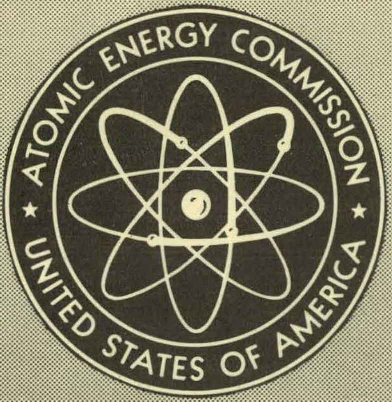

GEAP-3373

THE DETERMINATION OF URANIUM BURNUP IN MWD/TON

Technical Report

By
B. F. Rider
J. L. Russell, Jr.
D. W. Harris
J. P. Peterson, Jr.

March 17, 1960

Vallecitos Atomic Laboratory
General Electric Company
Pleasanton, California

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PHYSICS

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THE DETERMINATION OF URANIUM BURNUP IN MWD/TON

By

B. F. Rider, J. L. Russell, Jr., D. W. Harris, and J. P. Peterson, Jr.

I. INTRODUCTION AND PURPOSE

Nuclear fuel is occasionally warranted to produce a stipulated average Mwd/ton for discharged fuel. Mwd/ton is defined as the megawatt days of heat produced per 2000 pounds of total fissionable and fertile isotopes initially present.

In the history of nuclear power reactors, Mwd/ton has been a difficult number to measure accurately. Measurements performed in different laboratories are not always in agreement(1). A fuel burnup group in Committee E-10 of the American Society for Testing Material is preparing tentative procedures which will help standardize the field of burnup analysis. At present, methods differ from laboratory to laboratory. The purpose of this report is to evaluate some of the existing methods for burnup analysis and to select, if possible, the one best suited for warranty purposes. Most methods take one of three general approaches; namely, measurement of the amount of one or more fission products produced, measurement of the fuel composition before and after irradiation, or some other measurement which is indirect and non-destructive.

Several non-destructive methods for calculating burnup of a fuel element have been suggested. One method involves a heat balance obtained either from temperature and flow measurements of the coolant integrated over time or from electrical power production divided by the thermal efficiency factor for the plant. Another method involves remote gamma scintillation spectrometry for Zr + Nb-95 or Cs-137. Still another involves the measurement of decay heat of an element in a shielded calorimeter. Others involve measurements with ionization chambers or even flux monitors attached to the fuel elements. Burnup can also be calculated from an estimated flux assigned to a reactor position multiplied by the time of exposure.

Although each of these methods may serve a useful purpose, none of them was considered to give as reliable a value of burnup as a radiochemical or mass spectrographic analysis of the dissolved fuel. For this reason, only these two methods are evaluated in this report.

II. SUMMARY

A. RADIOCHEMICAL METHOD

The first approach to Mwd/ton determination is the measurement of a fission product to uranium ratio in the irradiated fuel. It is a direct measurement of the desired quantity, and for small exposures is preferred to the method which depends on small differences in the fuel's isotopic composition. At high exposures this advantage largely disappears. The method has been reviewed by Crouthamel, et al.(2) and Sunderman(3).

In principle, the number of fissions occurring in fuel is determined by measuring the number of atoms of a fission product isotope present and dividing by the fractional fission yield of that isotope. The yield of any fission product varies with the fissioning isotope but a proper choice of fission product will be one which has a nearly constant yield for all fissioning isotopes. The number of fissions occurring in U-235, Pu-239, Pu-241, as well as U-238, is subject to measurement. The resulting number of fissions is converted through a suitable heat of fission factor to Mwd which is in turn divided by the tons of fissionable and fertile atoms initially present to obtain Mwd/ton. Oxygen and other diluents are excluded from the calculations.

If a fission product to uranium ratio method is to be used, it is evident that no separation of uranium from its fission products should occur before withdrawing the sample for analysis.

B. MASS SPECTROMETRIC METHOD

Isotopic analyses of fuel are normally made before and after irradiation for accountability purposes, use charges, and plutonium credits. These data can also be used for the determination of Mwd/ton.

Mwd/ton is related to U-235 disappearance although at high exposures the relationship is not a direct one. The amount of U-235 which was destroyed in-pile by parasitic capture instead of fission must be excluded from the calculation. Then the contribution from fast fission of U-238 as well as the contribution from fission of the Pu-239 and Pu-241 formed during irradiation must be added in.

The parasitic neutron capture in U-235 can be directly measured by U-236 mass analysis. On the other hand, the contribution from fast fission of U-238 cannot be measured by isotopic analysis of the fuel. However, it can be estimated. Since this fast fission is normally a small contribution, it does not cause significant error in the experimentally determined value of Mwd/ton. An estimate of the plutonium contribution can be obtained from post-irradiation analysis of the fuel. Because of the strong dependence of the plutonium cross sections on reactor spectrum and the lack of adequate description of this spectrum, there is a large inherent uncertainty in the size of this plutonium fission contribution.

The calculation of Mwd/ton by analysis of fuel isotopes before and after irradiation is based on the difference of results obtained before and after irradiation. This procedure is necessarily limited in accuracy at low exposures when a small difference of two similar large numbers is involved. The method becomes increasingly reliable as the exposure becomes greater. However, at some high exposure, the large uncertainty of the plutonium contribution begins to dominate, thus decreasing the accuracy once again.

If this procedure is to be used, methods must be developed for obtaining representative samples of the fuel before as well as after irradiation.

III. CONCLUSIONS

Neither of the foregoing methods appears to be clearly superior to the other and each leaves something to be desired. It is concluded that:

1. For important samples where reliability is of great concern, it is wise to employ more than one method of analysis.
2. Careful plans must be made to obtain and preserve samples of fuel before irradiation. Equally careful plans must be made for the preparation of the post irradiation samples in order not to destroy the validity of the measurements.
3. Highly accurate measurement of burnup is an involved and expensive process and may be economically justified for only the most important samples.

IV. RECOMMENDATIONS

On the basis of the present study, it is recommended that:

1. Other methods, especially the heat balance method, should also be carefully studied and reported upon.
2. The half life of Cs-137 should be re-measured to reduce the uncertainty in this basic physical constant.
3. The use of Sr-90 as a burnup indicator should be evaluated.
4. The stable isotopes of fission products such as zirconium, molybdenum, and cerium which can be measured by isotope dilution technique should be evaluated as burnup indicators.

V. DISCUSSION

In the following technical discussion an attempt has been made to describe in detail two methods for measuring Mwd/ton. After presentation of each method a sample calculation is given which is intended to help illustrate and clarify the use of the method. Finally, there is a discussion of the problems, errors and uncertainties associated with the method. Insofar as it seemed practical, the mathematical derivations of equations and stepwise procedures have been removed to the appendix.

It has been the intention of the authors to describe what in their opinion is the present state of the technical development in this field. It is hoped that this document will stimulate interest in further improving the accuracy of methods for measuring burnup.

A. RADIOCHEMICAL METHOD

1. Fission Product to Uranium Ratio. One approach to the determination of Mwd/ton is the measurement of a fission product to uranium ratio in the irradiated fuel.

   A fission product suitable for fuel burnup work should have a long half life, a high fission yield which is constant for fast and thermal fission on all isotopes, have simple chemistry, have a known decay scheme, have a single isotope of the element present, and have a low cross section for formation from adjacent chains.

Some of the fission products suggested for measurement include stable isotopes of zirconium, molybdenum and cerium as well as radioisotopes such as Cs-137, Sr-90, Ce-144 and Zr-95.

Many stable elements are formed in high yield in fission. The yield of some of the more abundant elements in U-235 fission can be summarized as follows:

Element	Atoms/fission
Zr	0.32
Mo	0.25
Xe	0.24
Nd	0.22
Ce	0.12
Cs	0.12
Ru	0.11
Sr	0.10

Chemical analysis for stable fission products shows great promise, especially by the sensitive and accurate isotope dilution technique on a mass spectrometer. Zirconium, neodymium, and cerium in particular are relatively non-volatile at reactor fuel temperatures and are apt to remain associated with the uranium in the fuel. Stable isotope analysis has not been fully exploited and deserves considerably more attention than it has received. Much of the future work on burnup may be in this area.

Among radioisotopes, Cs-137 is almost ideally suited for fuel burnup measurements. Its virtues are: a known decay scheme, a low capture cross-section of less than 2 barns$^{(4)}$, a long half-life, a low yield of Cs-136 which could be converted into Cs-137 by neutron capture, a low absorption cross-section for all the 136 mass chain members that might be diverted into the 137 mass chain by neutron capture, and a high fission yield which is fairly accurately known and not greatly affected by the type of fissionable material or the neutron spectrum. For these reasons, Cs-137 is the almost universally used fission product for the measurement of fuel burnup. The detailed discussion that follows will bring out its occasional shortcomings.

Second choice among radioisotopes would be Sr-90. It has a half-life which is as long as Cs-137. It has not been as widely used for burnup measurements as Cs-137. As a result, its constants are less well known. In particular, little is known of its yield in Pu-239 fission. Although it remains a useful alternative for future development, it will be given no further consideration in this report.

Ce-144 and Zr-95 are too short lived to use for the long irradiations of 3 to 5 years considered possible for commercial power reactors.

a. Calculation of Megawatt Days per Ton. Megawatt days per ton is proportional to % burnup. If % burnup is expressed as fissions per hundred initial fissionable plus fertile atoms this relationship can be most simply expressed as follows:

$$\text{Mwd/ton} = \frac{\text{fissions}}{10^2 \text{ atoms}} \times \frac{1 \text{ Mwd}}{(2.63 \pm 0.09) \times 10^{21} \text{ fissions}} \times \frac{1 \text{ atom}}{4.353 \times 10^{-28} \text{ ton}}$$

$$= \% \text{ Burnup} \times (8.7 \pm 0.3) \times 10^3$$

Each of the values making up the proportionality constant (i.e. the energy released in fission and the weight of an average initial fissionable and fertile atom), as well as the measurement of burnup will be treated in turn.

b. Energy Release in Fission. According to Weinberg and Wigner(5) the distribution of fission energy can be summarized as in Table I.

TABLE I

ENERGY FROM AN AVERAGE FISSION

Kinetic energy of fission fragments	167 ± 5 Mev
Prompt gamma rays	6 ± 1
Kinetic energy of fission neutrons	5 ± 0.5
Fission product decay	
gamma	6 ± 1
beta	8 ± 1.5
Neutrinos	12 + 2.5
Total Energy per Fission	204 ± 7

The value of total fission energy derived from nuclear masses(6) is approximately 203 Mev. Considering the inaccuracy of some of the values of the table, the closeness of this agreement is fortuitous. In a nuclear chain reactor, the maximum available energy per fission is 193 Mev, that is, the total energy minus the neutrino energy. However, the capture of neutrons in the reactor, particularly the (n,γ) process, produces additional energy which brings the total available energy back to about 205 Mev. This last figure is also in good agreement with the measurements of the energy absorbed in the Argonne heavy-water and Oak Ridge graphite reactors. The value holds also for Pu-239. Utilizing this value, the number of fissions per megawatt-day can be expressed as:

$$\frac{1 \text{ fiss.}}{205 \text{ Mev}} \times \frac{6.2422 \times 10^{18} \text{ Mev}}{\text{megawatt-sec.}} \times \frac{86{,}400 \text{ sec.}}{\text{day}} = \frac{(2.63 \pm 0.09) \times 10^{21} \text{ fiss.}}{\text{Mwd}}$$

c. Weight of Initial Fissionable and Fertile Atoms. The atomic weight of uranium in slightly enriched uranium oxide fuel ranges from 238.07 for 0.72% U-235 to 237.94 for 6% U-235. The use of the value 238.00 for an average weight of uranium in this range introduces less than 0.03% error. An average atom of such uranium weighs $(4.353 \pm 0.001) \times 10^{-28}$ ton as shown below:

$$\frac{1 \text{ ton}}{2000 \times 453.59 \text{ gm}} \times \frac{238.00 \pm 0.07 \text{ gm}}{(6.0248 \pm 0.0003)^{(7)} \times 10^{23} \text{ atoms}} = \frac{(4.353 \pm 0.001) \times 10^{-28} \text{ ton}}{\text{atom}}$$

d. Percent Burnup. Percent burnup is here defined as the number of fissions per 100 initial fissionable and fertile atoms. This can also be expressed:

$$\% \text{ Burnup} = \frac{\text{fissions/ml solution}}{(\text{initial fissionable} + \text{fertile atoms})/\text{ml solution}} \times 100$$

The fissions per ml are determined by Cs-137 analysis and the initial fissionable and fertile atoms/ml are determined by careful post-irradiation analysis for uranium atoms/ml to which are added fissions/ml and Pu atoms/ml, to obtain the initial fissionable and fertile atoms/ml. The analyses are carried out on a carefully prepared solution of the irradiated fuel.

2. Method of Measurement

a. Sample Preparation. In the preparation of a sample for burnup analysis, a combined dissolution of cladding and core is preferred. Schemes which include dejacketing prior to dissolution of the uranium are apt to disturb the fission product to uranium ratio.

It is recommended that uranium oxide fuel clad in Zircaloy-2 be dissolved in nitric acid containing sufficient hydrofluoric acid to attack the zirconium cladding(8). The entire solution should be stirred and sampled. Such a sampling procedure will average the fuel both radially and axially and avoid problems caused by possible cesium migration within the fuel.

All analytical dilutions of the primary sample should be made in 1 to 2 molar nitric acid containing 1 to 10 ppm cesium carrier to reduce loss of cesium-137 by ion exchange with sodium and potassium centers in glassware. The acid serves to prevent uranium hydrolysis and subsequent adsorption of hydrated uranium oxides on the glassware.

b. Uranium Analysis. Many procedures have been used for analysis of uranium(9). However, not all are sufficiently accurate or sensitive for analysis of irradiated uranium after 10,000 Mwd/ton exposure. A serious problem is raised by the extreme radioactivity of the samples. Even after 130 days cooling, such a sample emits 2,200 R/hr gamma and 590,000 Rad/hr beta per gram of uranium at 1 cm. See Appendix VIII for the detailed fission product inventory calculations. Table II shows for each type of analysis the amount of uranium required and its associated dose rate.

TABLE II

A COMPARISON OF URANIUM METHODS AT 10,000 MWD/TON

Accuracy	Method	Total U Required, mg	Fission Products, millicuries	Mr/Hr @ 1 cm Gamma	Mrep/Hr @ 1 cm Beta
0.5%	Gravimetric	100	240	2.2×10^5	5.9×10^7
2%	Titrimetric	10	24	2.2×10^4	5.9×10^6
5%	Colorimetric	1	2.4	2.2×10^3	5.9×10^5
0.4%	Coulometric	0.1	0.24	2.2×10^2	5.9×10^4
10%	Fluorimetric	0.001	0.0024	2.2	5.9×10^2
1%	Mass Spectrometric	0.001	0.0024	2.2	5.9×10^2

Conventional gravimetric(10), titrimetric(11), and colorimetric(12, 13) methods require elaborate and cumbersome shielded facilities. Controlled potential coulometric analyses(14) appears to be promising even though it is not the most sensitive method available and may require some β-γ activity shielding. Of the highly sensitive methods for uranium, the fluorimetric method(15, 16) is not sufficiently accurate. The mass spectrometric isotope dilution method(17, 18) using U-233 tracer seems to be the most suitable method for highly irradiated samples because of its accuracy and high sensitivity. See Appendix IV for the detailed procedure. The one microgram of uranium required for the mass spectrometric method corresponds to 2 ml of a millionfold dilution of an initial 2M uranium solution. The Cs-137 content of this same size aliquot at 10,000 Mwd/ton is about 72,500 d/m, which is a suitable size for Cs-137 analysis. When cesium-137 and uranium can be determined on the same solution, no knowledge of the actual dilution factor, original volume, or concentration of the dissolver solution is required because only the cesium to uranium ratio is sought. The dilute solution can be easily handled in the laboratory because of its modest dose rate.

c. Cesium-137 Analysis. An aliquot of the sample solution and an aliquot of Cs-137 standard solution are analyzed concurrently according to Appendix V. Cesium carrier is added and chemical purification carried out. The final precipitates are weighed for chemical yield and counted on a multi-channel scintillation spectrometer employing a sodium iodide crystal. The number of counts per minute in the photopeak is obtained by summing the counts/minute in all channels under the 0.66 Mev Ba-137m photopeak in the sample and standard.

Standard Cs-137 was formerly distributed by the National Bureau of Standards. Recently they have discontinued distribution in favor of Nuclear-Chicago Co. in keeping with a government policy of not competing with private industry. The standard used in this analysis can be NBS #4931 Cs-137 solution where still available or Nuclear-Chicago Type RS-137 solution, both of which are certified in γ/m/ml at 0.66 mev, the former to ± 2% and the latter to ± 3%. The certified value should be corrected to the time of counting. The counting efficiency of the counter can be readily established and the γ/m/ml of the sample calculated. The value is converted to fissions/ml by multiplication by the Cs-137 "K" factor. The sample calculation in Table III will help to clarify these manipulations.

TABLE III

Cs-137 SAMPLE CALCULATION

Step	Sample Calculation	Est. Std. Dev. @ 10,000 Mwd/ton
1. Sample c/m in 0.66 Mev peak (Corrected for Cs-134 and background)	4.460×10^3	± 2%
2. ÷ Chemical Yield of the Sample	0.725	± 2%
3. ÷ ml of the sample	2.000	± 0.5%
4. = c/m/ml of the sample	3.076×10^3	
5. Standard c/m in 0.66 Mev peak (corrected for background)	3.394×10^3	± 1%
6. ÷ Chemical Yield of the Standard	0.930	± 2%
7. ÷ ml of the standard	1.000	± 0.5%
8. = c/m/ml of the standard	3.649×10^3	
9. Relative c/m/ml (line 4 ÷ line 8)	0.8429	
10. x γ/m/ml of standard at time of counting	3.746×10^4	± 1%(a)
11. = γ/m/ml of the sample	3.158×10^4	
12. ÷ $e^{-\lambda t}$ for decay since end of irradiation	0.976	± 0.05%
13. = γ/m/ml at end of irradiation	3.235×10^4	
14. $\div \frac{1 - e^{-\lambda t_2}}{\lambda t_2}$ which is the fraction remaining at end of irradiation time, t_2	0.960	± 1.5%
15. = γ/m/ml at 0.66 Mev	3.360×10^4	
16. F_{49}/F_T (see pp. 26 and 31, eq. 6 and 12)	0.25 ± 0.06	
17. Weighted Cs "K" factor in $\frac{\text{fissions}}{\gamma/\text{m at } 0.66 \text{ Mev}}$ (See Note b).	4.46×10^8	± 3.8%
18. = fissions/ml (line 15 x line 17)	1.499×10^{13}	
19. Mass ratio U-238/U-233	10.35	± 0.5%
20. Atoms U-233/ml spike	2.378×10^{14}	± 0.9%
21. x ml of U-233 spike added	1.000	± 0.5%
22. = atoms U-233 added	2.378×10^{14}	
23. Atoms U-238 = (line 19 x line 22)	2.460×10^{15}	
24. ÷ fraction of U-238 in irradiated U	0.973	± 0.05%

(Continued on page 11)

TABLE III (Continued)

Step	Sample Calculation	Est. Std. Dev. @ 10,000 Mwd/ton
25. = atoms total irradiated U	2.528×10^{15}	
26. ÷ ml of the sample	2.000	± 0.5%
27. = atoms irradiated U/ml	1.264×10^{15}	
28. + fissions/ml (step 18)	1.472×10^{13}	
29. + Pu atoms/ml	6.1×10^{12}	
30. = atoms original U/ml	1.285×10^{15}	
31. $= \frac{\text{fission/ml}}{\text{atoms original U/ml}}$ (line 18 ÷ line 30)	0.01166	
32. x 100 = % Burnup	1.166	
33. x $(8.7 \pm 0.3) \times 10^3$ Mwd/ton/% Burnup	8.7×10^3	± 3.5%
34. = Mwd/ton	10,144	± 6.7%

(a) The recommended Cs-137 standard is Nuclear-Chicago's RS-137. The quoted error includes only the 1% error which may be introduced by Nuclear-Chicago when it compares a new Cs-137 batch with NBS #4931. The absolute error in N-C RS-137 Batch #1 Cs-137 standard cancels out when the same value appears in the denominator of the Cs-137 "K" factor (see section on Cs "K" factor).

(b) Pu-239 "K" factor = $(5.14 \pm 0.20) \times 10^8$ fissions/γ/m at 0.66 Mev. (see p. 21).

Non-Pu-239 "K" factor = $(4.23 \pm 0.16) \times 10^8$ fissions/γ/m at 0.66 Mev. (see p. 20).

Weighted "K" factor = $0.91 \times 10^8 (F_{49}/F_T) + 4.23 \times 10^8$ fissions/γ/m at 0.66 Mev.

If $F_{49}/F_T = 0.25 \pm 0.06$, then "K" = $(4.46 \pm 0.17) \times 10^8$ fissions/γ/m at 0.66 Mev.

3. Sources of Error

a. Effect of Cesium-136. Cs-136 is formed in fission of U-235 in about one thousandth the fission yield of Cs-137. Cs-136 has a half-life of 12.9 days which is about one thousand times shorter than Cs-137 hence a specific activity which is about one thousand times as great as Cs-137. For this reason, the activity from Cs-136 about equals the activity from Cs-137 at the time of fission in U-235. For Pu-239 fission, the Cs-136 activity actually exceeds the Cs-137 activity by about fifteen fold at the time of fission. The actual fission yield for Cs-136 in U-235 and Pu-239 fission is 0.006% and 0.09%, respectively. It is customary to allow the Cs-136 to decay prior to the analysis. Ten half-lives or 130 days permits a thousand fold decay which is adequate even for plutonium fission. With U-235 irradiated three years, sufficient in-pile decay occurs to reduce the Cs-136 contribution to 1.7% of the Cs-137. For power reactor fuel with three years of service, the cooling requirements for Cs-136 need not dictate a lengthened fuel cycle or increased fuel inventory. However, if the cooling period were to be shortened from 130 days to as short as 26 days, the analyst would observe a substantial increase in radioactivity of the sample over that listed in Appendix VIII. A 250-fold increase in gamma dose from Ba + La-140 would be one of the sources of greatest concern. Figure 1 shows the gamma spectrum of a purified cesium fraction separated from U-233 shortly after irradiation as measured by Crouthamel(19). Although the Cs-136 fission yield is higher for U-233 than for U-235, the spectrum clearly shows the nature of the interference of the many Cs-136 gamma rays on the Cs-137 gamma ray at 0.661 Mev. where insufficient cooling time has been allowed.

b. Effect of Cesium-134. Cs-134 has a 2.3 year half-life and does not decay appreciably during the cooling period before analysis. It becomes a serious interference whenever a large fraction of the initial fissionable isotope is fissioned. It is formed by (n, γ) reaction on fission product Cs-133. Cs-133 has a 29 barn cross-section for thermal (n, γ) reaction. There is, however, a large resonance near 6 ev. The resonance integral is calculated to be approximately 400 barns. The effective pile cross-section will depend upon the ratio of epithermal to thermal flux in any particular reactor. It can be estimated for various reactors as follows:

Type	Epithermal/thermal ratio	Effective pile σ for Cs-133
High enrichment water moderated	0.2	110 barns
Low enrichment water moderated	0.1	70 barns
Graphite moderated	0.05	50 barns
D_2O moderated	0.03	40 barns

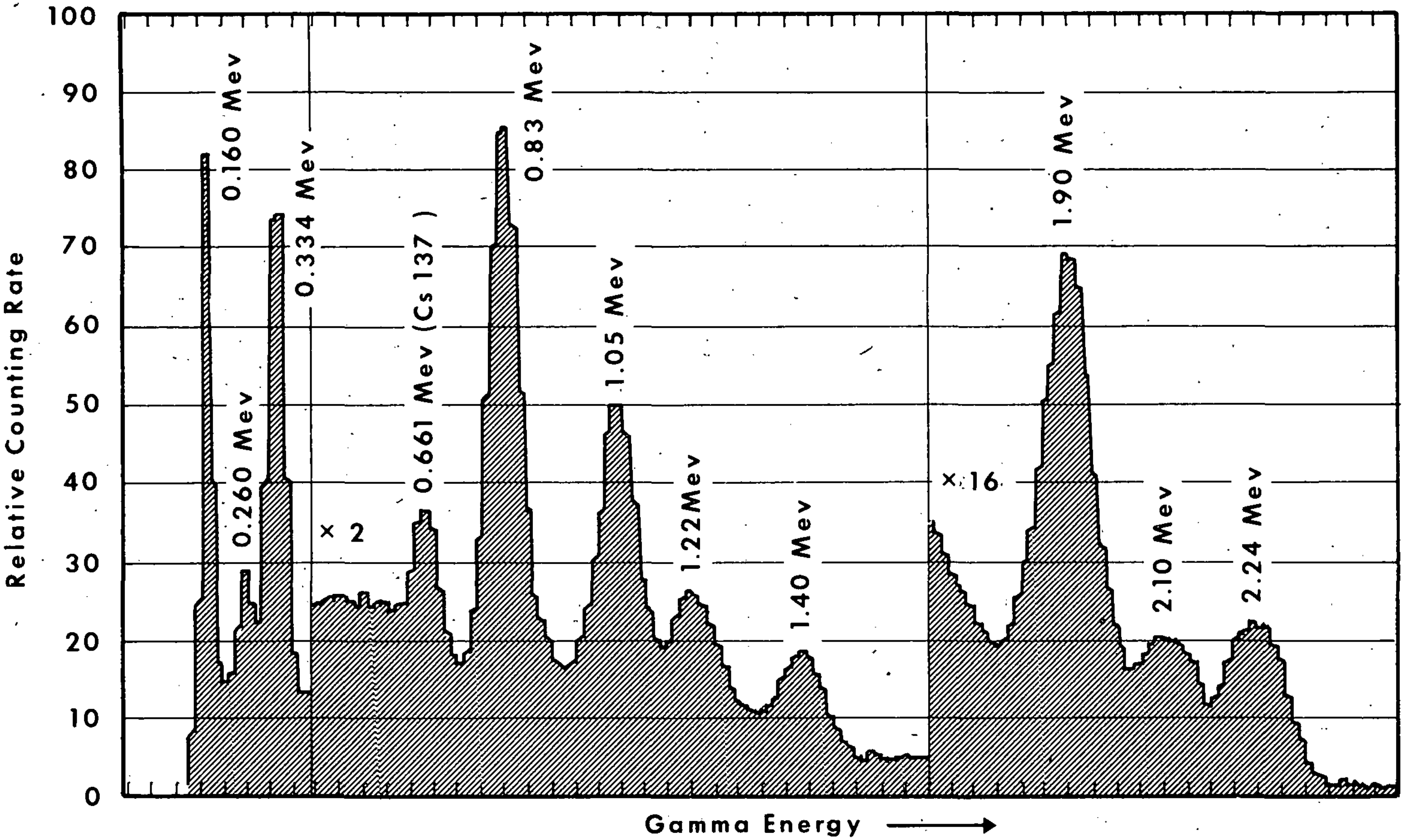

Figure 1. GAMMA SPECTRUM OF CESIUM FRACTION CONTAINING Cs 136 AND Cs 137

An attempt has been made in Appendix VI to estimate the extent of Cs-134 interference under specific reactor conditions. Figure 2 is a plot of the ratio of the activity of Cs-134 to Cs-137, as a function of fissions per initial fissionable atom. Three conditions are plotted where the plutonium conversion ratio, C, is 0.0, 0.2, and 1. In actual practice the plutonium conversion ratio will be about 0.6 or midway between 0.2 and 1.0. For our purposes, the dotted line in Figure 2 is a sufficient approximation. This line passes through Cs-134/Cs-137 activity of 0.5 at 10,000 Mwd/ton.

The Cs-134 interference is corrected for in the memory of the multi-channel analyzer. The mechanics of the correction can be briefly described as follows. Accumulate the combined Cs-137 plus Cs-134 spectrum for a selected live time. Complement (invert) the spectrum in the memory. Select from a library of pure Cs-134 sources one of slightly greater Cs-134 activity level than that of the sample. Substitute it in the same position and set the timer for the same live time as for the original sample. Proceed with accumulation. When the Cs-134 peaks at 0.8 and 1.4 Mev. have just disappeared from the spectrum as viewed on the oscilloscope display, remove the Cs-134 source but allow the background to continue to subtract until the live timer shuts off. Read out on tape the number of counts in each channel. Sum all the counts appearing under the 0.66 Mev. photopeak. This will represent the Cs-137 at 0.66 Mev. corrected for background and Cs-134.

The selection of a Cs-134 source of slightly greater Cs-134 activity allows the subtraction to be completed in less than the sample counting time. Any subtraction longer than the sample counting time would over subtract counter background. On the other hand, if the Cs-134 source is substantially more active than the sample, a shift in base line occurs in the photomultiplier tube and the spectrum shifts several channels. The subtraction then occurs several channels displaced from the original spectrum.

The position of the Cs-134 source must be identical with that of the sample since the ratio of the 0.8 Mev. peak to the 1.4 Mev. summation peak is strongly dependent on geometry.

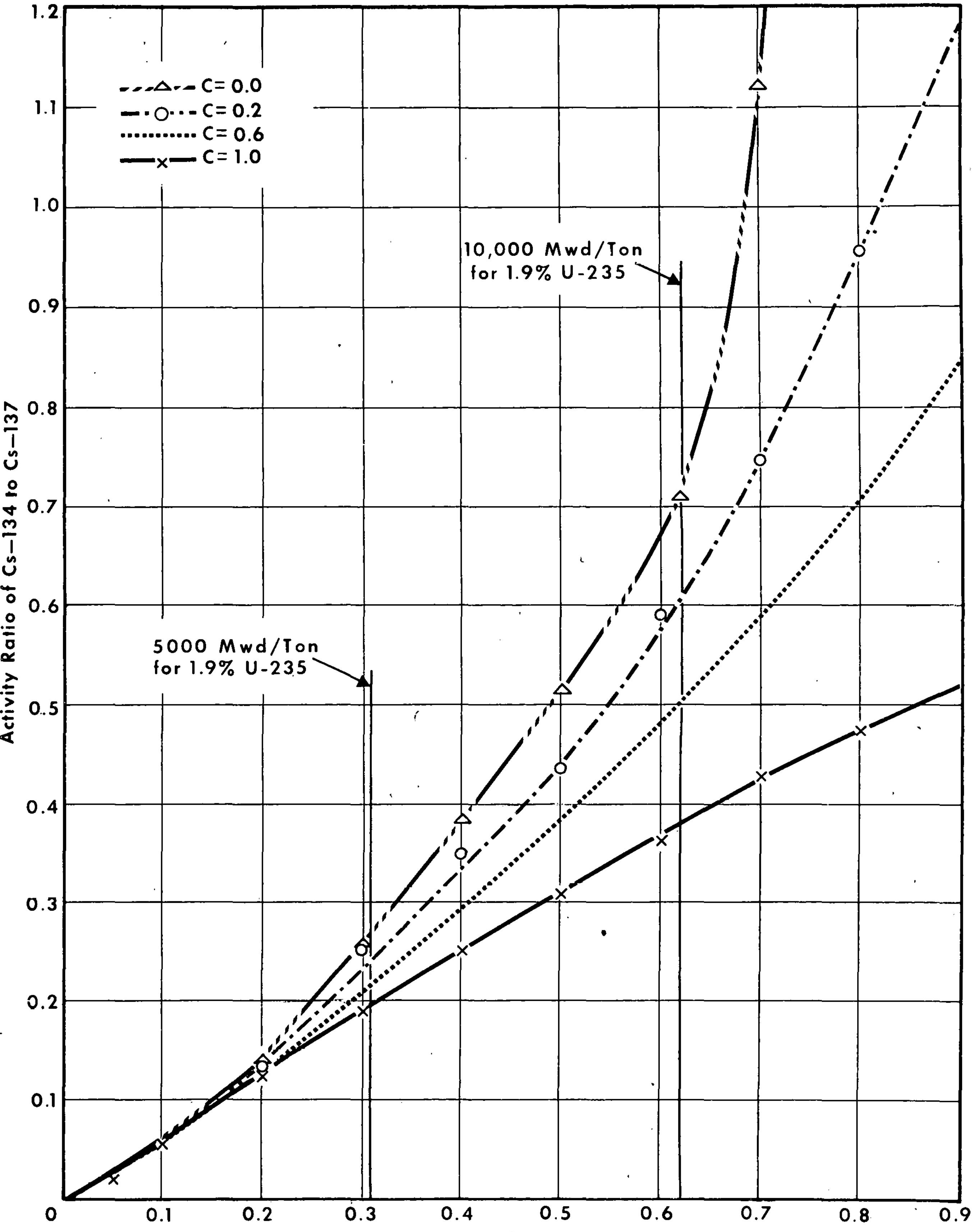

Figure 2. RATIO OF Cs134 TO Cs137 ACTIVITY

Summation of the counts in all channels under the photopeak is preferable to the measurement of peak height since a small displacement of the Cs-134 spectrum during the subtraction results in a Cs-137 peak which is too tall and too narrow but of correct area expressed as the total counts in all channels under the photopeak.

Figure 3 shows two gamma spectra of the same cesium fraction where the activity ratio of Cs-134 to Cs-137 is equal to 0.5. The upper half of the figure shows the spectrum obtained with a 3" diameter solid right cylindrical crystal of sodium iodide. Under this spectrum, the spectrum of pure Cs-134 has been indicated by the shaded region. The difference between the two curves (the unshaded area between the curves) represents the Cs-137 contribution.

The lower half of Figure 3 shows the spectrum obtained with a 5" diameter right cylindrical crystal of sodium iodide with a re-entrant well for the sample. The spectrum of pure Cs-134 has been indicated as before. It can be seen that the Cs-134 interference is minimized by use of the 5" diameter well crystal for counting. In such a crystal the interfering 0.6 Mev. Cs-134 gamma adds to its coincident 0.8 Mev. gamma to form a 1.4 Mev. summation peak. In this case, the interference of Cs-134 was reduced fourfold. The improvement results not only from the well geometry but from the large crystal size which reduces the Compton scattering from the summation peak and increases the efficiency for formation of the summation peak. A 3" diameter well crystal was tried in the interest of economy but was found to be insufficiently large to show any advantage over a 3" diameter solid crystal.

Experimentally it has been shown that for a Cs-134/Cs-137 ratio of approximately 5, the average error in Cs-137 is about 20%. In a more realistic case at 10,000 Mwd/ton where Cs-134/Cs-137 is 0.5, the error due to Cs-134 correction should average 2%.

c. <u>Effect of Cesium Volatility</u>. Cesium-137 is the daughter of Xe-137, a gaseous fission product of appreciable half life, i.e. 3.8 minutes. Thus, in fuels in which the percentage of fission gas released is significant, e.g. over 5%, there exists the danger that much of the Xe-137 has migrated radially out of the fuel and then decayed with the deposition of its Cs-137 daughter on the cooler surfaces.

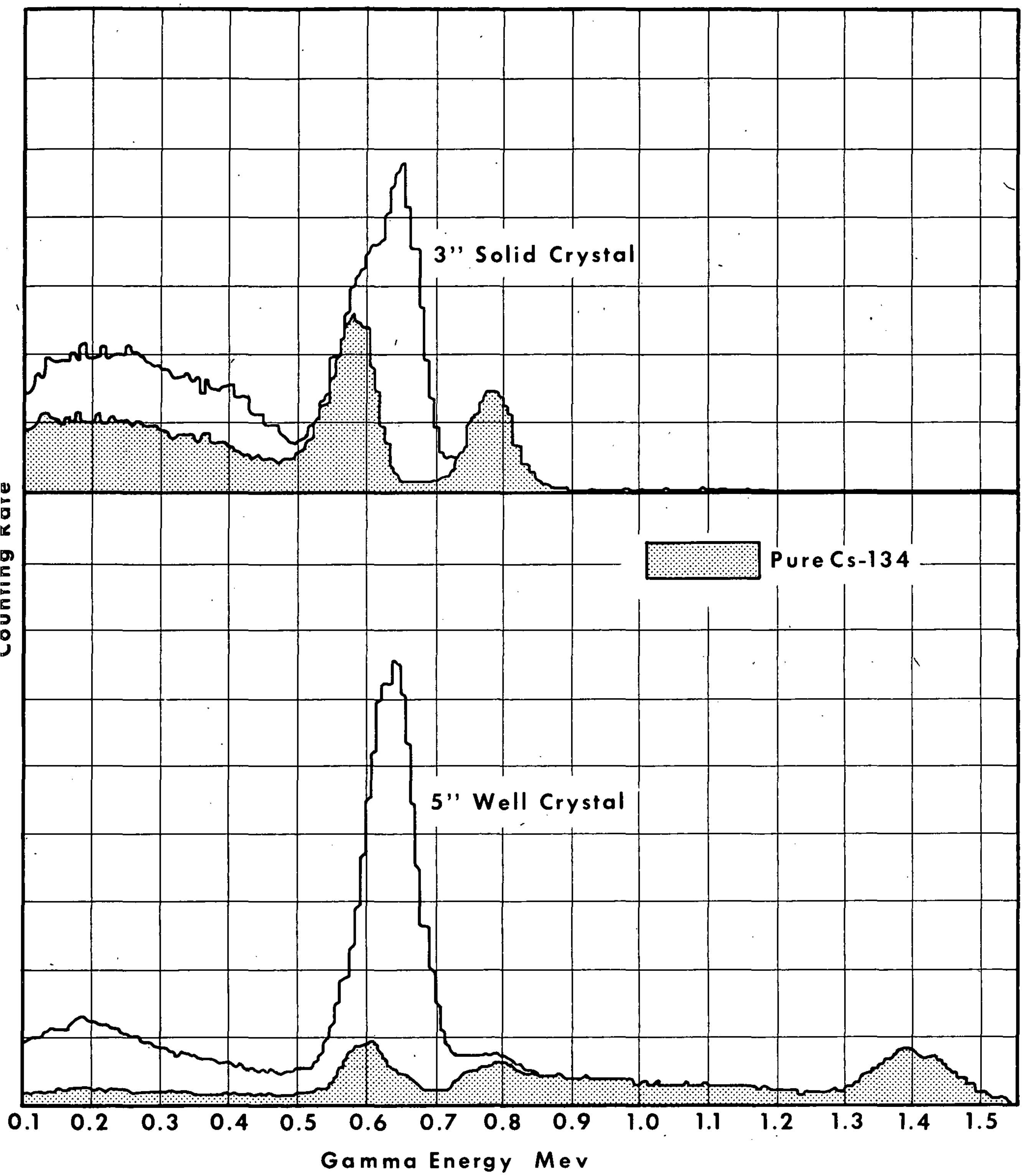

Figure 3. GAMMA SPECTRA OF CESIUM FRACTION
Cs-134/Cs-137 Ratio = 0.5

An example of this is cited by Slosek(20) where a majority of the Kr-85 was released from UO_2 to the voids and virtually all of the Cs-137 was found plated on the cladding wall.

This migration need not occur only while present as gaseous Xe-137. Cesium metal is also quite volatile. It boils at 670°C. Even cesium oxide which could be formed in a UO_2 fuel is not stable at reactor fuel temperatures. It dissociates between 360° to 400°C to volatile cesium plus oxygen. Since the central portion of uranium oxide fuels can achieve temperatures exceeding 2000°C, cesium is a gas throughout the fuel and would condense on the coolest region which is the cladding. The migration of cesium is not a problem in reprocessing sound irradiated fuel when entire fuel assemblies including cladding are dissolved. Such a dissolution gives an average burnup sample for the entire assembly. If the zirconium cladding is removed in NH_4F solution, the Cs-137 associated with the cladding may be lost to the decladding solution. Then a careful material balance of Cs-137 and U in all decladding solutions, washes, residues and head end wastes would be required to establish the actual Cs-137/U ratio.

d. <u>Burnout of Cesium-137</u>. The burnout of Cs-137 in the reactor is not a significant source of error. The cross section for destruction is between 0.09 and 0.23 barns(21), or less than 1% of the cross section for formation from U-235. Since the concentration of Cs-137 will seldom exceed 3% of the U-235 concentration, the rate of destruction will not exceed 0.03% of the rate of formation.

e. <u>Decay Scheme of Cesium-137</u>. The decay scheme for Cs-137 is somewhat uncertain. We have adopted the most recently published scheme which lists 92.4 ± 0.8%(22) as decaying to Ba-137m with the remainder proceeding directly to the ground state by beta decay. Earlier publications list 95.2 ± 0.3%(23), 92%(24), ~97%(25) and 95%(26) for this branching ratio. The Ba-137m decays by gamma emission at 0.66 Mev. This gamma ray is partially converted to K, L, and M electron emission. An average value for the K electron to γ ratio is 0.095 ± 0.002. An average L/γ ratio is 0.018 ± 0.01, and an average MN/γ ratio is 0.005 ± 0.0004. An average combined KLMN electron emission to gamma emission ratio is then 0.118 ± 0.003. Hence the d/m of Ba-137m per γ/m at 0.66 Mev. is 1.118 ± 0.003. Appendix VII is a summary of the values which were averaged.

f. Fission Yields of Cesium-137. Cs-137 fission yields for thermal fission of U-235 have been reported to be 0.0594 by Steinberg and Glendenin(27), 0.0615 by Petruska, et al.(28), and 0.0622 by Brown(29). The first two values have been determined mass spectrometrically, but Brown's value was determined radiometrically relative to a yield of 0.0632 for Ba-140. Katcoff(30) has recommended a value of 0.0644 for the fission yield of Ba-140. If Brown's result is normalized to this value, the resulting fission yield for Cs-137 is 0.0633. An average value is 0.0614 ± 0.0016.

Cs-137 fission yield for thermal fission of Pu-239 is reported to be 0.0524(30), 0.051(31), 0.0494(32), and 0.049(33) for an average of 0.051 ± 0.001, although some authors(34, 35) are not in agreement with this value.

g. Decay Constant of Cesium-137. A substantial uncertainty exists in the value of the decay constant for Cs-137. Table IV shows the recently reported half lives and their corresponding decay constants. All values prior to 1955 have been deleted due to their large uncertainties. The Table IV values still cover a spread of ± 13%. In fact the decay constant is so poorly known that it is frequently avoided in calculations.

TABLE IV

RECENTLY REPORTED VALUES FOR Cs-137 HALF LIFE AND DECAY CONSTANT

$t_{1/2}$, years	λ, days^{-1}
30.0 ± 0.4(36)	6.33×10^{-5}
26.6 ± 0.4(37)	7.14×10^{-5}
$28.6 \begin{smallmatrix} +2 \\ -1 \end{smallmatrix}$ (38)	6.64×10^{-5}
26 ± 1 (39)	7.30×10^{-5}

As a substitute, experiments have been performed at Argonne National Laboratory in cooperation with others to measure a "K" factor which would relate d/m of Cs-137 to the number of fissions occurring in a fission chamber. The product of this experiment was a Cs-137 "K" factor solution equivalent to (3.65 ± 0.08) x 10^{14} thermal U-235 fissions/ml on 1-1-57. This solution was recently compared to Nuclear-Chicago RS-137 Batch No. 1 which was certified to contain (3.80 ± 0.11) x 10^{7} γ/m/ml on 2-27-59, equivalent to (4.01 ± 0.12) x 10^{7} γ/m/ml on 1-1-57. The average of 30 comparisons of the two standards showed that the "K" factor solution was 0.0215 ± 0.0003 times as concentrated as the Nuclear-Chicago standard by Cs-137 gamma counting or (8.62 ± 0.28) x 10^{5} γ/m/ml on 1-1-57. The d/m/ml Cs-137 in the "K" factor solution can be calculated as follows:

$$(8.62 \pm 0.28) \times 10^{5}\ \underset{1\text{-}1\text{-}57}{\gamma/\text{m/ml}} \times \frac{1.118 \pm 0.003\ \text{d Ba-137m}/\gamma}{0.924 \pm 0.008\ \text{Ba-137m/Cs-137}} =$$

$$(1.04 \pm 0.04) \times 10^{6}\ \underset{1\text{-}1\text{-}57}{\text{d/m/ml}}$$

The decay constant of Cs-137 can be calculated from these observations as follows:

$$\lambda = \frac{(1.04 \pm 0.04) \times 10^{6}\ \text{d/m/ml}}{(3.65 \pm 0.08) \times 10^{14}\ \text{f/ml}} \times \frac{1440\ \text{min}}{\text{day}} \times \frac{1\ \text{fission}}{0.0614 \pm 0.0016\ \text{atoms Cs-137}} =$$

$$= (6.68 \pm 0.32) \times 10^{-5}\ \text{day}^{-1}$$

This is equivalent to 28.4 ± 1.4 year half-life which corresponds most closely to the 28.6 $^{+2}_{-1}$ year value given by Moses and Cook(40). The latter value is, therefore, taken at the best value presently available. Hence, λ for Cs-137 is taken as 6.64 x 10^{-5} days^{-1}.

h. Cs-137 "K" Factors for U-235 and Pu-239 Thermal Fission. For convenience a "K" factor relating fissions to γ/m can be calculated. The Cs-137 "K" factor for thermal fission of U-235 as obtained from the Argonne National Laboratory "K" factor solution is obtained as follows:

$$\frac{(3.65 \pm 0.08) \times 10^{14}\ \text{fiss./ml 1-1-57}}{(8.62 \pm 0.28) \times 10^{5}\ \gamma/\text{m/ml 1-1-57}} =$$

$$(4.23 \pm 0.16) \times 10^{8}\ \frac{\text{U-235 Thermal fiss.}}{\gamma/\text{m at 0.66 Mev.}}$$

For lack of better data U-238 and Pu-241 fissions are assumed to have the same Cs "K" factor as U-235 fissions.

The corresponding Cs-137 "K" factor for thermal fission of Pu-239 is obtained as follows:

$$\frac{1.118 \pm 0.003 \text{ d/m Ba-137m}}{1\ \gamma\text{/m at 0.66 Mev.}} \times \frac{1 \text{ d/m Cs-137}}{0.924 \pm 0.008 \text{ d/m Ba-137m}}$$

$$\times \frac{1 \text{ fission}}{0.051 \pm 0.001 \text{ atom Cs-137}} \times \frac{1}{(6.64 \pm 0.19) \times 10^{-5} \text{ day}^{-1}}$$

$$\times \frac{1440 \text{ minutes}}{1 \text{ day}} = (5.14 \pm 0.20) \times 10^{8} \frac{\text{Pu-239 thermal fiss.}}{\gamma\text{/m at 0.66 Mev.}}$$

For fuel samples which have fissions resulting from more than one isotope, a weighted "K" factor is calculated as shown in the footnote to Table III.

i. In-Pile and Out-of-Pile Decay. Small corrections need to be applied for decay of Cs-137 following irradiation as well as during the irradiation. The amount of Cs-137 which decays following the irradiation is corrected for by dividing by $e^{-\lambda t_1}$ where t_1 is the time in days between the end of irradiation and the time of counting, and λ is the decay constant for Cs-137 in days^{-1}. This correction is about 1% for 130 days of cooling time. The fraction of the Cs-137 remaining at the end of the irradiation is given by the expression:

$$\frac{1 - e^{-\lambda t_2}}{\lambda t_2}$$

where t_2 is the time in days the fuel was irradiated and λ is the decay constant of Cs-137 in days^{-1}. The activity of Cs-137 observed must be divided by this value to correct for the decay during irradiation. The simplifying assumption is made that the fuel was irradiated at a constant flux for the entire period of irradiation. Initial periods of very low power operation should not be included in the irradiation time. The total "in-pile" decay correction is about 1½% per year of irradiation. The normal irradiation time of an oxide fuel element will be 2 to 5 years.

If large batches contain elements of different irradiation histories or if a disproportionate amount of the heat production took place early or late in the irradiation, it is difficult to choose an equivalent irradiation time closer than 1 year for a 3 year irradiation. Such an error would contribute ± 1½% error to the final Mwd/ton result.

j. Cumulative Error. The errors involved in the calculation of Mwd/ton by Cs-137 to uranium ratio method are summarized in Table III. The errors are of two types: experimental errors and errors in the physical constants. The total combined error in Mwd/ton is estimated to be 6.4% at 5,000 Mwd/ton, 6.7% at 10,000 Mwd/ton and 7.6% at 15,000 Mwd/ton. Most of the total combined error results from errors in the physical constants.

B. MASS SPECTROMETRIC METHOD

One method of estimating total heat released from fissionable material is to measure the quantity of fissionable material present before and after irradiation. The difference so obtained is related to the number of fissions which occurred, and hence to the amount of heat produced. A combination of chemical and mass spectrometric measurements can provide the isotopic composition of the fuel before and after irradiation.

The results of a mass spectrometric analysis consists of the relative abundances of the various isotopes in a sample. These are usually expressed as the ratios of the amount of each isotope to that of a particular isotope of the sample. The problems associated with measurement of these mass ratios are discussed in Appendices III and IV. This section is devoted to a description of the mathematical manipulation required to relate the mass ratios to heat generated by the fuel. This includes tabulation of the equations required to relate the mass ratios to burnup based on the neutron capture processes in uranium fuel; a sample calculation to illustrate use of the equations; and a discussion of the error in the burnup due to uncertainties in the mass ratio data as well as the uncertainties in the reactor properties which relate mass ratios to burnup.

1. Neutron Capture Processes in Uranium Fuel. The neutron capture processes in uranium fuel are illustrated in Figure 4. This figure is not a complete listing of isotopes formed by the chain. It includes only those isotopes which are usually included in reactor calculations. The important thermally fissionable isotopes are U-235, Pu-239, and Pu-241. Present day thermal reactors, fueled with uranium slightly enriched in U-235, do not generate more than about 1 to 3 percent of their energy by Pu-241 fission because of the small amount of that isotope produced by the end of fuel life. However, fast fission of U-238 accounts for possibly 5 to 10 percent of the fission in these reactors. An isotopic

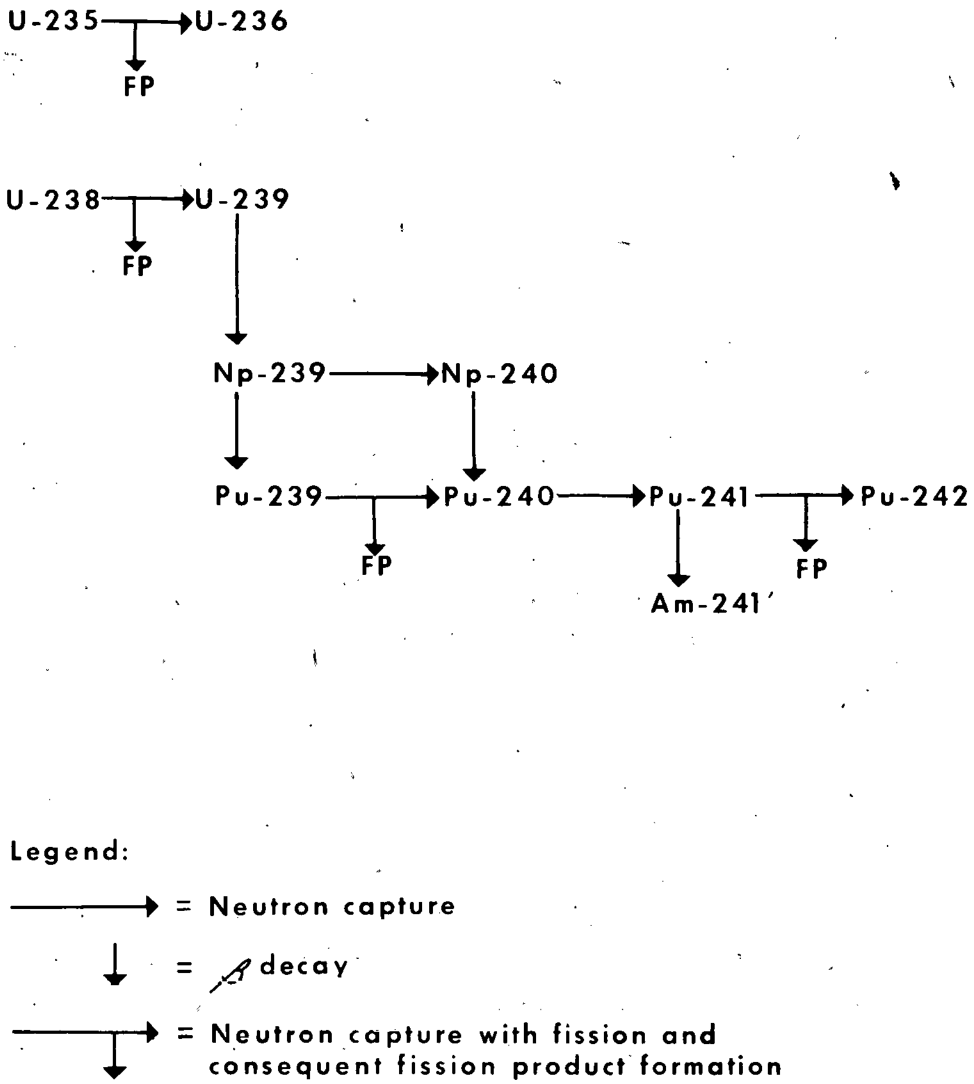

Figure 4. NEUTRON CAPTURE PROCESSES IN URANIUM FUEL

analysis of the fuel before and after irradiation provides: a direct determination of U-235 fission, no information about U-238 fission, and the final concentrations of the plutonium isotopes from which a rough estimate of plutonium fission can be obtained. These three topics are discussed in order.

a. U-235 Fissions. For the reactors under consideration, U-235 fissions are the predominate source of energy. The number of U-235 fissions which have occurred, F_{25} (see Appendix I for notation used), is equal to the total loss of U-235 less the U-236 gain (see Figure 4).

$$\begin{aligned} F_{25} &= (N^o_{25} - N_{25}) - (N_{26} - N^o_{26}) \\ &= (N^o_{25} + N^o_{26}) - (N_{25} + N_{26}) \end{aligned} \tag{1}$$

N^o_{25} and N^o_{26} are the numbers of U-235 and U-236 atoms, respectively, in the sample before irradiation, and N_{25} and N_{26} are the numbers after irradiation.

Because the U-235 capture-to-fission ratio, α_{25}, is well known and for thermal and near thermal reactors only slightly dependent on spectrum, it might be more accurate in a particular case to calculate the U-236 gain from the U-235 loss. This leads to:

$$F_{25} = \frac{N^o_{25} - N_{25}}{1 + \alpha_{25}} \tag{2}$$

For a small burnup it may be more appropriate to use as experimental data the ratio of U-236 to U-235 before (R_o) and after (R) irradiation, because for this case equations (1) and (2) involve the small difference of two relatively large numbers, N^o_{25} and N_{25}. This leads to:

$$F_{25} = N^o_{25} \frac{R \quad R_o}{R + \alpha_{25} (1 + R)} \tag{3}$$

The most reliable form of F_{25} to use in any particular measurement depends upon the properties of the sample under consideration as well as the accuracy of the data available. However, for low enrichment fuels with appreciable burnup, equation (1) is most satisfactory because it avoids entirely the physical properties of the reactor, while maintaining good accuracy.

b. U-238 Fissions. The number of U-238 fissions (related to the fast fission factor) which have occurred in a sample cannot be obtained from measurement of the loss of U-238 atoms because the fractional depletion of U-238 in slightly enriched reactors is very small and only part of this depletion is due to U-238 fission. This means that U-238 fission must be included as a calculated correction term for the mass spectrometric method. Because this correction to the total number of fissions is about 5 or 10 percent and fairly well understood, the uncertainty introduced in the final results by this correction is not as large as some other uncertainties of the method.

In this section fast fission is accounted for by a quantity, g. The value of g is not always found in a reactor design document. However, the fast fission factor, ϵ, can always be found in design documents, and g is simply related to ϵ by:

$$g = (\epsilon - 1) \frac{\nu_{25}}{(\nu_{28} - 1 - \alpha_{28})} \cong 1.6\ (\epsilon - 1) \tag{4a}$$

The number of U-238 fissions, F_{28}, is equal to the sum of non-U-238 fissions (corrected for the difference in number of neutrons produced by uranium and plutonium fission) multiplied by g. Hence:

$$F_{28} = g\ (F_{25} + \frac{\nu_{49}}{\nu_{25}} F_{49} + \frac{\nu_{41}}{\nu_{25}} F_{41}) \tag{4b}$$

c. Pu-239 and Pu-241 Fissions. An isotopic analysis does not provide, in practice, sufficient information to determine the plutonium burnup. Only in an idealized point reactor of constant known spectrum is it possible rigorously to relate plutonium burnup to isotopic data, and then only if several of the physical properties of the reactor are known. However, if several approximations are made (see Appendix II) the Pu-239 and Pu-241 burnup can be expressed in at least three different ways. First, the concept of conversion ratio leads to the following expression for F_{49}:

$$F_{49} = \frac{C\,(N_{25}^{o} - N_{25}) - N_{49}}{(1 + \alpha_{49})\,(1 - C)} \tag{5}$$

C is the average number of fuel atoms produced per fuel atom destroyed. This concept does not include, in a natural way, the Pu-241 fission.

Secondly, use can be made of the capture-to-fission ratio, α, of the fissionable isotopes to obtain the information about fission. This leads to:

$$F_{49} = \frac{1}{\alpha_{49}}\left[N_{40} + N_{41}\, e^{\lambda_{41} t} + N_{42}\, \frac{1 + \alpha_{41}}{\alpha_{41}}\right] \tag{6}$$

$$F_{41} = \frac{1}{\alpha_{41}}\, N_{42} \tag{7}$$

In this case, $e^{\lambda_{41} t}$ is a correction for the radioactive decay of Pu-241 to Am-241. This formulation neglects the possibility of Np-239 neutron capture (Figure 1). This is usually justified because a flux as high as 10^{14} nv is required to transmute 0.2% of the Np-239 before it β-decays to Pu-239.

Finally, the fission fractions can also be expressed in terms of the ratio of the plutonium fission cross sections to the U-235 absorption cross section.

$$F_{49} \cong \frac{\sigma_{49}}{(1 + \alpha_{49})\,\sigma_{25}}\, N_{49} \left(\frac{N_{25}^{o} - N_{25}}{N_{25} \ln \frac{N_{25}}{N_{25}}} \right) \tag{8}$$

$$F_{41} \cong \frac{\sigma_{41}}{(1 + \alpha_{41})\,\sigma_{25}}\, \frac{N_{41}}{4} \ln \frac{N_{25}^{o}}{N_{25}} \tag{9}$$

Which of the three methods is applicable to a given sample depends upon what information is available about the reactor in which the sample was irradiated, as well as the accuracy of the isotopic analysis. Equations (6) and (7) require the least amount of information about the reactor. Equations (5), (8) and (9) require a detailed description of the reactor as well as the irradiation history and for this reason may be impractical as bases for measurement techniques. Also, equations (8) and (9) break down for mathematical reasons at very high burnup (greater than 10,000 or 15,000 Mwd/ton) and/or conversion ratios outside the range 0.3 to 0.8.

2. Sample Calculation. In order to illustrate the use of the method and to provide a typical case for estimate of errors, the method is applied to a hypothetical fuel sample. An IBM-650 program was used to calculate the isotopic composition of a fuel element in a water moderated reactor after various exposure times. The program includes self-shielding and spectrum shift effects, but does not treat spatial variation. These calculated isotopic compositions were taken as data and the number of fissions at each exposure calculated from these isotopic compositions.

The experimental data available from a mass spectrometric analysis of the fuel consist of the atom ratios of U-235, U-236, Pu-239, Pu-240, and Pu-241 to U-238 after irradiation; and U-235 and U-236 to U-238 before irradiation. The data from the IBM calculation is tabulated in Table V for 5,000 Mwd/ton, 10,000 Mwd/ton and 15,000 Mwd/ton.

TABLE V

CALCULATED MASS RATIO DATA WITH ERRORS ESTIMATED AS THOSE ATTAINABLE BY AVAILABLE EXPERIMENTAL TECHNIQUES

Ratio to U-238	0 Mwd/ton	5,000 Mwd/ton	10,000 Mwd/ton	15,000 Mwd/ton
25/28	0.01937 ± 0.00020	0.01393 ± 0.00014	0.00994 ± 0.00010	0.00693 ± 0.00007
26/28	0.00000 ± 0.00000	0.00086 ± 0.00007	0.00148 ± 0.00007	0.00193 ± 0.00007
49/28	0.00000 ± 0.00000	0.00239 ± 0.00012	0.00350 ± 0.00018	0.00397 ± 0.00020
40/28	0.00000 ± 0.00000	0.00038 ± 0.00002	0.00096 ± 0.00005	0.00149 ± 0.00007
41/28	0.00000 ± 0.00000	0.00011 ± 0.00001	0.00039 ± 0.00003	0.00067 ± 0.00006
42/28	0.00000 ± 0.00000	0.000014 ± 0.00007	0.00010 ± 0.00001	0.00030 ± 0.00003

Other data necessary for application of the method are defined in Table VI.

TABLE VI

DATA REQUIRED FOR APPLICATION OF METHOD

Reactor-dependent Properties	Constants
$g = \frac{\text{U-238 fission rate}}{\text{non-U-238 fission rate}}$	k = Mwd from complete fission of 1 ton uranium = $(8.7 \pm 0.3) \times 10^5$ Mwd/ton
α_{49} = effective ratio of Pu-239 capture to fission	$\frac{\nu_{49}}{\nu_{25}}$ = ratio of number neutrons per fission of Pu-239 to U-235 = 1.17 ± 0.02
α_{41} = effective ratio of Pu-241 capture to fission	$\frac{\nu_{41}}{\nu_{25}}$ = ratio of number of neutrons per fission of Pu-241 to U-235 = 1.24 ± 0.02
	λ_{41} = rate of Pu-241 decay to Am-241 = 0.0525 year^{-1}

The constants listed in Table VI are obtained from standard references; k is based on an estimated energy release of 205 ± 7 Mev per fission (see page 6 of this report); the two ratios of neutron production per fission and λ_{41} are taken from BNL-325(41). For simplicity in this sample calculation, both in preparation of the data and in analysis, λ_{41} is assumed to be zero.

This report is not sufficiently voluminous to include a complete description and evaluation of methods for estimating the quantity g listed in Table VI. For a real problem, g would be obtained from the pertinent reactor design document. The reactor dependent properties used in this example are:

$$g = 0.06 \pm 0.02$$
$$\alpha_{49} = 0.57 \pm 0.13$$
$$\alpha_{41} = 0.40 \pm 0.15$$

The values of α_{49} and α_{41} are averages of possible extremes and the errors are sufficient to overlap the extremes. These values reflect no information about the reactor except that it is a thermal power reactor. The first step of the calculation is to convert the isotopic ratios to atom fractions of initial fuel loading. To do this, there must be some estimate of the fraction of fuel lost by fission during irradiation. This is a very small correction for low enrichment fuels so that a crude guess at the average exposure is adequate. The fractional loss is the estimated burnup in Mwd/ton times 1.15×10^{-6}. The ratios before irradiation are divided by

$$1 + R_{25-28} + R_{26-28} \tag{10}$$

to obtain atom fractions. The ratios after irradiation are divided by

$$1 + R_{25-28} + R_{26-28} + R_{Pu-28} + \left[1.15 \times 10^{-6} \times \text{Mwd/ton (est.)}\right] \tag{11}$$

to obtain atom fractions where R_{xx-yy} refers to the ratio of isotope xx to isotope yy.

The resulting atom fractions can then be inserted into equations (1), (6), and (7) to obtain the non-fast fission fraction. These together with fast fission fraction from equation (4b) then give the total fraction of fuel which has fissioned. This multiplied by k of Table VI gives the Mwd/ton of the fuel.

The following are the numerical substitutions for each of these steps for the 10,000 Mwd/ton case of Table V.

The atom fractions are obtained by dividing the ratios by equations (10), initial, or (11), irradiated:

$$1 + 0.01937 + 0 = 1.01937$$

$$1 + 0.00994 + 0.00148 + 0.00350 + 0.00096 + 0.00039 + 0.00010 + 010115 = 1.02787$$

Now substituting in equation (1) to obtain F_{25}, the U-235 contribution gives:

$$F_{25} = 0.01900 + 0 - 0.00967 - 0.00144 = 0.00789 \pm 0.00070$$

Substituting in equation (6) to obtain Pu-239 contribution gives:

$$F_{49} = \frac{1}{0.57}\left[0.00093 + 0.00038 + 0.00010\left(\frac{1 + 0.4}{0.4}\right)\right] = 0.00291 \pm 0.00070$$

Substituting in equation (7) to obtain Pu-241 contribution gives:

$$F_{41} = \frac{1}{0.4}(0.00010) = 0.00025 \pm 0.00010$$

Substituting in equation (4) to obtain U-238 contribution gives:

$$F_{28} = 0.06\left[0.00789 + 1.17\ (0.00291) + 1.24\ (0.00025)\right] = 0.00070 \pm 0.00023$$

Therefore, the total fraction, F_T, of the initial fuel sample which has fissioned is:

$$F_T = F_{25} + F_{49} + F_{28} = F_{41} = 0.01175 \pm 0.00079 \qquad (12)$$

This is converted to Mwd/ton by multiplying by the constant, k, from Table VI:

$$\begin{aligned} \text{Mwd/ton} &= (0.01175 \pm 0.00079) \times (8.7 \pm 0.3) \times 10^5 \\ &= 10{,}200 \pm 770\ \text{Mwd/ton} \end{aligned} \qquad (13)$$

Table VII lists the fission fractions for 5,000, 10,000, and 15,000 Mwd/ton and their associated errors.

TABLE VII

Mwd/ton FOR IRRADIATED FUEL DESCRIBED BY DATA OF TABLE V

Item	5,000 Mwd/ton	10,000 Mwd/ton	15,000 Mwd/ton
F_{25}	0.00455 ± 0.00026	0.00789 ± 0.00024	0.01042 ± 0.00022
F_{49}	0.00093 ± 0.00023	0.00291 ± 0.00070	0.00544 ± 0.00125
F_{28}	0.00034 ± 0.00012	0.00070 ± 0.00023	0.00106 ± 0.00035
F_{41}	0.00003 ± 0.00002	0.00025 ± 0.00010	0.00075 ± 0.00029
F_T	0.00585 ± 0.00037	0.01175 ± 0.00079	0.01767 ± 0.00132
kF_T = Mwd/ton	5,100 ± 370	10,200 ± 770	15,400 ± 1,280
% Uncertainty	7.2%	7.5%	8.3%

3. Sources and Sizes of Error. The sources of error in the mass spectrometric method are discussed in terms of the equation:

$$\text{Mwd/ton} = k\ (F_{25} + F_{49} + F_{28} + F_{41}) \qquad (14)$$

The errors associated with each term in the equation are discussed separately. The individual sources of error are listed in Table VIII.

TABLE VIII

DISTRIBUTION OF ERRORS SHOWN IN TABLE VII

Term	Error in Mwd/ton		
	5,000 Mwd/ton	10,000 Mwd/ton	15,000 Mwd/ton
F_{25}	± 4.4%	± 2.0%	± 1.2%
F_{49}	± 4.0%	± 6.0%	± 7.0%
F_{28}	± 2.0%	± 2.0%	± 2.0%
F_{41}	± 0.3%	± 0.9%	± 1.6%
k	± 3.5%	± 3.5%	± 3.5%
kF_T or Mwd/ton	± 7.2%	± 7.5%	± 8.3%

It will be shown in this discussion that, although all of the terms contribute to the error in determination of heat produced by the fuel, it is the Pu-239 fission term, F_{49}, which is the most serious offender and the greatest single obstacle to the use of the mass spectrometric method for determination of fuel burnup.

a. Errors in k. The constant, k, relates the number of fissions which have occurred to the total heat produced by these fissions. It is, therefore, the amount of heat produced per fission. This number is slightly different for each of the fissionable isotopes. It is known to only ± 3.5 percent and the variation with type of fissionable material is about the same amount. For this method we have assumed that each fission produces the same amount of heat.

The uncertainty in k is limiting regardless of how accurately the number of fissions is determined by chemical or physical analysis. The accuracy of the heat determination can be no better than the accuracy with which k is shown. A more detailed discussion of the uncertainties in k appears on page 6.

b. Errors in F_{25}. The determination of the U-235 fission fraction, F_{25}, depends upon the accuracy with which the ratios of U-235 and U-236 to U-238 can be determined before and after irradiation. One real difficulty in this determination is that this ratio must be known for the fuel before, as well as after, irradiation. Some reactor systems utilize mixed fuels. If these are all processed in the same batch, appropriately averaged values for the experimental ratios before irradiation must be derived. Also, although all uranium fuel utilized in the United States will have been analyzed by Oak Ridge as to U-235 content before the manufacturing process, this may be modified by mixing batches during the manufacturing process, either intentionally or at times accidentally. The U-236 is not normally specified, hence the availability of a reliable ratio of isotopic composition of the fuel before irradiation cannot be pre-supposed.

If the mass spectrometric method is to be used to analyze the fuel, care should be taken to record the history of the fuel during manufacture and irradiation so that these numbers will be available several years later at the time of fuel analysis. Because of the batch nature of fuel production, it would not be adequate to save a single fuel sample for analysis at the same time the irradiated fuel is analyzed. However, consideration might be given to preserving a statistical sampling of reactor fuel for later analysis.

The accuracy obtainable for mass ratios depends upon several variables, such as sample purity, size of the ratios, and the accuracy with which tracers can be prepared. Appendix III is a discussion of the sources of error in determination of the mass ratios. The errors listed in Table V are only indicative of the reliability of available experimental techniques and are not applicable to any particular determination. Any experimental determination must include an estimate of its error if the data are to be useful.

c. Errors in F_{49}. The Pu-239 fission fraction, F_{49}, amounts to a significant portion of the fission energy produced. For the reactors considered, this isotope is not present at the beginning of the fuel cycle, and only that fraction is left which has not been used to produce heat at the end of the run. What must be done is to deduce how much plutonium fissioned during the run from this remaining fraction. The relationship between the fission fraction and the remaining plutonium fractions depends upon the spectrum in which the irradiation was made.

Now α_{49} in equation (6) is a time and position average which depends strongly upon the reactor properties. It can differ by a factor of 1.5 for two different thermal reactors. Unfortunately, the isotopic data does not provide information about this coefficient. Its variation is due to the low energy resonance in Pu-239 cross section. The maximum value α_{49} can have in a thermal reactor is about 0.70, and the minimum value is about 0.44. Unless other information is available, it can only be assumed that α_{49} is the average of these numbers and has an uncertainty which overlaps the extremes. This is

$$\alpha_{49} = 0.57 \pm 0.13$$

d. Errors in F_{28}. The U-238 fission fraction is small compared with the total fission fraction. The fact that it can only be estimated and not measured is not a serious restriction on the method. The reactor parameter, ϵ , can always be obtained from the pertinent reactor design document. This provides g to within ± 30 percent. A large reduction in this uncertainty would result in only a negligible improvement in the heat determination.

e. Errors in F_{41}. The Pu-241 fission fraction, F_{41}, is such a small term that its error is unimportant. The model used to derive F_{49} in equation (6) probably contains an inherent error of the order of 5 percent because it neglects the burnup of Pu-242. The α_{41} is not a well known physical constant and its behavior with energy is not known. Available cross section data indicates a variation of α_{41} with energy that is opposite to that of α_{49}. For this report, α_{41} at 0.025 ev is taken as the best known number, and the maximum variation from this, as indicated by the BNL-325 cross section data, is taken as the uncertainty. This leads to

$$\alpha_{41} = 0.40 \pm 0.15$$

However, F_{41} only amounts to about 1 percent of the total fission fraction, so that this 38 percent uncertainty in F_{41} introduces only a 0.4 percent uncertainty in the heat produced.

f. Errors in Sampling. If an isotopic analysis procedure is adopted for burnup measurements, methods must be developed for obtaining representative samples of the fuel before and after irradiation. The after-irradiation samples can be obtained by dissolving the entire batch of fuel in a single vessel--the averaging process being accomplished by stirring. The before-irradiation sample must be obtained mathematically by a prodigious bookkeeping system which is capable of tracing every fuel element in a given batch from the dissolving vessel, through the reactor, the manufacturer, to Oak Ridge National Laboratory where the original mass spectrometric measurements were made. The bookkeeping system can never be a simple one. The problem is compounded because most power reactors utilize fuels of more than one enrichment. Careful planning must be given to sampling in order to preserve the validity of the measurements.

g. Cumulative Errors. The errors involved in calculation of Mwd/ton by the mass spectrometric method were summarized in Table III. The total combined error in Mwd/ton is estimated to be 7.2% at 5,000 Mwd/ton, 7.5% at 10,000 Mwd/ton, and 8.3% at 15,000 Mwd/ton. From the form of the equations used in this method, it is clear that the uncertainty will rise rapidly both above 15,000 Mwd/ton and below 5,000 Mwd/ton.

APPENDIX I

NOTATION USED IN THE TEXT

Conventional notation is used where applicable. A subscript of "ab" refers to a uranium or transuranic isotope of atomic number "xa" and atomic mass "xxb". Also N_{xx} and F_{xx} refer to numbers per number of pre-irradiation fuel atoms (both fissionable and fertile) so that, strictly speaking, they should be referred to as fractions. The following table of definitions does not define isotope-dependent parameters, e.g., cross section, but rather defines the symbol for arbitrary subscript xx.

$A = \frac{q\epsilon}{(1 + \alpha_{25})(G - 1)}$; lumped constants.

C = conversion ratio; number of Pu-239 atoms produced per fuel atom destroyed.

$D = \sigma_{25}E$

$E = \int_0^t \phi dt$; exposure.

F_{xx} = fission fraction for isotope xx.

F_T = total fission fraction; sum of all F_{xx}.

$G = \bar{\sigma}_{49}\left(1 - \frac{q\epsilon\nu_{49}}{\nu_{25}(1 + \alpha_{49})}\right)$; lumped constants.

g = initial (clean) reactor ratio of U-238 fission rate to U-235 fission rate.

k = constant for converting total fission fraction to Mwd/ton.

"K" = factor to convert γ/m at 0.661 Mev to fissions.

M = number of Pu-239 atoms produced, per original fuel atom, during irradiation.

N_{xx} = number of atoms of isotope xx per original fuel atom, extant at end of irradiation.

N_{xx}^{o} = number of atoms of isotope xx, per original fuel atom, extant at beginning of irradiation.

q = constant of proportionality between number of fission neutrons produced and number of resulting Pu-239 atoms.

R = ratio of number of U-236 atoms to U-235 atoms after irradiation.

R_o = ratio of number of U-236 atoms to U-235 atoms before irradiation.

R_{xx-yy} = ratio of number of isotope xx to isotope yy after irradiation.

R_{xx-yy}^{o} = ratio of number of isotope xx to isotope yy before irradiation.

α_{xx} = capture-to-fission ratio of isotope xx.

ϵ = reactor fast fission factor.

λ_{xx} = radioactive decay constant of isotope xx.

ν_{xx} = number of neutrons per fission of isotope xx.

Φ = neutron flux; nv.

σ_{xx} = absorption cross section of isotope xx.

$\bar{\sigma}_{xx}$ = ratio of absorption cross section of isotope xx to the absorption cross section of U-235.

APPENDIX II

DERIVATION OF EQUATIONS FOR PU-239 BURN-UP

Burn-up and production of various plutonium isotopes are described by the following equations:

$$\frac{dN_{25}}{dE} = - \sigma_{25}N_{25} \tag{1}$$

$$\frac{dN_{49}}{dE} = - \sigma_{49}N_{49} + q\left(\frac{\sigma_{25}N_{25}}{1 + \alpha_{25}} + \frac{\nu_{49}}{\nu_{25}} \frac{(\sigma_{49}N_{49})}{(1 + \alpha_{49})}\right) \tag{2}$$

$$\frac{dN_{40}}{dE} = - \sigma_{40}N_{40} + \sigma_{49}N_{49} \frac{\alpha_{49}}{1 + \alpha_{49}} \tag{3}$$

$$\frac{dN_{41}}{dE} = - \sigma_{41}N_{41} + \sigma_{40}N_{40} \tag{4}$$

where E is exposure defined as $E = \int_0^t \Phi dt$. In deriving these equations the assumption of a point reactor (i.e., a flat flux) was made. This assumes the same flux for an equal time on all irradiated fuel. This is the most serious approximation limiting the equations.

Before the differential equations which govern fuel composition can be listed, the nature of the dependence of conversion of U-238 to Pu-239 on spectrum must be specified. It is assumed that the production of Pu-239 is approximately proportional to the number of fission neutrons produced.

Finally, it is assumed that the lifetime of the Np isotope (see Fig. 1) is negligibly short, and also the production of Pu-239 due to fission neutrons from Pu-241 may be neglected.

Solution of Eq. (1) leads to a determination of E:

$$\sigma_{25}E = D = \ln \frac{N_{25}^{\circ}}{N_{25}} \tag{5}$$

The numbers $\frac{N_{49}}{N_{25}^{\circ}}$, $\frac{N_{40}}{N_{25}^{\circ}}$, and $\frac{N_{41}}{N_{25}^{\circ}}$ may be determined from Eqs. (2), (3), and (4) respectively:

$$\frac{N_{49}}{N_{25}^{\circ}} = A\left(e^{-D} - e^{-GD}\right) \tag{6}$$

$$\frac{N_{40}}{N_{25}^{\circ}} = \frac{\bar{\sigma}_{49}\alpha_{49}A}{1 + \alpha_{49}}\left[\frac{1}{\bar{\sigma}_{40} - 1}\left(e^{-D} - e^{-\bar{\sigma}_{40}D}\right) - \frac{1}{\bar{\sigma}_{40} - G}\left(e^{-GD} - e^{-\bar{\sigma}_{40}D}\right)\right] \tag{7}$$

$$\begin{aligned}\frac{N_{41}}{N_{25}^{\circ}} = \frac{\bar{\sigma}_{40}\bar{\sigma}_{49}\alpha_{49}A}{1 + \alpha_{49}} & \left\{\frac{1}{\bar{\sigma}_{40} - 1}\left[\frac{1}{\bar{\sigma}_{41} - 1}\left(e^{-D} - e^{-\bar{\sigma}_{41}D}\right) - \frac{1}{\bar{\sigma}_{41} - \bar{\sigma}_{40}}\left(e^{-\bar{\sigma}_{40}D} - e^{-\bar{\sigma}_{41}D}\right)\right]\right. \\ & \left. - \frac{1}{\bar{\sigma}_{40} - G}\left[\frac{1}{\bar{\sigma}_{41} - G}\left(e^{-GD} - e^{-\bar{\sigma}_{41}D}\right) - \frac{1}{\bar{\sigma}_{41} - \bar{\sigma}_{40}}\left(e^{-\bar{\sigma}_{40}D} - e^{-\bar{\sigma}_{41}D}\right)\right]\right\}\end{aligned} \tag{8}$$

where:

$$G = \bar{\sigma}_{49}\left(1 - \frac{q\epsilon\nu_{49}}{\nu_{25}(1 + \alpha_{49})}\right) \tag{9}$$

$$A = \frac{q\epsilon}{(1 + \alpha_{25})(G - 1)} \tag{10}$$

$$\bar{\sigma}_{xx} = \frac{\sigma_{xx}}{\sigma_{25}} \tag{11}$$

These solutions may be somewhat simplified without introducing errors larger than those incorporated in the derivation of the differential equations.

N_{49}/N_{25}^{o} may be expanded in powers of D(G - 1) to give:

$$\frac{N_{49}}{N_{25}} = \frac{q\epsilon D}{1 + \alpha_{25}}\left(1 - \frac{D}{2}(G - 1) + \frac{D^2(G - 1)^2}{3!} + \ldots\right) \tag{12}$$

For reactors with conversion ratios in the range of 0.3 to 0.8,

$$\left|\frac{G - 1}{2}\right|$$

is less than about 1/4. Some reactors fall outside this range. For example, conversion ratio in the PWR blanket fuel is about 1.2.

Neglecting the second term and all higher terms introduces a fractional uncertainty in Pu-239 burn-up of about 1/8. Very high exposures, 10,000 to 15,000 Mwd/ton, are required for D to exceed unity. Therefore, the lowest order term in the expansion is adequate for the purposes of calculating Pu-239 burn-up to accuracies of better than ± 15 percent exclusive of the much larger cross section and theoretical errors, within the specified range of validity. This gives:

$$N_{49} = \frac{q\epsilon D}{1 + \alpha_{25}} N_{25} = \frac{q\epsilon D}{1 + \alpha_{25}} N_{25}^{o} e^{-D} \tag{13}$$

which can be integrated over exposure to obtain:

$$F_{49} \approx \frac{\bar{\sigma}_{49}}{1 + \alpha_{49}} N_{49} \left(\frac{N_{25}^{o} - N_{25}}{N_{25} \ln \frac{N_{25}^{o}}{N_{25}}}\right) \tag{14}$$

F_{41} because of its relative unimportance is approximated by a much less accurate form based upon first order expansion of all the exponentials in the solution. This leads to:

$$F_{41} \approx \frac{\bar{\sigma}_{41}}{1 + \alpha_{41}} \left(\frac{N_{41}}{4}\right) \ln \frac{N_{25}^{\circ}}{N_{25}} \qquad (15)$$

An alternative approach to representing burn-up is to utilize a conversion ratio, C, which is defined as the number of Pu-239 atoms produced for each fuel atom (either Pu-239 or U-235) destroyed. If M is the total number of Pu-239 atoms produced in a sample, then:

$$M = C[F_{25}(1 + \alpha_{25}) + F_{49}(1 + \alpha_{49})] \qquad (16)$$

Also, F_{49} is the total number of Pu-239 atoms produced during irradiation, M, less the number remaining at the end of the irradiation, N_{49}, divided by $(1 + \alpha_{49})$.

$$F_{49} = \frac{M - N_{49}}{(1 + \alpha_{49})} \qquad (17)$$

Eliminating M gives:

$$F_{49} = \frac{CF_{25}(1 + \alpha_{25}) - N_{49}}{(1 - C)(1 + \alpha_{49})} \qquad (18)$$

This expression for F_{49} is very sensitive to uncertainties in the conversion ratio. Because C is a function of the fuel burn-up, as well as the other design parameters of the reactor, there is some question as to the applicability of this form to measurement of burn-up.

Another description of burn-up can be made in terms of the capture-to-fission ratio, α, for each fissionable isotope. If α is known for a fissionable isotope, then the number of fissions which occur can be found by dividing the number of non-fission captures by α. The number of non-fission captures in Pu-239 is the sum of all higher plutonium isotopes, corrected for their losses by neutron capture or decay. The number of non-fission captures in Pu-239 is the sum of:

$$N_{40} + N_{41}e^{\lambda t} + \frac{N_{42}}{\alpha_{41}} + N_{42} \qquad (19)$$

which, divided by α_{49}, gives the Pu-239 fissions:

$$F_{49} = \frac{1}{\alpha_{49}} \left[N_{40} + N_{41} e^{\lambda t} + N_{42} \left(\frac{1 + \alpha_{41}}{\alpha_{41}} \right) \right] \tag{20}$$

Similarly, for F_{41}:

$$F_{41} = \frac{1}{\alpha_{41}} N_{42} \tag{21}$$

The largest uncertainties in these last forms are in the capture-to-fission ratios. However, the possible extreme values of α can be estimated, and even if the uncertainties are assumed to be sufficiently large to overlap these extremes, the approach remains the best of the three described in this appendix for representing burn-up of Pu-239. This approach has the added advantage of requiring the least amount of specific information about the spectrum in which the sample was irradiated.

APPENDIX III

SOURCES OF ERROR IN MASS SPECTROMETRY

Errors in mass spectrometry may be classified as sampling errors, operator errors, calculational errors, and instrumental errors.

Sampling Errors. Sampling may well be the largest single source of error. Since a very microscopic sample is used in the analysis, unusual care must be taken to assure that it is truly representative of the total specimen which is being analyzed. The best method is to dissolve the specimen and aliquot the stirred solution.

One sampling error which cannot be overemphasized is the contamination error common to all methods of trace analysis(42). In a single analysis one cannot determine whether the uranium came from the sample or from contamination in reagents. This problem can be handled by processing two parts of the sample differing in mass by a factor of ten through the same amount of reagents. If contamination is negligible, they will exhibit total uranium in the ratio of their starting volumes. If contamination is present, crude reagent corrections could be applied. However, these corrections could only be applied if the chemical recovery were identical in all samples. Furthermore, if the contamination comes from dust particles and is not introduced from reagents, there is no reason to assume that the contamination introduced in one sample is the same as that in another. The safest way to correct for contamination is to have none present, i.e. use extremely clean laboratory techniques. The best techniques with the procedure in Appendix IV will still carry 0.002 ugm of natural uranium contamination. The effect of this contamination can be minimized by working with 1 ugm or more of uranium in the sample.

Operator Errors. Operator errors occur in measuring the volume of the sample aliquot and the volume of the tracer aliquot as well as in calibration of the absolute concentration for the tracer solutions. If micro pipets are thoroughly cleaned, and mercury calibrated, and if each aliquot measured in them is thoroughly rinsed into the sample, this error can be minimized. It has been reported that 21% of the error in isotopic dilution analysis is found to be in the variation among pipets(43). The same authors studied the precision of the analysis as a function of sample to spike ratio. The optimum ratio of sample/spike was found to be 1:1 but introduced 1% or less error from 100:1 down to 0.1:1. With the proper selection of sample to spike they found the error for a single determination to be ± 3.7% for total uranium at the 95% confidence level.

Calculation Errors. The method of calculation should allow for U-238 and U-235 impurities in the U-233 tracer. Such a method is provided by the following equation reported by Inghram(44). Neglecting the difference in atomic weight,

$$W_1 = \frac{(R_1 + 1)\ (1 - R_3/R_2)}{(R_3 - R_1)\ (1 + 1/R_2)}\ W_2$$

where:

$R_1 = \frac{\text{U-233}}{\text{U-238}}$ sample

$R_2 = \frac{\text{U-233}}{\text{U-238}}$ tracer

$R_3 = \frac{\text{U-233}}{\text{U-238}}$ mixture

W_1 = Weight of U-238 in the sample

W_2 = Weight of U-233 added as tracer

From this equation, it is apparent that the best tracer is one which differs from the samples by the greatest possible factor so that R_3/R_2 can be very different from one. The ideal tracer is a monoisotope in which case $R_2 = \infty$. U-233 can be obtained in which $R_2 \geq 1000$.

The final result, W_1, depends only on isotopic ratios. It does not depend on its chemical recovery. Chemical recovery is not important, except where contamination is a factor, as long as enough material is recovered to serve for isotopic analysis.

Many of the errors, including the differences in atomic weight between sample and tracer mentioned above, can be cancelled out in the calibration of the tracer. A typical procedure is as follows:

1. Prepare a solution of the tracer by dissolving about 1 mg of U-233 in a convenient amount of dilute nitric acid.

2. Prepare a standard solution of chemically pure NBS #950 U_3O_8 by dissolving carefully weighed gram amounts in nitric acid and diluting with dilute nitric acid to an exact volume which is about 1000 times that in Step 1. Record weight of U-238 per ml on this standard solution, as follows:

$$\frac{\text{gm U-238}}{\text{ml}} = \frac{\text{gm } U_3O_8}{\text{ml soln}} \times \frac{0.8480 \text{ gm U}}{\text{gm } U_3O_8} \times \frac{0.9928 \text{ gm U-238}}{\text{gm U}}$$

3. Combine equal aliquots of the solution from Step 1 and Step 2 and measure the resulting isotopic composition on the mass spectrometer.

From the isotopic composition observed in Step 3, the concentration of the tracer can be calculated. The advantages of this method are that large amounts of tracer are not necessary for standardization. The chemical purity of the tracer does not enter, the result depends only on the purity of the NBS standard used in Step 2. The mass spectrometer discrimination introduced in the isotopic measurement of Step 3 is later cancelled when the isotopic composition resulting from an isotopic dilution analysis is made.

The final calculational error to be mentioned is that due to the statistical nature of the data obtained. Instruments using counting techniques to measure and record ion beams will be subject to all errors inherent to counting techniques. These include coincidence losses at high counting rates and statistical fluctuations in low counting rates. In instruments using current measuring devices, the precision and accuracy will be sensitive to the number of individual scans made, as well as the amplitude of the signals recorded.

Instrumental Errors. Errors associated with any type of mass spectrometer may be caused by improper focus of the ion beam on the collector. Drift in the accelerating voltage or magnetic flux may cause the beam to shift position. Insufficient resolution results in contribution of one peak to another. Any fluctuation of the source filament temperature would result in unstable ion emission during the analysis period. Chemical impurities in the source filament or in the sample may contribute in an irregular manner to the ion peaks being studied. Examples are polymers of potassium (K_6^+) and hydrocarbons.

If a direct current measuring device is used and peak amplitude are transmitted to a recorder, there may be non-linear response in the recorder over various sensitivity ranges. Secondary ions formed at the collector may contribute to the peak signal. Voltage scanning may cause mass discrimination. Insufficient sample size may limit analysis time, hence precision and accuracy.

If individual ions are counted as pulses, an insufficient sample size may not afford sufficient counts to obtain good statistics. If voltage scanning is used with such an instrument, a discrimination effect occurs at the electron multiplier (collector) due to differences in energy absorbed over the range of accelerating voltages used to scan the sample. The electron multiplier may become unstable. Spurious noise from external sources may seriously affect the total counts received.

Cumulative Errors. Much time and care is normally spent to reduce errors in analysis to a minimum. Random errors remaining in the determination should be 0.1 to 1%. Systematic errors such as might be caused by mass discrimination are perhaps 0.5 to 1%. The cumulative error is the sum of errors in the determination and the calibration. Unless there is a large error caused by contamination, this may be ± 1 to 5%(45). Additional calibration errors are introduced when one desires ratios of plutonium isotopes to uranium isotopes since different elements have different emission characteristics and must be related through the relative concentrations of Pu and U tracers added.

Table V has listed some mass ratio data with errors estimated to be those attainable by present experimental techniques. For the procedure used in the mass spectrometry of uranium and plutonium refer to Appendix IV.

APPENDIX IV

URANIUM AND PLUTONIUM ANALYSIS

Samples of dissolved irradiated fuel contain highly radioactive fission products. For this reason, uranium and plutonium are separated prior to analysis. The following procedure gives a good yield together with a good decontamination factor.

Reagents:

1. Distilled conc. HNO_3.
2. 2 M HNO_3 - distilled conc. HNO_3, double distilled H_2O.
3. U-233 solution, standardized.
4. Pu-236 solution, standardized.
5. $KBrO_3$ - Crystals, Reagent Grade. Low natural U blank.
6. 8 M NH_4NO_3 in 2 M HNO_3 - Place 200 ml distilled 16 M HNO_3 + 100 ml double distilled H_2O in a large beaker. Bubble NH_3 gas through solution until basic to pH paper. Boil off excess NH_3 (solution neutral). Transfer to mixing cylinder, add 50 ml of distilled 16 M HNO_3, dilute to 400 ml. Check density of solution (1.31 ± 0.01 @ 20°C.).
7. Hexone - distilled.
8. HCl - C.P. reagent. Low natural U blank.
9. 1 M HNO_3 - distilled conc. HNO_3, double distilled H_2O.
10. 30% H_2O_2 - meets A.C.S. specification, low natural U blank.
11. 0.2 M T.T.A. in xylene - 4.44 gm T.T.A. dissolved in 100 ml distilled xylene.
12. Xylene - distilled.
13. Ether - distilled.
14. 0.05 M HNO_3 - distilled conc. HNO_3, double distilled H_2O.
15. H_2O - double distilled.

Glassware:

All glassware used is Pyrex which has been soaked overnight in 50% HNO_3 and rinsed with double distilled water. Pipets are rinsed with 50% HNO_3 and double distilled water before using.

Separation and Decontamination Procedure:

1. Place the aliquot for analysis in a 15 ml cone and evaporate to about 1 ml. Add a suitable U-233 and Pu-236 spike, one drop conc. nitric acid, and several $KBrO_3$ crystals. Allow to stand for 1 hour to allow oxidation of Pu to PuO_2^{++}.
2. Add 1.5 ml 8 M NH_4NO_3 in 2 M HNO_3, and evaporate to about 2 ml.
3. Prepare 2 scrub solutions in separate 15 ml cones, containing 1 ml of 8 M NH_4NO_3 in 2 M HNO_3 and about 10 mgc $KBrO_3$. Preoxidize about 10 ml hexone with 2 ml of 2 M HNO_3 and $KBrO_3$. Keep covered until ready for use.
4. Extract the U and Pu four times for five minutes with 2 ml portions of hexone (methyl isobutyl ketone), adding 1 drop of 16 M HNO_3 to the original solution after each extraction. Scrub each extract in turn with the two solutions prepared in step 3.
5. Strip the combined hexone extracts with five 2 ml portions of H_2O. Evaporate the combined aqueous portions to dryness, add a few drops of HNO_3 and HCl, take to dryness. Evaporate to dryness with HNO_3 under a gentle stream of pure nitrogen on a boiling water bath.
6. Prepare 3 ml of 1 M HNO_3 and 1 drop of 30% H_2O_2, add 1 ml to the Pu and U residue from step 5 and two 1 ml portions to separate 15 ml cones.
7. Extract immediately the Pu 2 times for 20 min. with 2 ml portions of 0.2 M T.T.A. (thenoyltrifluoroacetone) in xylene. Scrub each in turn with solutions prepared in step 6. Save the aqueous phase for uranium. Combine the T.T.A. extracts and add a few crystals of trichloroacetic acid.
8. Mount the combined T.T.A. extracts on a platinum plate for alpha pulse analysis.
9. After pulse analysis, remove the Pu for mass analysis as follows: Cover disc with HF. Evaporate to dryness under a heat lamp. Again cover disc with HF and evaporate to dryness. Cover disc with conc.

HNO_3 and evaporate to dryness. Repeat 3 or 4 times. Cover disc with conc. nitric, reflux a few seconds, and transfer with a pipet to a 15 ml cone. Repeat 3 or 4 times.

10. Evaporate the combined conc. HNO_3 refluxes to dryness. Treat residue with aqua regia and evaporate to dryness. Evaporate to dryness with conc. HNO_3 on a boiling water bath several times. Add 50 λ of 0.01 $\underline{M}$ HNO_3 to the evaporated sample and submit sample for mass spectrographic analysis.

11. Wash the original 1 $\underline{M}$ HNO_3 uranium fraction (Step 7) with xylene. Add 1 drop of HNO_3 and 3 drops of HCl to the washed 1 $\underline{M}$ HNO_3 and reflux for about one-half hour to destroy the organic present. Evaporate to dryness, flame gently to destroy organic matter and dissolve the residue with 2 drops HNO_3 and evaporate to dryness on a water bath.

12. Pipette three 1 ml portions of 8 $\underline{M}$ NH_4NO_3 in 2 $\underline{M}$ HNO_3, dissolve the evaporated U fraction in one 1 ml portion. Place the other 2 portions in two 15 ml cones for scrub solutions.

13. Extract the U with four 2 ml portions of diethyl ether, adding 100 λ of conc. HNO_3 before each extraction. Scrub each extract in turn with 2 scrub solutions prepared in Step 12.

14. Evaporate the combined ether extracts over 1 ml of H_2O in a 15 ml cone. Evaporate to dryness.

15. Add 3 drops of HCl and 1 drop of HNO_3, and evaporate to dryness repeatedly until the organic is destroyed. Flame gently to expell ammonium salts. Then dissolve in HNO_3 and evaporate to dryness on a water bath. Add 50 λ of 0.05 $\underline{M}$ HNO_3 to the dry cone and submit sample for mass spectrographic analysis.

Plutonium Calculation:

To determine the amount of Pu in the original sample, it is necessary to measure in a Frisch chamber the alpha spectrum of the plate prepared in Step 8. The ratio of Pu-239 and Pu-240 activity to Pu-236 activity is calculated. If the ratio is multiplied by the original activity of Pu-236 added, the original activity of Pu-239 plus Pu-240 can be obtained. From the mass analysis a Pu-239 to Pu-240 atom ratio is obtained. The specific activity of the mixture is calculated from that of the individual isotopes. The Pu-239 plus Pu-240 activity can be converted to Pu-239 plus Pu-240 weight by dividing this activity by the specific activity of the mixture.

Uranium Calculation:

The ratio of the various U isotopes to U-233 from the mass spectrometer data is multiplied by the amount of U-233 spike originally added to the sample to obtain the amount of each uranium isotope present in the original sample.

APPENDIX V

CESIUM-137 ANALYSIS

Principle of Method

Cesium is precipitated as the perchlorate; scavenged with iron, cerium, and zirconium; and finally precipitated as the chloroplatinate.

Reference

UCRL-432
LA-1721

Reagents and Apparatus

1. Cesium carrier, 10 mg/ml standardized.
2. Iron, cerium, zirconium, carriers (10 mg/ml).
3. Chloroplatinic acid (5% aq.)
4. Thymolphthalein indicator (0.1% in ethanol).
5. HCl and NaOH (1N).
6. Whatman #540 filter paper, 2.4 cm. dia.
7. $HClO_4$ acid (conc.)
8. HNO_3 acid (conc.)
9. Absolute ethanol.

Procedure

1. Prepare a dilution of the radioactive sample in 2 M nitric acid containing 10 ppm cesium carrier.

2. Add 10 ml H_2O, exactly 2 ml cesium carrier, and an aliquot of the diluted sample to a 50 ml erlenmeyer flask.

3. Add 0.5 ml conc. HNO_3 and 5 ml conc. $HClO_4$ and boil until dense white fumes appear. Cool to room temperature. Add 15 ml absolute ethanol. Transfer to a 50 ml centrifuge cone.

4. Centrifuge. Discard the supernatant liquid into cold running water. Wash the precipitate 2 times with absolute ethanol.

5. Dissolve the precipitate in 15 ml water.

6. Add 5 drops of iron carrier and one drop each of zirconium and cerium carriers.

7. Add 3 drops of thymolphthalein indicator.

8. Add 1 N NaOH while swirling until a blue end point is reached.

9. Centrifuge and decant the supernatant liquid through an 11 cm. dia. #40 Whatman filter paper into a clean centrifuge cone. Discard the precipitate.

10. Add 2 ml of 5% chloroplatinic acid. Swirl gently to mix.

11. Heat briefly in a beaker of boiling water to coagulate the precipitate.

12. Cool contents in an ice bath to decrease the solubility of the precipitate.

13. Centrifuge and discard the supernatant liquid.

14. Slurry the precipitate with distilled H_2O onto a dried and weighed filter paper disc, 2.4 cm. dia.

15. Dry at 110°C. for 15 min., cool for 15 minutes in a dessicator, weigh for yield, count for gamma activity on a multichannel scintillation spectrometer.

Note 1: If Cs-137 is to be used as a burnup indicator in nuclear fuel, the fuel should be totally sealed in a gas tight clad to prevent escape of Xe-137 parent. The cladding must be completely dissolved with the fuel since the fission product is driven or diffused to surprising depth in the cladding walls and cannot be removed by leaching or etching. Finally, all acids used to dissolve the fuel and cladding must contain 1 to 10 ppm of inert cesium carrier to discourage loss of radiocesium by ion exchange on glassware. All dilutions made from the original acid dissolution must also contain 1 to 2 M nitric or hydrochloric acid and 1 to 10 ppm cesium carrier.

Note 2: Macro amounts of Rb, K, NH_4^+ salts interfere as do excessive amounts of Na salts. Silicotungstic acid effects a separation. Where Cs-137 is a very minor constituent, several preliminary perchlorate precipitations may be required to improve decontamination. Both of these decontamination steps are described in LA-1721. Normally 130 days cooling is allowed to permit Cs-136 to decay.

APPENDIX VI

CALCULATION OF Cs-134 TO Cs-137 RATIO

It is desirable to be able to estimate the extent of Cs-134 interference under actual reactor conditions. Figure 2 is a plot of the activity ratio of Cs-134 to Cs-137 as a function of the fissions per initial fissionable atom. A family of curves are shown for various plutonium conversion ratios, C. The case corresponding to an actual reactor with $C \approx 0.6$ is indicated by a dotted line.

Derivation of Equations for Cs-134/Cs-137 Activity Ratio. The differential equations governing the concentrations of Cs-133, Cs-134, and Cs-137 can be expressed:

$$\frac{dN_f}{dE} = - \sigma_f N_f (1 + \alpha)(1 - C) \tag{1}$$

$$\frac{dN_3}{dE} = - \sigma_3 N_3 + 0.06\ \sigma_f N_f \tag{2}$$

$$\frac{dN_4}{dE} = - (\sigma_4 + \frac{\lambda_4}{\Phi}) N_4 + \sigma_3 N_3 \tag{3}$$

$$\frac{dN_7}{dE} = 0.06\ \sigma_f N_f \tag{4}$$

where:

C = conversion ratio

N_f = atoms of U-235

N_f^o = initial atoms of U-235

N_3 = atoms of Cs-133

N_4 = atoms of Cs-134

N_7 = atoms of Cs-137

σ_f = cross section of U-235 for fission, barns

σ_4 = capture (n,γ) cross section of Cs-134, barns

$\sigma_4' = \sigma_4 + \frac{\lambda_4}{\Phi}$

σ_3 = capture (n,γ) cross section of Cs-133, barns
α = ratio of capture-to-fission cross section for U-235
λ_4 = decay constant of Cs-134, sec^{-1}
λ_7 = decay constant of Cs-137, sec^{-1}
Φ = flux of reactor (3×10^{13} $n/cm^2/sec$ for the example)
E = total exposure in n/cm^2
A_4 = activity of Cs-134, dps
A_7 = activity of Cs-137, dps

Several assumptions are made in writing the differential equations. They include: an over-simplification of the concept of conversion ratio, the concept of a point reactor with cross sections independent of exposure and position in the core, and negligible burn-out of Xe-133 and Cs-137. Results based on these equations are, therefore, only semi-quantitative. However, the mathematical description is adequate for the purposes of this report.

The following solutions to the above equations are for the case of zero initial concentrations of N_3, N_4, and N_7.

$$N_f = N_f^{\circ} e^{-\sigma_f(1+\alpha)(1-C)E} \tag{5}$$

$$N_3 = \frac{0.06\ \sigma_f N_f^{\circ}}{\sigma_3 - \sigma_f(1+\alpha)(1-C)} \left(e^{-\sigma_f(1+\alpha)(1-C)} - e^{-\sigma_3 E} \right) \tag{6}$$

$$N_4 = \frac{0.06\ \sigma_f N_f^{\circ} \sigma_3}{\sigma_3 - \sigma_f(1+\alpha)(1-C)} \left[\frac{e^{-\sigma_f(1+\alpha)(1-C)E} - e^{-\sigma_4' E}}{\sigma_4' - \sigma_f(1+\alpha)(1-C)} - \frac{e^{-\sigma_3 E} - e^{-\sigma_4' E}}{\sigma_4' - \sigma_3} \right] \tag{7}$$

$$N_7 = \frac{0.06\ N_f^{\circ}}{(1+\alpha)(1-C)} \left(1 - e^{-\sigma_f(1+\alpha)(1-C)E} \right) \tag{8}$$

which can be solved for:

$$\frac{N_4}{N_7} = \frac{\sigma_3 \sigma_f (1 + \alpha)(1 - C)}{\sigma_3 - \sigma_f (1 + \alpha)(1 - C)} \left(\frac{1}{1 - e^{-\sigma_f (1 + \alpha)(1 - C)E}} \right)$$

$$\times \left(\frac{e^{-\sigma_f (1 + \alpha)(1 - C)E} - e^{-\sigma_4 ' E}}{\sigma_4 ' - \sigma_f (1 + \alpha)(1 - C)} - \frac{e^{-\sigma_3 E} - e^{-\sigma_4 ' E}}{\sigma_4 ' - \sigma_3} \right) \qquad (9)$$

$$\frac{A_4}{A_7} = \frac{\lambda_4 N_4}{\lambda_7 N_7} \qquad (10)$$

The number of fissions which occurred can be obtained by integration of $\sigma_f N_f$ in Eq. (5) over exposure. The number of fissions per initial number of fissionable atoms is:

$$\frac{\text{fissions}}{\text{initial number of fissionable atoms}} = \frac{N_f^{\,o}\left(1 - e^{-\sigma_f (1 + \alpha)(1 - C)E}\right)}{(1 + \alpha)(1 - C)} \qquad (11)$$

Figure 2 is a plot of the activity ratio of Cs-134/Cs-137 vs. the fissions per initial number of fissionable atoms, for $C = 0$, $\alpha/(1 + \alpha)$, $\approx .6$ and 1. The assumed reactor dependent parameters are

$$\sigma_f = 580$$

$$\sigma_3 = 70 \text{ barns}$$

$$\left(\sigma_4 + \frac{\lambda_4}{\phi}\right) = 450 \text{ barns}$$

$$\phi = 3 \times 10^{13} \text{ nv}$$

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APPENDIX VII

CESIUM-137 AND Ba-137m DECAY SCHEME CONSTANTS

Cs-137

92.4 ± 0.8%	0.514 Mev β	(46)
7.6 ± 0.8%	1.18 Mev β	(46)

Ba-137m

	K/γ	K/L	L/MN	
	0.098	5.66	3.85	(46)
	0.095			(47)
	0.093			(48)
		5.9	3.6	(49)
	0.096	4.6		(50)
		5.2	3.6	(51)
	0.092	5.8	4.5	(52)
		5.43	3.7	(53)
		5.5	3.7	(54)
	0.095			(55)
	0.097			(56)
Average	0.095 ± 0.002	5.4 ± 0.4	3.8 ± 0.3	
e^-/γ	0.095 ± 0.002	0.018 ± 0.001	0.005 ± 0.004	

APPENDIX VIII

FISSION PRODUCT INVENTORY OF FUEL AT 10,000 Mwd/ton

The methods of analysis which can be applied to irradiated fuel are somewhat restricted by the level of activity present. Calculations were made for the fission product inventory and resulting beta and gamma dose rates at 10,000 Mwd/ton, representing 0.012 fissions/gm U, a 2 year irradiation, and a cooling period of 130 days. The total number of millicuries/gm U can be calculated:

$$\frac{mc}{gm\ U} = \frac{\dfrac{1 - e^{-\lambda t_1}}{\lambda t_1} \times e^{-\lambda t_2} \times F \times Y_f \times \lambda}{3.7 \times 10^7}$$

where

t_1 = time of irradiation, sec.

t_2 = cooling time, sec.

λ = decay constant of fission product of interest, sec^{-1}.

F = fissions/gram uranium.

Y_f = fission yield of fission product of interest.

The total gamma radiation dose was calculated:

$$R/hr\ @\ 1\ cm = 5.57 \times 10^3 \times C \times E$$

where

C = curies

E = total energy of gamma per disintegration in Mev.

The total beta radiation dose was calculated according to Fitzgerald(57):

$$Rep/hr = \frac{2.06 \times 10^5\ E_{max}\ C}{3\ R^2\ (0.543\ E_{max} - 0.16)}$$

where

C = curies

R = cm from source

E_{max} = maximum beta energy, Mev.

The following gives a summary of these calculations. In the calculation it was assumed that the fuel solution is a point source and there is no beta shielding. The dose is calculated at 1 cm.

FISSION PRODUCT INVENTORY IN IRRADIATED URANIUM

AT 10,000 Mwd/ton COOLED 130 DAYS

Fission Product	Millicuries/gram of U	R/Hr/gm U at 1 cm gamma dose	Rep/Hr/gm U at 1 cm beta dose
Ba-137m	33.2	95.6	--
Cs-137	33.2	--	0.64×10^4
Ce-144	475.0	79.4	14.06×10^4
Pr-144	475.0	76.0	6.46×10^4
Sr-90	33.2	--	0.95×10^4
Y-90	33.2	--	0.48×10^4
Pm-147	131.1	--	3.70×10^4
Ru-106	178.6	--	11.02×10^4
Rh-106	178.6	206.7	2.28×10^4
Zr-95	133.0	513.0	2.85×10^4
Nb-95	266.0	1024.0	9.78×10^4
Y-91	190.0	2.5	3.14×10^4
Sr-89	114.0	--	1.90×10^4
Ru-103	43.7	122.0	0.84×10^4
Rh-103	43.7	49.0	0.42×10^4
Ce-141	47.5	28.3	0.91×10^4
Ba-140	0.8	0.9	0.01×10^4
La-140	0.8	8.4	0.01×10^4
Total/gm U	2410.6	2205.8	594,500

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