slight modification of the method of Newton (67) and of Goeckermann (32), aliquots of powdered thorium were dissolved in concentrated HCl which contained the tellurium carrier, the tellurium being precipitated as the metal as the thorium dissolved. The tellurium metal was then dissolved in HNO_3, scavenged with $Fe(OH)_3$ from a solution made alkaline with NaOH, and reprecipitated as tellurium metal with six per cent H_2SO_3. The cycle of dissolving and precipitating was repeated; then the tellurium metal was filtered, weighed and counted.

Iodine (8.0 d I^{131})

Iodine was separated by dissolving aliquots of the powdered thorium target in HCl containing I^- carrier, oxidizing I_2 with a nitric acid solution of cerium(IV) and extracting into CCl_4. Purifying after the manner of Newton (68), the I_2 was reduced with $NaHSO_3$, stripped into aqueous solution and stored for ten days to permit short-lived iodine activities to decay out. At the end of this period the iodine was run through two more extraction cycles, oxidizing with $NaNO_2$ and reducing with $NaHSO_3$, and was finally precipitated, weighed and counted as AgI.

Barium (13.4 d Ba^{140})

In all cases, barium and strontium were precipitated simultaneously as the nitrates from the matrix solution, as reported above. After the precipitation of $BaCrO_4$, the precipitate was dissolved in dilute HCl and scavenged with $Fe(OH)_3$. The fact that barium carries with it large quantities of 3.64 d Ra^{224}, with its daughters 10.6 hr Pb^{212} and 60.5 min Bi^{212}, made precipitation and counting of a barium sample futile. The relatively small amount of active barium present in the sample made the fractional precipitation method of Ballou et al. (8) impractical in this instance. The greatest success was obtained by "milking" the 41.4 hr La^{140} daughter from the barium solution by precipitation as $La(OH)_3$ from ammoniacal solution, followed by gravimetric determination of barium as $BaSO_4$. The precipitation of $La(OH)_3$ was never quite complete, which made the experimental fission yield determination for nucleon number 140 somewhat too small.

Cerium (32.5 d Ce^{141} and 33 hr Ce^{143})

The large quantities of thorium (3.5 grams per aliquot) present in the matrix solution made it impossible to follow the procedure of Newton (69) in precipitating Th^{+4} away from Ce^{+3} as the iodate. Instead, it was necessary to develop the new procedure herein described.

Ce^{+3}, La^{+3} and Y^{+3} carriers were added to aliquots of the HCl-Th matrix solution, which were then saturated with $Al(NO_3)_3 \cdot 9H_2O$. The thorium was extracted from this solution into mesityl oxide (48). The rare earths were precipitated from the aqueous phase with excess NaOH (leaving any aluminum in solution as the aluminate), centrifuged off, and redissolved in dilute HNO_3. The solution was once again saturated with $Al(NO_3)_3 \cdot 9H_2O$. The rare earths were then extracted into tributyl phosphate and stripped with very dilute HNO_3 to which a little H_2O_2 has been added to keep cerium in the trivalent state. The rare earth hydroxides were then precipitated from strong NaOH solution to remove aluminum.

The cerium was separated from other rare earths and residual fission products by the method of Boldridge and Hume (11), in which the process of $KBrO_3$ oxidation, $Ce(IO_3)_4$ precipitation and dissolving with H_2O_2 in HCl was carried out and repeated, followed by a $Zr(IO_3)_4$ scavenging and a double $Ce(OH)_3$ precipitation. The cerium was finally weighed, mounted and counted as $Ce_2(C_2O_4)_3 \cdot 10\ H_2O$, with an overall recovery of about 3/4 of the carrier originally added.

Conversion of Counting Data to Absolute Activities

The work of L. R. Zumwalt (102) on absolute beta counting was the primary source of the corrections used in these experiments. Zumwalt's correction is as follows:

$$(c/m) = (d/m)G\ f_W\ f_A\ f_B\ f_H\ f_S\ f_C$$

where G = geometry factor

f_W = air, counter window and sample covering absorption

f_A = air-scattering

f_C = forescattering by sample cover

f_H = scattering by walls of mount and housing

f_B = backscattering

f_S = self-absorption and self-scattering

Several modifications were made to this equation. First, f_H was set equal to unity. This may be justified by the fact that, for short distances from the counter window (such as were used in the present work), f_H deviates from unity only slightly even when the shelves are made of aluminum, as they were in the experiments of Zumwalt. Since the shelves used in the present work were made of Lucite, the average atomic number of which is less than half that of aluminum, the above approximation appears justified.

Second, it was noted that Englekemeir et al. (20) observed that in their work, except for experiments performed on the first shelf (4 mm from the counter window), the absorption and forescattering effects of the cellophane sample covering effectively cancelled each other. Therefore, the function f_W', standing for only air and window absorption, was substituted for f_W and f_C was set equal to unity.

Third, it was necessary to use the correction data of Englekemeir et al. (20) for the backscattering, self-absorption and self-scattering factors because cardboard mountings were used in the present work instead of the polystyrene backings which Zumwalt used.

Last, an additional factor was inserted to compensate for the fact that the preparation of the counting samples never resulted in quantitative removal of the inert carrier and the corresponding activities from the matrix solution.

The correction equation actually used in this work is:

$$a = (d/m) = (c/m)\ g\ F_W'\ F_A\ F_{BS}\ F$$

where a = activity

c/m = counts per min. actually recorded

$F_W' = 1/f_W'$

$F_A = 1/f_A$

F = wt carrier added/wt carrier recovered

F_{BS} = self-absorption, self and back-scattering factor

$= 1/f_S\ f_B$

The actual values used are tabulated in Table 1.

Table 1

Factors used to convert raw counting data to absolute activities.

Sample	Wt(mg)**	F	Isotope	Radiation(Mev)	$F_A{}^h$	$F_W{}^i$	Distance from window(mm)	F_{BS}
H-7	12.5	2.13	7.5d Ag^{111}	1.04 β^-	0.992	1.121^i	11	0.83 e,f
			3.2h Ag^{112}	3.6 β^-	1.0	1.00 *	11	0.83 e,f
			5.3h Ag^{113}	2.1 β^-	0.996	1.017*	11	0.83 e,f
H-9	35.3	1.171	9.7h Sr^{91}	3.2 β^-	0.996	1.041*	16	0.72 c
				1.3 β^-	0.996	1.041*	16	0.81 d
			57d Y^{91}	1.5 β^-	0.994	1.03 ^{i}	16	0.77 c
			53d Sr^{89}	1.5 β^-	0.994	1.03 ^{i}	16	0.77 c
H-10	16.3	1.63	7.5d Ag^{111}	1.04 β^-	0.992	1.114^i	11	0.83 f
			3.2h Ag^{112}	3.6 β^-	1.0	1.017*	11	0.83 f
			5.3h Ag^{113}	2.1 β^-	0.996	1.017*	11	0.83 f
H-13	33.5	1.240	9.7h Sr^{91}	3.2 β^-	0.996	1.035*	16	0.72 c
				1.3 β^-	0.996	1.035*	16	0.81 d
			57d Y^{91}	1.5 β^-	0.994	1.03 ^{i}	16	0.77 c
			53d Sr^{89}	1.5 β^-	0.994	1.03 ^{i}	16	0.77 c
H-14	33.0	1.258	9.7h Sr^{91}	3.2 β^-	0.996	1.035*	16	0.72 c
				1.3 β^-	0.996	1.035*	16	0.81 d
			57d Y^{91}	1.5 β^-	0.994	1.03 ^{i}	16	0.77 c
			53d Sr^{89}	1.5 β^-	0.994	1.03 ^{i}	16	0.77 c
H-21	---	1	41.4h La^{140}	Total	0.990	1	16	0.81 f
H-24	---	1.30	41.4h La^{140}	"	0.990	1	16	0.77 g
H-32	24.9	1.89	2.4h Br^{83}	1.0 β^-	0.990	1.11 *	13	0.81 c
H-33	15.9	2.96	2.4h Br^{83}	1.0 β^-	0.990	1.11 *	13	0.82 c
H-34	20.0	1.915	67h Mo^{99}	1.23,0.445β^-	0.994	1.00 *	13	0.81 c
H-35	8.1	4.73	67h Mo^{99}	1.23,0.445β^-	0.994	1.00 *	13	0.85 c
H-45	11.1	1.54	1.95h In^{117}	1.73 β^-	0.995	1.037^i	13	0.81 c,e
H-46	11.7	1.32	1.95h In^{117}	1.73 β^-	0.995	1.037^i	13	0.81 c,e
H-47	18.2	2.10	67h Mo^{99}	1.23,0.445β^-	0.994	1.00 *	13	0.81 c
H-48	21.1	1.815	67h Mo^{99}	1.23,0.445β^-	0.994	1.00 *	13	0.81 c

Table 1 (Continued)

Sample	Wt(mg)**	F	Isotope	Radiation(Mev)	F_A^h	F_W'	Distance from window(mm)	F_{BS}
H-49	11.8	3.98	2.4h Br^{83}	1.0 β^-	0.990	1.09*	13	0.84^c
H-50	12.8	3.67	2.4h Br^{83}	1.0 β^-	0.990	1.09*	13	0.84^c
H-51	33.7	1.251	9.7h Sr^{91}	3.2 β^-	0.995	1.039*	13	0.76^c
				1.3 β^-	0.995	1.039*	13	0.80^d
			57d Y^{91}	1.5 β^-	0.994	1.03^i	13	0.80^c
			53d Sr^{89}	1.5 β^-	0.994	1.03^i	13	0.80^c
H-52	31.0	1.362	9.7h Sr^{91}	3.2 β^-	0.995	1.039*	13	0.76^c
				1.3 β^-	0.995	1.039*	13	0.80^d
			57d Y^{91}	1.5 β^-	0.994	1.03^i	13	0.80^c
			53d Sr^{89}	1.5 β^-	0.994	1.03^i	13	0.80^c
H-53	13.5	2.84	67h Mo^{99}	1.23,0.455β^-	0.994	1.00*	13	0.82^c
H-54	9.1	4.21	67h Mo^{99}	1.23,0.455β^-	0.994	1.00*	13	0.86^c
H-59	13.4	1.836	32.5d Ce^{141}	0.581 β^-	0.988	1.251^i	13	0.83^b
				0.442 β^-	0.987	1.340^i	13	0.94^a
				0.103 e^-	0.986	$1.515^{k,l}$	13	$1.47^{e,f,g}$
			33h Ce^{143}	1.1 β^-	0.993	1.075*	13	0.82^c
H-60	17.7	1.390	32.5d Ce^{141}	0.581 β^-	0.988	1.251^i	13	0.82^b
				0.442 β^-	0.987	1.340^i	13	0.97^a
				0.103 e^-	0.986	$1.515^{k,l}$	13	$1.65^{e,f,g}$
			33h Ce^{143}	1.1 β^-	0.993	1.070*	13	0.81^c
H-61	12.3	3.11	67h Mo^{99}	1.23,0.455β^-	0.994	1.00*	13	0.83^c
H-62	14.9	2.57	67h Mo^{99}	1.23,0.455β^-	0.994	1.00*	13	0.82^c
H-63	32.3	1.061	4.5h Ru^{105}	1.4 β^-	0.992	1.14*	13	0.79^c
H-64	33.4	1.027	4.5h Ru^{105}	1.4 β^-	0.992	1.14*	13	0.79^c
H-65	25.1	1.528	67h Mo^{99}	1.23,0.455β^-	0.994	1.00*	13	0.81^c
H-66	20.4	1.88	67h Mo^{99}	1.23,0.455β^-	0.994	1.00*	13	0.81^c
H-67	20.7	1.020	30h Te^{*131}	0.144 e^-	0.986	$1.25^{j,k}$	13	0.93^g
				0.172 e^-	0.987	$1.19^{j,k}$	13	0.87^g
			25m Te^{131}	1.8 β^-	0.997	1.03^i	13	0.81^g

Table 1 (Continued)

Sample	Wt(mg)**	F	Isotope	Radiation(Mev)	F_A[h]	F'_W	Distance from window(mm)	F_{BS}
H-68	19.4	1.088	8.0d I^{131}	Total	0.987	1.222[i]	13	0.82[b]
			30h Te^{*131}	0.144 e^-	0.986	1.25[j,k]	13	0.93[g]
				0.172 e^-	0.987	1.19[j,k]	13	0.87[g]
			25m Te^{131}	1.8 β^-	0.997	1.03[i]	13	0.81[g]
			8.0d I^{131}	Total	0.987	1.222[i]	13	0.82[b]
H-69	7.3	5.25	67h Mo^{99}	1.23,0.445β^-	0.994	1.00*	13	0.88[c]
H-70	16.4	2.34	67h Mo^{99}	1.23,0.445β^-	0.994	1.00*	13	0.81[c]
H-71	29.8	1.250	8.0d I^{131}	Total	0.987	1.222[i]	13	0.89[b]
H-72	30.6	1.217	8.0d I^{131}	Total	0.987	1.222[i]	13	0.89[b]

*Experimentally determined by back-extrapolation to zero

**All samples had an area of 2 sq. cm.

[a] Fig. 4.3, (20)

[b] Fig. 4.4, (20)

[c] Fig. 4.7, (20)

[d] Fig. 4.8, (20)

[e] Fig. 4.9, (20)

[f] Fig. 4.10, (20)

[g] Fig. 4.11, (20)

[h] Table 1.3, (102)

[i] Table 1.1, (102)

[j] (27)

[k] Fig. VII-8-(b), p. 163, (25)

[l] Fig. 1-24, p. 52 (21)

RESULTS

Only relative fission yields were determined in the present investigation. An internal standard, wither Sr^{91} or Mo^{99}, was separated from each bombarded sample. (The yield ratio of the two internal standards was determined on two independent occasions.) After the relative formation rates had been determined, a symmetrical curve was drawn and normalized so that the area beneath it totalled 200 per cent, the assumption having been made that only binary fission occurred. (See Figure 4.) The data are shown in Table 2.

Assuming that the experimentally determined yield of a given nucleon number and the yield of its mirror nucleon number were equal, the best symmetrical curve is formed by placing the line of symmetry at nucleon number 114.5. Thus it appears that an average of three neutrons are emitted during the photofission of Th^{232}. From the points which have been determined, although these are fewer in number than might be desired, it does not appear that the photofission of Th^{232} can be said to involve the emission of less than 2.5 or more than 3.5 neutrons.

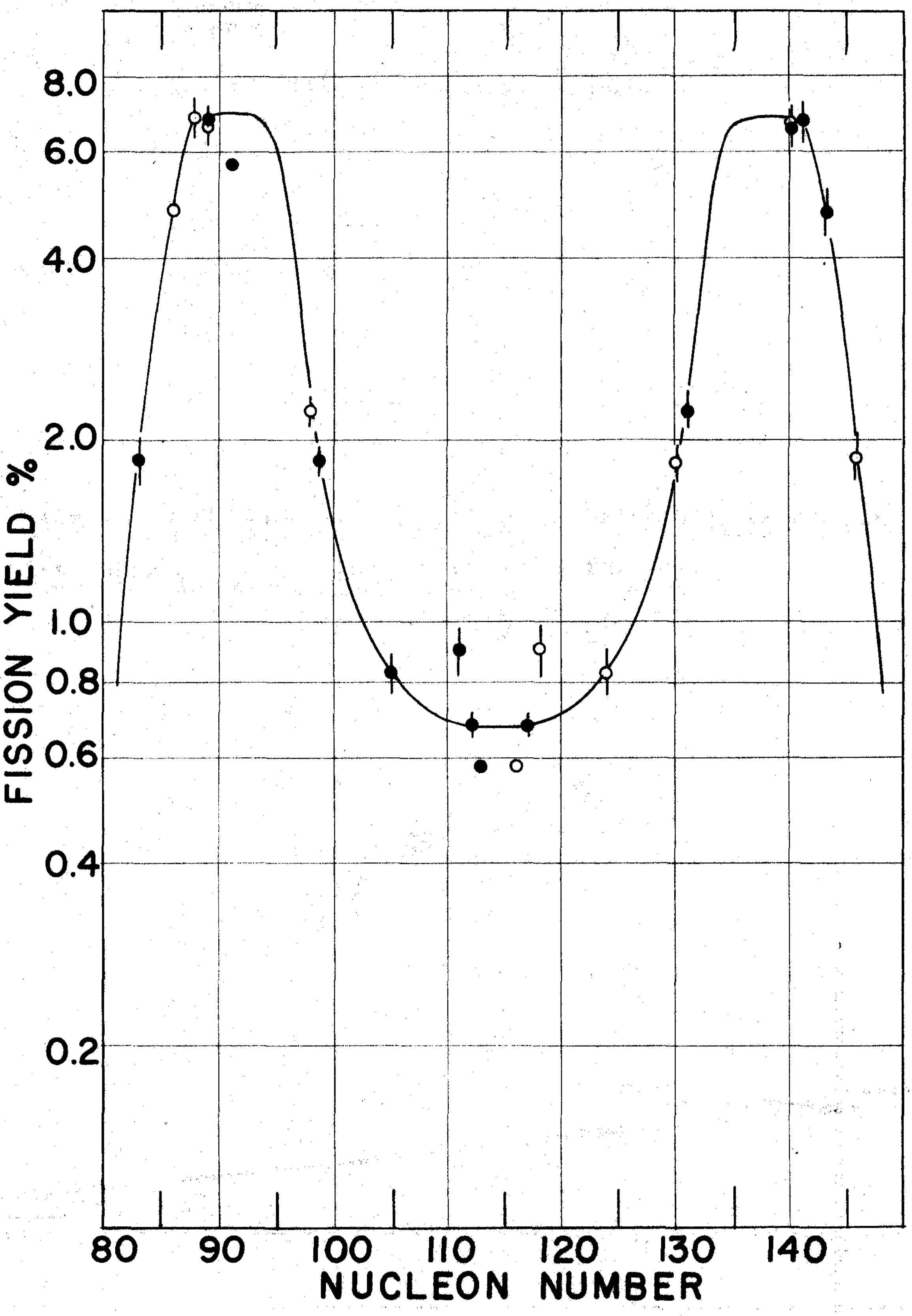
The points lie on a smooth, 'double-humped" curve. Exceptions are the cases of Sr^{91} and Ag^{113}, which lie below the curve because they do not represent the complete chain yields of their respective nucleon numbers, and of Ag^{111}, which appears to have been contaminated with some other longlived activity and thus lies above the curve. The maxima of the curve lie at nucleon numbers 91 and 138, giving a value of 1.52 for the most probable mass ratio. The widths of the peaks at half-height are 12 mass units. The most probable products are formed ten times more frequently than are the products of symmetrical fission. The height of the maxima of the normalized curve, i. e., the estimated value of the yield of the most probable fission fragments, is seen to be 6.9 per cent.

Table 2

Photofission yields of thorium

Nucleon Number	Nuclides Isolated and Measured	Yields (%)	Estimated Reliability (%)
83	2.4h Br^{83}	1.89	± 0.15
89	53d Sr^{89}	6.7	± 0.1
91	9.7h Sr^{91} 51m Y^{*91}	5.7	± 0.1
99	67h Mo^{99}	1.85	± 0.10
105	4.5h Ru^{105}	0.83	± 0.07
111	7.5d Ag^{111}	0.90	± 0.09
112	3.2h Ag^{112}	0.68	± 0.02
113	5.3h Ag^{113}	0.58	± 0.01
117	2.72h Cd^{117} 1.95h In^{117}	0.68	± 0.02
131	30h Te^{*131} 25m Te^{131} 8d I^{131}	0.81	± 0.06
	Total	2.25	± 0.10
140	13.4d Ba^{140} 41.4m La^{140}	6.56	± 0.5
141	32.5d Ce^{141}	6.8	± 0.5
143	33h Ce^{143}	4.85	± 0.5

Figure 4. Photofission yields of thorium. Solid circles represent experimental data; open circles represent minor points (229-A).


8.0
6.0
4.0
2.0
1.0
0.8
0.6
0.4
0.2
FISSION YIELD %
80
90
100
110
120
130
140
NUCLEON NUMBER

DISCUSSION

The yield curves for the fission of Th^{232} by photons, by pile neutrons (93) and by 37.5-Mev α-particles (60) are shown in Figure 5 along with the well-known curve for thermal neutron fission of U^{235} (85). The most noteworthy feature of this comparison is that symmetrical fission is ten times more probable in photofission than it is in pile neutron fission, but still about three times less probable than in fission induced by α-particles.

Data are also available on the photofission of U^{238} (14-b, 76), U^{235} (83) and Bi^{209} (87). In all cases, including the present work, the number of points determined have been so few in number that the fission yield curves, when they can be drawn at all (See Figure 6.), are not sufficiently precise to be subject to fine interpretation. However, certain tendencies can be detected which seem to justify some general statements.

The half-width of the photofission yield curve is 14 in the case of U^{235} and 12 in the case of Th^{232}. The thermal neutron fission yield curve of U^{235} has a half-width of 15.5, whereas the pile neutron fission yield curve of Th^{232} has a half-width of 14. Thus it appears that, as in the case of neutron fission, the half-width increases with the mass of the compound nucleus. In addition, the cases of U^{238}, U^{235} and Th^{232} seem to indicate that photofission results in

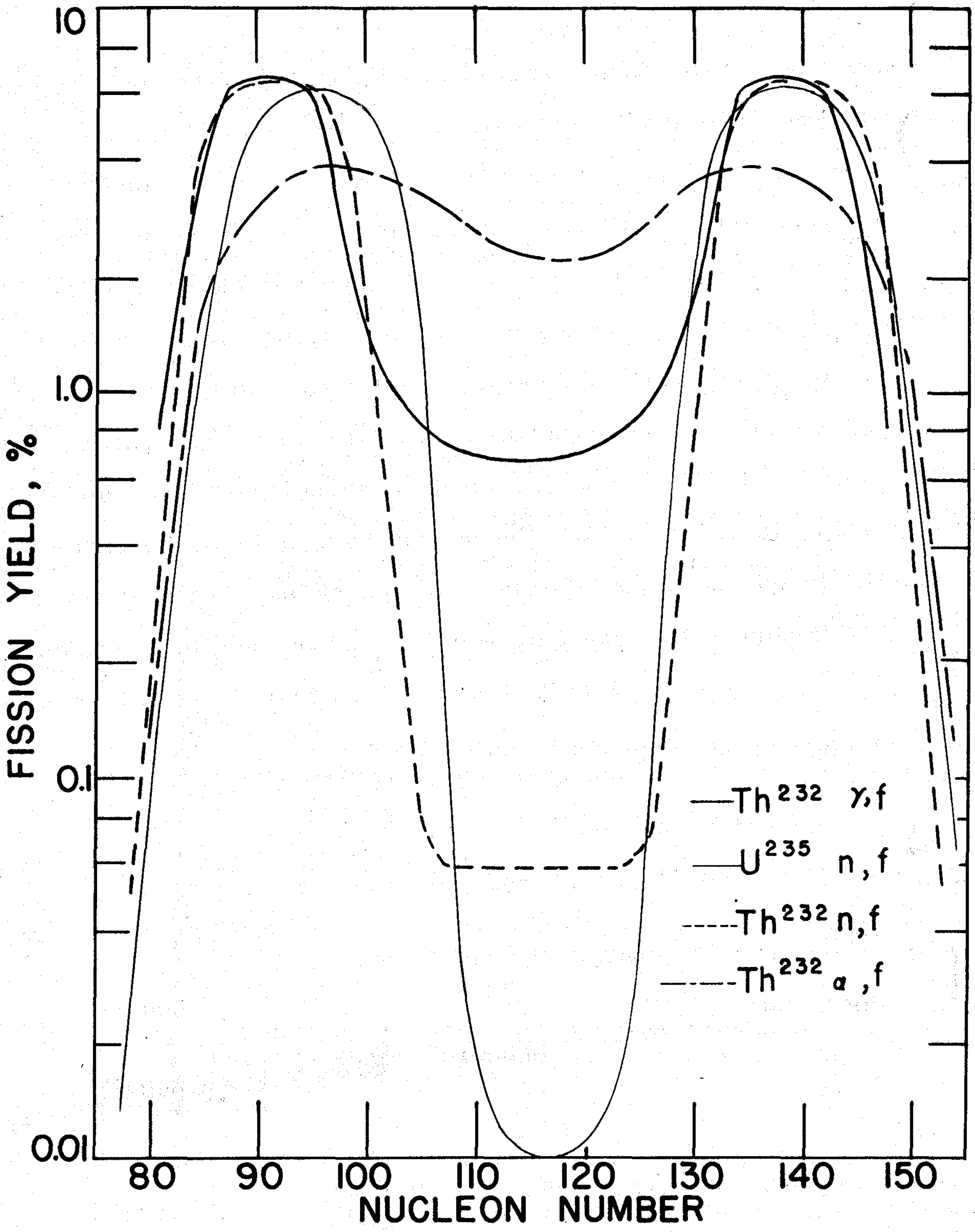


Figure 5. Thermal neutron fission yield in U^{235}; (γ,f), (n,f) and (α,f) yields in Th^{232}.

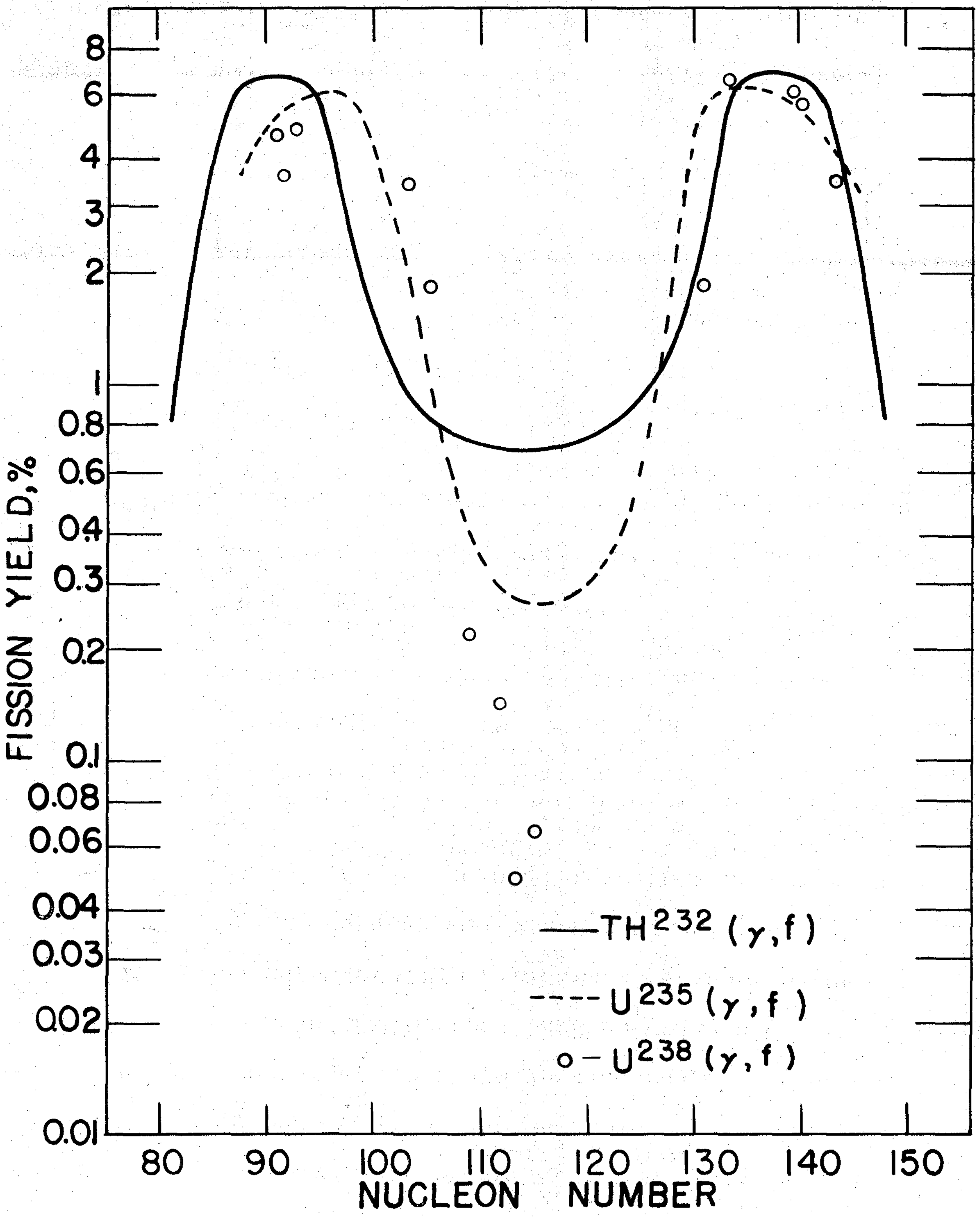


Figure 6. Photofission yields in Th^{232}, U^{235} and U^{238}.

definitely smaller half-widths than does neutron fission. It may also be worth noting in this connection that the photofission yield curve of Bi^{209}, having only a single peak, was distinctly narrower than the yield curve resulting from fission of Bi^{209} with 190-Mev deutrons (87).

The most probable mode of Bi^{209} photofission is symmetrical (87). The photofission yield ratio of most probable mode to symmetrical mode is ten in the case of Th^{232}, over 20 in the case of U^{235} (83) and about 100 in the case of U^{238} (76). The very high ratio reported for U^{238} may be partly caused by the fact that photofission was induced by brehmstrahlung with a maximum energy of only 16 Mev, so that this datum is not strictly comparable with the others. In spite of this qualification, the above data seem to justify the general statement that the tendency towards symmetrical photofission decreases as the nucleon number of the excited nucleus increases.

Further comparison of the photofission yield curves of U^{235} and Th^{232} with their respective neutron fission yield curves reveals that in both cases the heavy peak of the curve is shifted in the light direction by an amount which, though small, appears to be too large to be accounted for merely by the difference of one neutron in the composition of the respective compound nuclei. Present preliminary data indicate that the photofission yield curve of U^{238} also follows this trend.

Previous reports that the Th^{232} photofission cross-section has its peak at 17-18 Mev and practically vanishes above 30 Mev (6,54) led to the belief that in the present experiments the average amount of photoexcitation leading to fission was about 15 Mev, an excitation which is too low to cause emission of many neutrons from the excited nucleus prior to fission. This prediction is corroborated by the fact that the heavy branch of the experimental yield curve is symmetrical with the light branch, which would not be the case if the neutron yield were high. In addition, comparison of the reported neutron yield of 2.6 per spontaneous Th^{232} fission event (9) with the value of 3 ± 0.5 neutrons per Th^{232} photofission event obtained in the present investigation shows that the difference is small at most and may in fact not exist at all. If photofission actually does result in a higher neutron yield than does spontaneous fission, the increase is small and may be attributed to that fraction of fission events resulting from relatively high excitation. Further experiments would be required to resolve the doubt which remains as to whether or not photoexcitation ever causes a nucleus to emit neutrons prior to fission.

The attempt to correlate the reports of Price and Kerst (74) and of Goward et al. (34) led to the prediction that photofission of U^{238} results in the emission of 5.5 neutrons per event. In the face of the present data on Th^{232} and the data of Coryell and Richter (14-b, 76) on U^{238}, this prediction seems to be definitely discredited. The reasons for this are not apparent. Further experiments, preferably all using the same photon source, would be required to settle this point.

BIBLIOGRAPHY

1. Anderson, R. E. and R. B. Duffield, Phys. Rev., 85, 728 (1952).

2. Arakatsu, B., Y. Uemura, M. Sonoda, S. Shimizu, K. Kimura and K. Muraoka, Proc. Phys.-Math. Soc. (Japan), 32, 440 (1941).

3. Arnold, J. R. and N. Sugarman, J. Chem. Phys., 15, 703 (1947).

4. Aston, F. W., Proc. Roy. Soc., A115, 487 (1927).

5. Baldwin, G. C. and F. R. Elder, Phys. Rev., 78, 76 (1950).

6. _____ and G. S. Klaiber, Phys. Rev., 71, 3 (1947).

7. Ballou, N. E. Paper 257. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 1538-41. N. Y., McGraw-Hill Book Co., Inc. 1951.

8. _____ and others. Paper 225. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 1410-6. N. Y., McGraw-Hill Book Co., Inc. 1951.

9. Barclay, F. R., W. Galbraith and W. J. Whitehouse, Proc. Phys. Soc. (London), A65, 73 (1952).

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

11. Boldridge, W. F. and D. N. Hume. Paper 294. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 1693-1701. N. Y., McGraw-Hill Book Co., Inc. 1951.

12. Bonardi, J. P. and E. P. Barret, U. S. Bur. Mines Tech. Paper 230, (1920).

13. Chiotti, P. and B. A. Rogers, Metal Progress, 60, 60 (1951).

14a. Christensen, O. T., J. Prakt. Chem., (2)45, 213 (1892).

14b. Coryell, C. D., Private communication, May 5, 1952.

15. Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. N. Y., McGraw-Hill Book Co., Inc. 1951.

16. Courant, E. D., Phys. Rev., 82, 703 (1951).

17. Day, R. A. and R. W. Stoughton, J. Am. Chem. Soc., 72, 5662 (1950).

18. DeBenedetti, S., J. E. Francis, Jr., and T. W. Bonner, MDDC-1699, Jan. 28, 1948.

19. Dressel, R., M. Goldhaber and A. O. Hanson, Phys. Rev., 77, 754 (1950).

20. Engelkemeir, D. W., J. A. Seiler, E. P. Steinberg and L. Winsberg. Paper 4. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 56-65. N. Y., McGraw-Hill Book Co., Inc. 1951.

21. Evans, R. D. Fundamentals of nuclear physics. In Goodman, C., ed. The science and engineering of nuclear power. p. 1-75. Cambridge, Mass., Addison-Wesley Press, Inc. 1947.

22. Eyges, L., UCRL-1581, Nov. 30, 1951.

23. Frankel, S. and N. Metropolis, Phys. Rev., 72, 914 (1947).

24. Frenkel, J., J. Phys. U. S. S. R., 10, 533 (1946).

25. Friedlander, G. and J. W. Kennedy. Introduction to radiochemistry. N. Y., John Wiley and Sons, Inc. 1949.

26. Gaertner, E. R. and M. L. Yeater, Phys. Rev., 76, 363 (1949).

27. Glendenin, L. E., Nucleonics, 2, 16 (1948).

28. _____. Paper 260. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 1549-56. N. Y., McGraw-Hill Book Co., Inc. 1951.

29. _____ and C. D. Coryell, Phys. Rev., 77, 755 (1950).

30. _____, C. D. Coryell and R. R. Edwards. Paper 52. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 489-516. N. Y., McGraw-Hill Book Co., Inc. 1951.

31. _____, R. R. Edwards and H. Gest. Paper 232. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 1451-2. N. Y., McGraw-Hill Book Co., Inc. 1951.

32. Goeckermann, R. H. Separation method 52-2. In Meinke, W. W., ed. AECD-2738. p. 158. Aug. 30, 1949.

33. _____ and I. Perlman, *Phys. Rev.*, *76*., 628 (1949).

34. Goward, F. K., E. J. Jones, H. H. H. Watson and D. J. Lees, *Proc. Phys. Soc. (London)*, *A64*, 95 (1951).

35. _____, E. W. Titterton and J. J. Wilkins, *Nature*, *164*, 661 (1949).

36. Grummitt, W. E. and G. Wilkinson, *Nature*, *161*, 520 (1948).

37. _____, J. Geron, G. Wilkinson and L. Yaffe, *Can. J. Research*, *B25*, 357 (1947).

38. _____, J. Geron, G. Wilkinson and L. Yaffe, *Can. J. Research*, *B25*, 364 (1947).

39. Haxby, R. O., W. F. Shoupp, W. E. Stephens and W. H. Wells, *Phys. Rev.*, *58*, 92 (1940).

40. Heyn, R. A., A. H. W. Aten, Jr. and C. J. Bakker, *Nature*, *143*, 516 (1939).

41. Hirzel, O. and H. Wäffler, *Helv. Phys. Acta*, *20*, 373 (1947).

42. Jungerman, J. and S. C. Wright, *Phys. Rev.*, *76*, 1112 (1949).

43. Kerst, D. W. In Proc. Int'l. Conf. Nuclear Physics and the Physics of Fundamental Particles. p. 197-8. Sept. 17-22, 1951.

44. Koch, H. W. Ph. D. thesis. U. of Illinois. 1944 (unpublished).

45. _____, J. McElhinney and E. L. Gasteiger, *Phys. Rev.*, *77*, 329 (1950).

46. Kraus, K. A. and R. W. Holmberg, AECD-2919, 1950.

47. Langer, A. and W. E. Stephens, Phys. Rev., 58, 759 (1940).

48. Levine, H. and F. S. Grimaldi, AECD-3186, Feb. 1950.

49. Levinger, J. S. and H. A. Bethe, Phys. Rev., 78, 115 (1950).

50. _____ and H. A. Bethe, Phys. Rev., 85, 577 (1952).

51. Magnusson, L. B., Jr., R. Huizenga, P. R. Fields and M. H. Studier, Phys. Rev., 84, 166 (1951).

52. Mahr, C. and H. Ohle, Z. Anal. Chem., 109, 1 (1937).

53. Marquez, L., Phys. Rev., 81, 897 (1951).

54. McElhinney, J. and W. E. Ogle, Phys. Rev., 81, 342 (1951).

55. Meinke, W. W., ed., AECD-2738, Aug. 30, 1949.

56. Metcalf, R. P. Paper 47. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 478-9. N. Y., McGraw-Hill Book Co., Inc. 1951.

57. _____. Paper 51. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 487-8. N. Y., McGraw-Hill Book Co., Inc. 1951.

58. _____. Paper 268. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 1584-5. N. Y., McGraw-Hill Book Co., Inc. 1951.

59. Moeller, T., G. K. Schweitzer and D. D. Starr, Chem. Revs., 42, 63 (1948).

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

61. _____. Separation method 35-3. In Meinke, W. W., ed. AECD-2738. p. 98. Aug. 30, 1949.

62. _____. Separation method 38-5. In Meinke, W. W., ed. AECD-2738. p. 107. Aug. 30, 1949.

63. _____. Separation method 40-2. In Meinke, W. W., ed. AECD-2738. p. 113. Aug. 30, 1949.

64. _____. Separation method 42-3. In Meinke, W. W., ed. AECD-2738. p. 117. Aug. 30, 1949.

65. _____. Separation method 47-5. In Meinke, W. W., ed. AECD-2738. p. 136. Aug. 30, 1949.

66. _____. Separation method 48-5. In Meinke, W. W., ed. AECD-2738. p. 142. Aug. 30, 1949.

67. _____. Separation method 52-4. In Meinke, W. W., ed. AECD-2738. p. 160. Aug. 30, 1949.

68. _____. Separation method 53-4. In Meinke, W. W., ed. AECD-2738. p. 164. Aug. 30, 1949.

69. _____. Separation method 58-1. In Meinke, W. W., ed. AECD-2738. p. 195-6. Aug. 30, 1949.

70. O'Connor, P. R., MDDC-1706, Aug. 18, 1947.

71. _____ and G. T. Seaborg, Phys. Rev., 74, 1189 (1948).

72. Ogle, W. E. and J. McElhinney, Phys. Rev., 81, 344 (1951).

73. Parsons, R. W. and C. H. Collie, Proc. Phys. Soc. (London), A63, 839 (1950).

74. Price, G. A. and D. W. Kerst, Phys. Rev., 77, 806 (1950).

75. Reinecke, A., Ann., 126, 113 (1863).

76. Richter, H. G. In Laboratory for Nuclear Science and Engineering Progress Report. p. 30-1. M.I.T. Nov. 30, 1951.

77. Roberts, R. B., R. C. Meyer and L. R. Hafstad, Phys. Rev., 55, 416 (1939).

78. Rodden, C. J. and J. C. Warf. Thorium. In Rodden, C. J., ed. Analytical Chemistry of the Manhattan Project. p. 160-207. N. Y., McGraw-Hill Book Co., Inc. 1950.

79. Seaborg, G. T. and others, Phys. Rev., 72, 740 (1947).

80. Seiler, J. A. Paper 48. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 480-1. N. Y., McGraw-Hill Book Co., Inc. 1951.

81. Sheline, R. K., Phys. Rev., 84, 1064 (1951).

82. Sidgwick, N. V. The chemical elements and their compounds. p. 628-53. London, Oxford University Press. 1950.

83. Spence, R. W. In BNL-C-9. p. 43-51. July 14-15, 1949.

84. Steinberg, E. P. Paper 49. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 482-4. N. Y., McGraw-Hill Book Co., Inc. 1951.

85 _____ and M. S. Freedman. Paper 219. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 1378-90. N. Y., McGraw-Hill Book Co., Inc. 1951.

86. _____, J. A. Seiler, A. Goldstein and A. Dudley, ANL-353, 1947.

87. Sugarman, N., Phys. Rev., 79, 532 (1950).

88. _____ and R. Peters, Phys. Rev., 81, 951 (1951).

89. Sullivan, W. H. Trilinear chart of nuclear species. N. Y., John Wiley and Sons, Inc. 1949.

90. Swiatecki, W. J., Phys. Rev., 83, 178 (1951).

91. Titterton, E. W. and T. A. Brinkley, Phil. Mag., 41, 500 (1950).

92. _____ and F. K. Goward, Phys. Rev., 76, 142 (1949).

93. Turkevich, A. and J. B. Niday, Phys. Rev., 84, 52 (1951).

94. Waggener, W. C. and R. W. Stoughton, J. Phys. Chem., 56, 1 (1952).

95. Way, K. and N. Dismuke, AECD-2817, Aug. 29, 1949.

96. _____, L. Fano, M. R. Scott and K. Thew, eds. Nuclear data. NBS Circular 499. Washington, D. C., U. S. G. P. O. 1951.

97. _____, M. Wood and K. Thew, eds. Nuclear data. Supplement 1 to NBS Circular 499. Washington, D. C., U. S. G. P. O. 1951.

98. _____, G. Fuller, M. Wood, K. Thew and A. Jurgens, eds. Nuclear data. Supplement 2 to NBS Circular 499. Washington, D. C., U. S. G. P. O. 1951.

99. Winhold, E. J., P. T. Demos and I. Halpern, Phys. Rev., 85, 728 (1952).

100. Winsberg, L. Paper 50. In Coryell, C. D. and N. Sugarman, eds. Radiochemical Studies: The Fission Products. p. 485-6. N. Y., McGraw-Hill Book Co., Inc. 1951.

101. Wilson, R. R., Phys. Rev., 72, 189 (1947).

102. Zumwalt, L. R., AECU-567, no date.

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APPENDIX:

CHEMICAL PROCEDURES

Bromine

(1) Dissolve the irradiated sample of 13 g Th metal in 22 ml HCl*, 3 ml $HClO_4$, 5 ml H_2O and a few drops of fluosilicate soln. Collect HCl fumes in a trap containing 5 ml 6N NaOH, adding the contents of the trap to the main soln. after the Th is dissolved. Dil. to 50 ml and take duplicate 12-ml aliquots into 60-ml separatory funnels.

(2) Add 20 mg bromide carrier and 10 mg iodide carrier. Add 10 ml CCl_4, followed by 4 drops of a nitric acid soln. of 2M cerium(IV). Extract. Reextract with 1 or 2 2-ml portions of CCl_4 until CCl_4 layer is clear; then add 1 more drop 2M cerium(IV) and extract. Discard the CCl_4 layers. (See Note 1.)

(3) Add 10 ml CCl_4 and 10 drops 2M cerium(IV). Extract Br_2 into clean separatory funnels and save. Store aq layer as fission residue. Record time.

(4) Add 10 ml H_2O and 0.1N $NaHSO_3$ dropwise until CCl_4 layer decolorizes. Discard CCl_4 layer.

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*When concentrations are not specified, the concentrated laboratory reagent is used.

(5) Add 10 mg iodide carrier, 2 ml HNO_3 and 4 drops 2M cerium(IV). Extract. Add another 10 mg iodide carrier and 4 drops 2M cerium(IV). Extract with 10 ml CCl_4. Test with 2 ml CCl_4 and 1 drop 2M cerium(IV) for complete I_2 extraction. Extract twice more with 2-ml portions of CCl_4.

(6) Add 10 ml CCl_4 and 10 drops 2M cerium(IV). Extract Br_2 and discard aq phase.

(7) Add 10 ml H_2O and enough 0.1M $NaHSO_3$ to extract Br_2 into the aq phase. Transfer to 50-ml beaker. Add 1 ml HNO_3, heat, add 3 ml 0.1N $AgNO_3$, stir and digest briefly. Filter on tared paper, wash 3 times each with 5-ml portions of H_2O, EtOH and Et_2O. Dry 10 min at 110° C. Weigh as AgBr.

10 mg Br = 23.5 mg AgBr.

Note 1. A little Br may be lost here and in step 5, but it is more important to get complete purification from I activities.

Strontium

(1) Dissolve duplicate 5-g powdered Th samples in HNO_3 plus a few drops of fluosilicate. (See Note 1.) Add 20 mg Sr carrier and 20 mg Ba carrier. Transfer to 50-ml glass centrifuge tubes.

(2) Add 30 ml fuming HNO_3 with stirring, colling in an ice bath. Centrifuge. Draw off supernate carefully and store as fission residue.

(3) Dissolve ppt. in 2 ml warm water. Transfer to 15 ml centrifuge tubes with 15 ml fuming HNO_3, stir and cool in ice bath. Centrifuge. Discard supernate.

(4) Dissolve ppt. in 5 ml H_2O. Add 5 mg iron(III) carrier and ppt. $Fe(OH)_3$ with fresh, carbonate-free NH_4OH. Centrifuge. Repeat with another 5-mg portion of iron(III) carrier.

(5) Transfer supernate to new 15-ml tubes. Add 6N HNO_3 until the pink color of phenolphthalein disappears. Add 1 ml 6N acetic acid and 2 ml 6N ammonium acetate. Heat nearly to boiling. Add 1 ml 1.5M Na_2CrO_4 and a few drops of dilute Aerosol soln. and let stand hot for 1/2 hr. Centrifuge. Transfer supernate to 50-ml beakers through S&S 589 Red Ribbon filter paper for Sr detn. Save $BaCrO_4$ for subsequent Ba detn. if desired.

(6) Add 2 ml concd. NH_4OH to beakers. Heat nearly to boiling. Add 5 ml satd. aq $(NH_4)_2C_2O_4$ slowly with

stirring. Stir 1-2 min, filter on tared paper, wash 3 times each with 5-ml portions of hot dil. NH_4OH, EtOH and Et_2O. Dry in vacuum desiccator by exhausting for 2 min, then for 5 min. Weigh as $SrC_2O_4 \cdot H_2O$.

10 mg Sr = 22.1 mg $SrC_2O_4 \cdot H_2O$.

Note 1. If the Th sample has been dissolved in HCl, as is customary if solid pellets are bombarded, then aliquots are taken and the HCl is driven out by heating with HNO_3. Failure to do this results in the violent evolution of Cl_2 upon the addition of fuming HNO_3.

Molybdenum

(1) Dissolve the 13-20-g sample of Th metal in HCl plus a few drops of fluosilicate. Dilute to 50 ml and take duplicate 12-ml aliquots for Mo detn. into 30-ml beakers.

(2) Add 10 mg Mo carrier and 3 drops Br_2. Heat gently until all of the Br_2 is boiled out. (See Note 1.)

(3) Transfer to 60-ml separatory funnels. Make 6N in HCl. Extract 4 times with HCl-satd. Et_2O. Combine Et_2O portions in clean separatory funnels and wash twice with 2-ml portions of 6N HCl. Store aq phase as fission residue.

(4) Decant ether layers into 30-ml beakers and evap. over 5 ml H_2O under air stream; then boil out the last of the Et_2O.

(5) Transfer to 15-ml centrifuge tubes with 1 ml satd. oxalic acid soln. and 5 ml 6N HNO_3. Add 5 ml fresh 2% tincture of α-benzoinoxime slowly with stirring. Centrifuge, wash with 15 ml 1N HNO_3. Discard supernates.

(6) Dissolve ppt. in 5 ml 6N NaOH with stirring. Re-acidify with HNO_3. Add 2-3 ml tincture of α-benzoinoxime, centrifuge and discard supernate. Wash with 15 ml 1N HNO_3. Discard supernate.

(7) Perform wet oxidation of ppt. with 2 ml HNO_3 and 1 ml $HClO_4$, heating to white fumes of $HClO_4$. (See Note 2.)

(8) Cool and add 10 ml H_2O plus enough NH_4OH to dissolve the MoO_3. Reacidify with HCl and scavenge with 5 mg iron(III) carrier and NH_4OH. Centrifuge. Transfer supernate to 250-ml beakers and dil. to 150 ml.

(9) Make acid to methyl orange with HCl. Add 5 ml excess HCl plus 8 drops HNO_3. Dissolve 8 g NaOAc in the soln. Add 1.5 ml 0.1M $Pb(OAc)_2$. Heat at near boiling for 2 hr or more, till ppt. digests.

(10) Filter on tared paper. Wash 3 times each with 5-ml portions of hot 2% NH_4NO_3, hot H_2O and EtOH. Dry 15 min at 110° C and weigh as $PbMoO_4$.

10 mg Mo = 38.3 mg $PbMoO_4$.

Note 1. This Br_2 oxidation is necessary in order to bring all the active Mo to the hexavalent state so that it will exchange with the Mo carrier and be extracted into the Et_2O.

Note 2. If all the organic matter is not oxidized, it will become insoluble again when the soln. is made basic, resulting in the loss of considerable Mo when the soln. is scavenged with $Fe(OH)_3$.

Ruthenium

(1) Dissolve the irradiated sample of 13-20 g Th metal in HCl plus a few drops of fluosilicate soln. Dil. to 50 ml and take duplicate 5-ml aliquots into 50-ml distilling flasks for Ru analysis.

(2) To the distilling flasks add 10 mg iodide carrier, 20 mg Ru carrier ($RuCl_3.RuCl_4$ in dil. HCl), 1/2 g $NaBiO_3$, 3 glass beads and 10 ml $HClO_4$. Place 15 ml 6N NaOH and 10 mg Mo carrier in the receiver tubes and cool them in ice baths. (See Note 1.) Assemble distn. apparatus. (See Note 2.)

(3) Distill slowly at first, then quite rapidly, stopping when all the orange RuO_4 and 1-2 ml $HClO_4$ have passed over into the receiving tubes.

(4) Add 5 ml EtOH to receiving tubes and boil gently to ppt. black RuO_2. Centrifuge. Discard clear colorless supernate.

(5) Wash with 10 ml H_2O, 1 ml 6N NaOH and 10 mg Pb carrier. (See Note 3.) Boil, centrifuge and discard supernate.

(6) Dissolve RuO_2 by heating with 2 ml 6N HCl. Add 10 ml H_2O. Add 0.2 g Mg powder in small increments, stirring well. (Solution goes from brown to blue to colorless.) Add a few drops of dil. Aerosol soln. and boil gently to digest until the supernate is clear and colorless. (See Note 4.) Cool. Add 5 ml HCl slowly to remove

excess Mg, then boil again until supernate is clear and colorless. (See Note 4.)

(7) Filter on tared paper. Wash 3 times each with 5-ml portions of hot H_2O, EtOH and Et_2O. Dry 10 min at 110° C. Weigh as Ru metal.

Note 1. Some active Mo distills over with the $HClO_4$. The Mo carrier in the receiver serves to prevent it from contaminating the RuO_2 ppt.

Note 2. The joints of the all-glass apparatus should be greased with concd. $HClO_4$ and <u>never</u> with any type of organic stop-cock grease.

Note 3. Pb carrier is used in this wash solution to remove any traces of Pb^{212} which might have been physically carried over during the distn.

Note 4. If color remains at this point, add further small increments of Mg to the acid soln. until the soln. becomes and remains colorless upon boiling.

Silver

(1) Place 10 ml HCl in two 100-ml Lusteroid centrifuge tubes. Add 5-g portions of irradiated Th powder in small portions. Then warm in a water bath until the evolution of H_2 subsides and add a few drops of fluosilicate soln. to clear up the solutions.

(2) Add $AgNO_3$ carrier (20 mg Ag) and dil. to 90 ml. Transfer with stirring to glass 150-ml beakers. Wash with 10 ml H_2O to complete the transfer. Digest in beakers on hot plates for a few minutes.

(3) Centrifuge in portions in 50-ml glass tubes, saving supernate as fission residue.

(4) Dissolve AgCl in 2 ml 6N NH_4OH, heating if necessary. Dil. to 10 ml and scavenge with 5 mg iron(III) carrier. Repeat $Fe(OH)_3$ scavenging. Transfer supernate to new tubes.

(5) Add a few drops of 1M thioacetamide soln. and heat in oil bath to ppt. Ag_2S. Decant. Wash ppt. with H_2O.

(6) Dissolve ppt. in 1 ml boiling HNO_3. Dil. to 10 ml, neutralize with 6N NH_4OH and add 2 ml excess NH_4OH plus 2 drops dil. KI soln. Scavenge with 5 mg iron(III) carrier.

(7) Decant to new tubes and repeat steps 5 and 6.

(8) Transfer supernate to 50-ml beakers. Add 2 ml 6N HNO_3, a few drops of dil. Aerosol soln., and 5 drops 6N HCl.

Digest. Filter on tared paper. Wash 3 times each with 5-ml portions of H_2O, EtOH and Et_2O. Dry at 110° C and weigh as AgCl.

10 mg Ag = 13.3 mg AgCl.

Cadmium

(1) Dissolve 13 g irradiated Th metal in HCl plus a few drops of fluosilicate soln. Dil. to 50 ml and take duplicate 12-ml aliquots into 50-ml glass centrifuge tubes for Cd analysis.

(2) Add 20 mg Cd carrier, 5 mg Sn carrier, 2 mg Pd carrier and 5 mg Sb carrier. Add 1 ml NH_4OH, 6 ml H_2O and 6 ml 5% thiourea soln. Centrifuge and transfer to new 50-ml centrifuge tubes.

(3) Add an excess of a soln. which is 1% in thiourea and satd. with Reinecke's salt, $NH_4[Cr(NH_3)_2(SCN)_4] \cdot H_2O$, cool in an ice bath, centrifuge and wash with cold 1% thiourea soln. Store supernate as fission residue.

(4) Dissolve ppt. in 20 ml H_2O and 1.5 ml 6N HCl. Ppt. CdS by heating with a few drops of thioacetamide soln. (See Note 1.) Centrifuge. Discard supernate.

(5) Dissolve CdS with 2 ml hot 6N HCl. Boil out H_2S. Transfer to 15-ml centrifuge tubes. Add 10 mg Pb carrier. (See Note 2.)

(6) Add 6N NaOH soln. dropwise, to ppt. $Cd(OH)_2$. Stir and centrifuge. Discard supernate. Dissolve $Cd(OH)_2$ with several drops 6N HCl. Dil. to 5 ml. Reppt with 6N NaOH. Centrifuge. Discard supernate.

(7) Dissolve in 2 drops 6N HCl. Dil. to 5 ml. Add 5 ml iron(III) carrier. Add NH_4OH until $Fe(OH)_3$ starts to

ppt., then redissolve with a drop of 6N HCl, heat and add several crystals of NaOAc. Centrifuge off the basic ferric acetate. Transfer supernate to new tubes.

(8) Repeat the basic ferric acetate scavenging.

(9) Scavenge with basic indium acetate, pptd. at a pH of 7-8. Record time. Transfer supernate to new tubes and dil. to 14 ml. Add a few drops 6N HCl and 10 mg In carrier.

(10) 3 hr and 20 min after the time recorded in step 9, ppt. basic In acetate. Centrifuge. Store supernate in clean 50-ml beakers and add to it the 10 ml dil. NaOAc soln. with which the basic In acetate is washed. The combined solutions are saved for subsequent gravimetric detn. of Cd.

(11) Dissolve In ppt. in 2 drops 6N HCl. Add Cd holdback carrier and transfer with H_2O to clean 30-ml beakers. Repeat the pptn. of basic In acetate, adding a little filter pulp. Filter on 9-cm S&S 589 Black Ribbon paper. Wash with dil. NH_4OH. Char off with care in porcelain crucibles; ignite at 800° C for 15 min. Cool and weigh.

(12) Slurry the In_2O_3 with EtOH, deposit sample on filter paper, mount and count. Dry, reignite and reweigh the crucibles to determine the wt of In_2O_3 in the samples.

(13) Add HCl dropwise to the combined Cd solns. from step 10

until the soln. has a pH of about 1. Make soln. 1% in thiourea. Add large excess of the thiourea-Reinecke's salt soln. used in step 3. Place in refrigerator for several hours, stirring occasionally.

(14) Filter in tared 2001 Selas crucibles, wash with ice-cold 1% thiourea soln., then with cold EtOH. Dry to constant wt (20 min) at 110° C. The factor for Cd is 0.1247.

Note 1. It may be necessary to add a few drops of NH_4OH in order to initiate the pptn. of CdS.

Note 2. The addition to Pb holdback carrier is necessary to remove fairly large amounts of Th decay products which carry through to this point.

Tellurium

(1) Place duplicate 3.5-g portions of irradiated Th powder in 30-ml beakers. Add 3 ml H_2O, 20 mg Te carrier (HCl soln. of Te(IV)) and finally, in small increments, 7 ml HCl plus a few drops of fluosilicate soln. (See Note 1.) Complete the dissolving action by heating for a few min, then transfer to 15-ml centrifuge tubes.

(2) Centrifuge. Test supernate for completeness of pptn. with H_2SO_3. Wash with 10 ml H_2O and a little Aerosol. Store supernate as fission residue.

(3) Dissolve Te^0 in 10 drops 6N HNO_3. Evap. to dampness by heating in an oil bath under an air stream.

(4) Add 3 drops 6N HCl and dil. to 10 ml. Heat nearly to boiling. Neutralize by adding 6N NaOH dropwise. Add more reagent till white H_2TeO_3 disappears, then 10 drops excess. Add 1-2 mg iron(III) carrier dropwise with stirring; digest briefly and centrifuge. Repeat. (See Note 2.) Transfer supernate to 50-ml centrifuge tubes.

(5) Add to supernate an equal vol. of 6N HCl. Heat nearly to boiling. Ppt. Te^0 by adding 1/2 ml 6% H_2SO_3. Centrifuge. Discard supernate.

(6) Dissolve Te^0 in 10 drops 6N HNO_3. Evap. to dampness. Add 2 ml HCl and reevap. Repeat HCl evapn.

(7) Add 5 ml 6N HCl and 5 ml H_2O. Transfer to 30-ml

beakers. Filter on tared paper. Wash 3 times each with 5-ml portions of H_2O, EtOH and Et_2O. Dry at 110° C for 10 min. Weigh as Te^{0}.

Note 1. Evolution of H_2 causes pptn. of Te^{0}. However, enough Te remains in soln. to give exchange with the active Te.

Note 2. Ppt. contains $Fe(OH)_3$, Rh activity and Th insoluble residue.

Iodine

(1) To the irradiated Th sample add sufficient iodide carrier to give 20 mg I per aliquot. Then dissolve in HCl plus a few drops of fluosilicate soln., collecting the acid fumes in a trap containing 5 ml 6N NaOH. Add the contents of the trap to the main soln., dil. to 50 ml and take duplicate 12-ml aliquots into 60-ml separatory funnels for iodine analysis.

(2) Add 15 ml CCl_4 to separatory funnels. Oxidize iodide to I_2 by adding 8 drops of a nitric acid soln. of cerium(IV). Extract CCl_4 layer into clean separatory funnels. Record time. Extract aq phase with 2 more 5-ml portions of CCl_4. Wash the combined CCl_4 portions twice with 5-ml portions of H_2O. Store aq phase as fission residue.

(3) Add 15 ml H_2O. Then add a sufficient number of drops of 0.1M $NaHSO_3$ to decolorize both layers. Draw off CCl_4 and discard.

(4) Add 1 ml 6N HNO_3 and 5 drops 1M $NaNO_2$. Extract I_2 into 10 ml CCl_4. Place CCl_4 in clean separatory funnels and discard aq phase.

(5) Shake CCl_4 with 10 ml H_2O to which sufficient 0.1M $NaHSO_3$ has been added to decolorize both phases. Discard CCl_4.

(6) Repeat steps 4 and 5.

(7) Transfer aq phase to 50-ml beakers. Add 10 ml H_2O and 1 ml 6N HNO_3. Heat nearly to boiling to expel SO_2. Add 2 ml 0.1M $AgNO_3$ dropwise with stirring. Filter on tared paper. Wash 3 times each with 5-ml portions of H_2O and EtOH. Dry 15 min at 110° C. Weigh as AgI. 10 mg I = 18.5 mg AgI.

Barium

(1) Dissolve duplicate 5-g powdered Th samples in HNO_3 plus a few drops of fluosilicate soln. (See Note.) Add 20 mg Sr carrier and 20 mg Ba carrier. Transfer to 50-ml glass centrifuge tubes.

(2) Add 30 ml fuming HNO_3 with stirring, cooling in an ice bath. Centrifuge. Draw off supernate carefully and store as fission residue.

(3) Dissolve ppt. in 2 ml warm H_2O. Transfer to 15 ml centrifuge tubes with 15 ml fuming HNO_3. Stir and cool in ice bath. Centrifuge. Discard supernate.

(4) Dissolve ppt. in 5 ml H_2O. Add 5 mg iron(III) carrier and ppt. $Fe(OH)_3$ with fresh, carbonate-free NH_4OH. Centrifuge. Repeat with another 5-mg portion of iron(III) carrier.

(5) Transfer supernate to new 15-ml tubes. Add 6N HNO_3 until the pink color of phenolphthalein disappears. Add 1 ml 6N acetic acid and 2 ml 6N ammonium acetate. Heat nearly to boiling. Add 1 ml 1.5M Na_2CrO_4 and 2 drops dil. Aerosol soln. Let stand hot for 1/2 hr. Centrifuge. Discard supernate. (See Note 2.)

(6) Wash $BaCrO_4$ ppt. in 10 ml hot H_2O. Centrifuge for a long time. Discard supernate.

(7) Dissolve $BaCrO_4$ in 3 ml hot 6N HCl. Add 15 ml 4-1 HCl-Et_2O reagent, cool stir and centrifuge. Discard

supernate.

(8) Dissolve $BaCl_2$ in min. of H_2O. Repeat $HCl-Et_2O$ pptn.

(9) Dissolve in 10 ml H_2O. Add a little HNO_3 and 1 ml Pb carrier. Ppt. PbS by heating with a few drops of satd. thioacetamide soln. Centrifuge and transfer supernate to other tubes. Wash ppt. with H_2O and combine wash soln. with supernate. Boil H_2S out of soln.

(10) Repeat step 9. (See Note 3.)

(11) Add 10 mg La carrier. Add NH_4OH till ppt. begins to form, then 1 ml excess. Centrifuge. Add a few more drops La carrier and recentrifuge. Record time. Decant supernate to new tubes.

(12) Dissolve $La(OH)_3$ ppt. from step 11 in min. amount 6N HNO_3. Dil. to 3 ml, reppt. with NH_4OH. Centrifuge and combine supernate with the supernate from step 11. Discard $La(OH)_3$.

(13) Add 10 mg La carrier to combined supernates and acidify with HNO_3 till $La(OH)_3$ dissolves. After allowing time for La^{140} to grow into the soln., ppt. $La(OH)_3$ by addition of 10% excess NH_4OH. Centrifuge. Retain supernate for future milkings if desired.

(14) Dissolve $La(OH)_3$ in min. amount HNO_3 and reppt. Filter with suction, wash with very dil. NH_4OH, EtOH and Et_2O, mount and count. (See Note 4.)

Note 1. If the Th sample has been dissolved in HCl, as is customary if solid pellets are bombarded, then aliquots are taken and the HCl is driven out by heating with HNO_3. Failure to do this results in the violent evolution of Cl_2 upon the addition of fuming HNO_3.

Note 2. The supernate may be filtered to remove traces of $BaCrO_4$ and retained for subsequent detn. of Sr if desired.

Note 3. The sulfide scavenging is for the purpose of removing Pb and Bi decay products of Th, which grow out of the Ra^{224} which is carried along with the Ba.

Note 4. The assumption is made here that all of the La carrier which was added in step 13 is recovered by hydroxide pptn.

Cerium

(1) Dissolve the 13-g sample of irradiated Th in 25 ml HCl plus a few drops of fluosilicate soln. Dil. to 50 ml and take duplicate 12-ml aliquots for Ce analysis.

(2) Add 10 mg of Ce^{+3}, La and Y carriers, bringing the vol. of soln. to 15 ml. Add 28.5 g $Al(NO_3)_3 \cdot 9H_2O$. (See Note 1.) Heat to dissolve; then cool and transfer to 100-ml separatory funnels.

(3) Extract with 40 ml mesityl oxide. Extract a second time with 30 ml mesityl oxide, drawing off aq phase into 50-ml glass centrifuge tubes.

(4) Add NaOH to aq phase till $Al(OH)_3$ redissolves, leaving R. E. hydroxides. (See Note 2.) Cool. Centrifuge. Discard supernate.

(5) Dissolve in 2 ml 6N HNO_3. Add a little H_2SO_3. (See Note 3.) Dil. to 10 ml and add 19 g $Al(NO_3)_3 \cdot 9H_2O$. Heat to dissolve; then cool. Transfer to 60-ml separatory funnels.

(6) Extract with 25 ml tributyl phosphate. Strip into 50-ml centrifuge tubes with successive 20, 10 and 10-ml portions of H_2O, the last two portions containing a little HNO_3 and a drop of 30% H_2O_2. (See Note 4.)

(7) Add NaOH until $Al(OH)_3$ redissolves, leaving R. E. hydroxides. (See Note 4.) Cool under tap and centrifuge. Discard supernate.

(8) Add 8 ml HNO_3 and 1/4 g $KBrO_3$. Heat to complete oxidation of Ce. Then add 20 ml 0.35M HIO_3. Centrifuge. Discard supernate.

(9) Dissolve $Ce(IO_3)_4$ with 1 drop HCl and 5 drops H_2O_2. Then repeat step 8.

(10) Dissolve ppt. with 1 drop HCl and 3 drops H_2O_2. Add 8 ml HNO_3 and 10 mg Zr carrier. Add 20 ml 0.35M HIO_3. Centrifuge off $Zr(IO_3)_4$. Transfer supernate to new 50-ml tubes.

(11) Ppt. $Ce(OH)_3$ by adding solid NaOH with stirring. Cool. Centrifuge. Discard supernate.

(12) Dissolve in 1 ml 6N HCl and a little H_2SO_3. (See Note 3.) Reppt. $Ce(OH)_3$ with NH_4OH.

(13) Dissolve in 1 ml 6N HCl. Transfer to 50-ml beakers with 14 ml H_2O (in portions). Bring to boil on hotplate. Add 15 ml satd. $H_2C_2O_4$ soln. slowly with stirring. Cool in ice bath 10 min. Filter on tared paper, wash 3 times each with 5-ml portions of H_2O, EtOH and Et_2O. Dry in vacuum desiccator by exhausting for 2 min, 2 min and 3 min periods. Weigh as $Ce_2(C_2O_4)_3 \cdot 10H_2O$. 10 mg Ce = 25.9 mg $Ce_2(C_2O_4)_3 \cdot 10H_2O$.

Note 1. This amount of $Al(NO_3)_3 \cdot 9H_2O$ saturates the aq soln. and doubles its vol.

Note 2. Some insoluble Th residue will also remain.

Note 3. H_2SO_3 is added to keep Ce in the trivalent state. In spite of this, a faint yellow color due to traces of Ce^{+4} will be noticed.

Note 4. The reducing agent is necessary because tetravalent Ce remains in the tributyl phosphate and is not stripped by H_2O.

Note 5. Some $Al(NO_3)_3$ carries over into this soln. by purely physical means. It does not actually extract into the tributyl phosphate.