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PREPARATION AND CHARACTERIZATION OF NEUTRON DOSIMETER MATERIALS *

by

E. H. Kobisk and H. L. Adair

Introduction

There is a need for both stable and radioactive materials which can be placed in reactors and activated by neutrons to determine the neutron energy, spectra, flux, and fluence at a particular location. In addition, deposits of various radioactive materials are needed for use in precision neutron cross-section measurements. The materials used for neutron monitors or for precision cross-section measurements must be accurately defined and contain minimum amounts of impurities. The Isotopes Division at the Oak Ridge National Laboratory has established a program for providing neutron dosimeters as well as materials used for precision neutron cross-section measurements.

Preparation of Dosimeters

In addition to being well defined and containing minimum amounts of impurities, the encapsulated dosimeter materials should meet the following criteria.[1]

1. The materials should have peak activation characteristics at different neutron energies.

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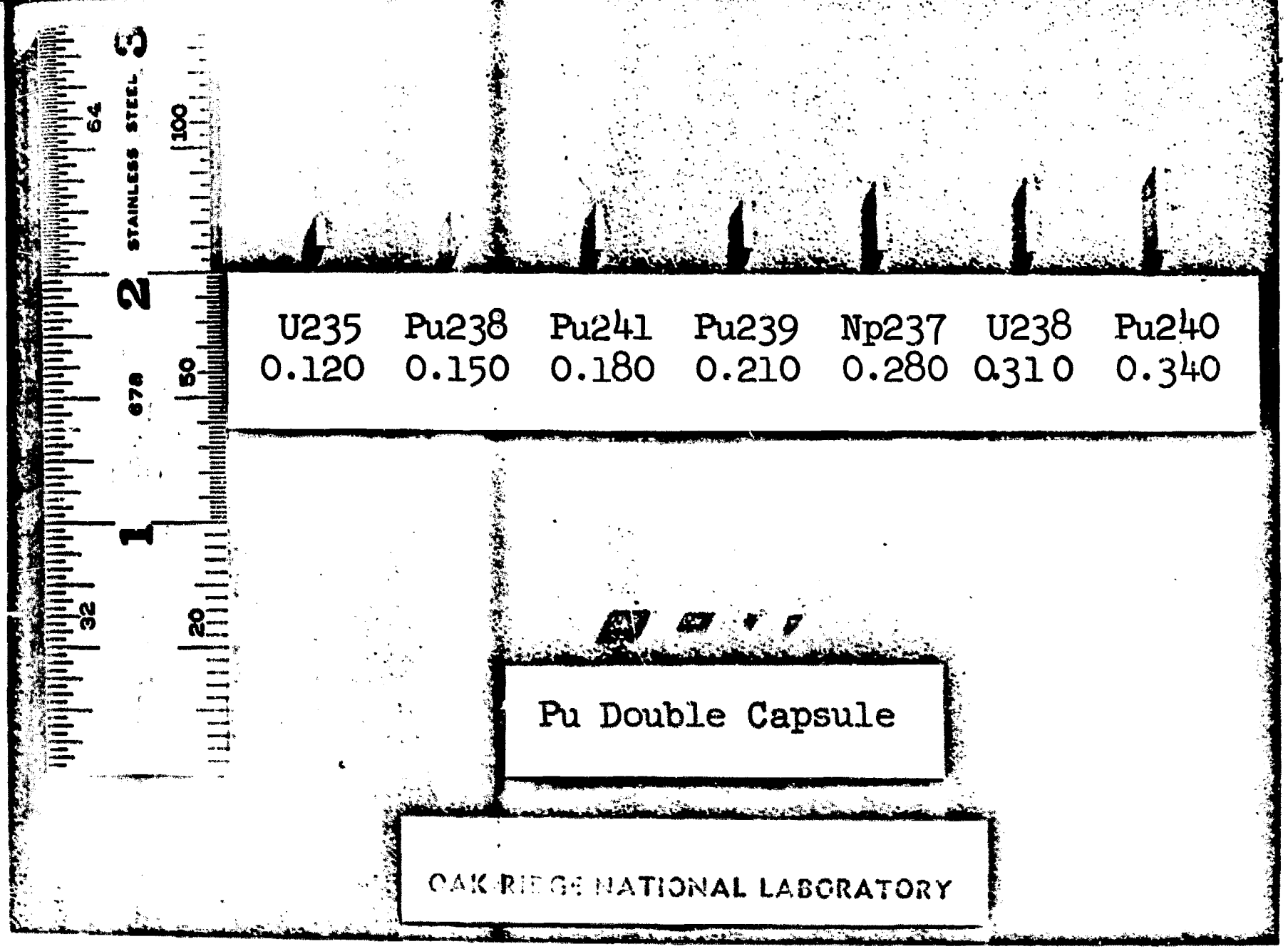
Table 1. Vanadium Metal Used for Dosimeter Capsules

V - 99.995%

Spark Source Mass Analysis

	ppm
Al	0.05
B	<0.02
Ca	0.8
Co	<1.0
Cr	<10.0
Cu	0.5
Fe	<3.0
Hf	3.0
K	2.0
Mg	0.1
Mn	<3.0
Na	<0.5
Ni	<3.0
P	0.2
Si	3.0
Ta	10.0
Zr	1.0


U235 Pu238 Pu241 Pu239 Np237 U238 Pu240
0.120 0.150 0.180 0.210 0.280 0.310 0.340
Pu Double Capsule
OAK RIDGE NATIONAL LABORATORY

2. The dosimeter and encapsulating materials should have high melting points, normally >1000°F.
3. The dosimeter materials should produce product radioisotopes whose half lives and radiation characteristics are accurately known and are amenable to direct counting through the capsule without dissolution.

The dosimeters prepared by the Isotopes Division at the Oak Ridge National Laboratory are encapsulated in high purity vanadium (99.995%) which contains ≤10 ppm tantalum. The low tantalum content is necessary because tantalum has a high cross section for fast neutrons and the activation products produced interfere with the analysis of the activation products produced in the dosimeter material. A typical spark-source mass spectrographic analysis of the vanadium is shown in Table 1. Thus far, dosimeters of ^{6}Li, ^{10}B, ^{45}Sc, ^{232}Th, ^{235}U, ^{238}U, ^{237}Np, ^{238}Pu, ^{239}Pu, and ^{241}Pu have been prepared. Normally, the elemental form is used for the stable materials and the radioactive materials are in oxide form.

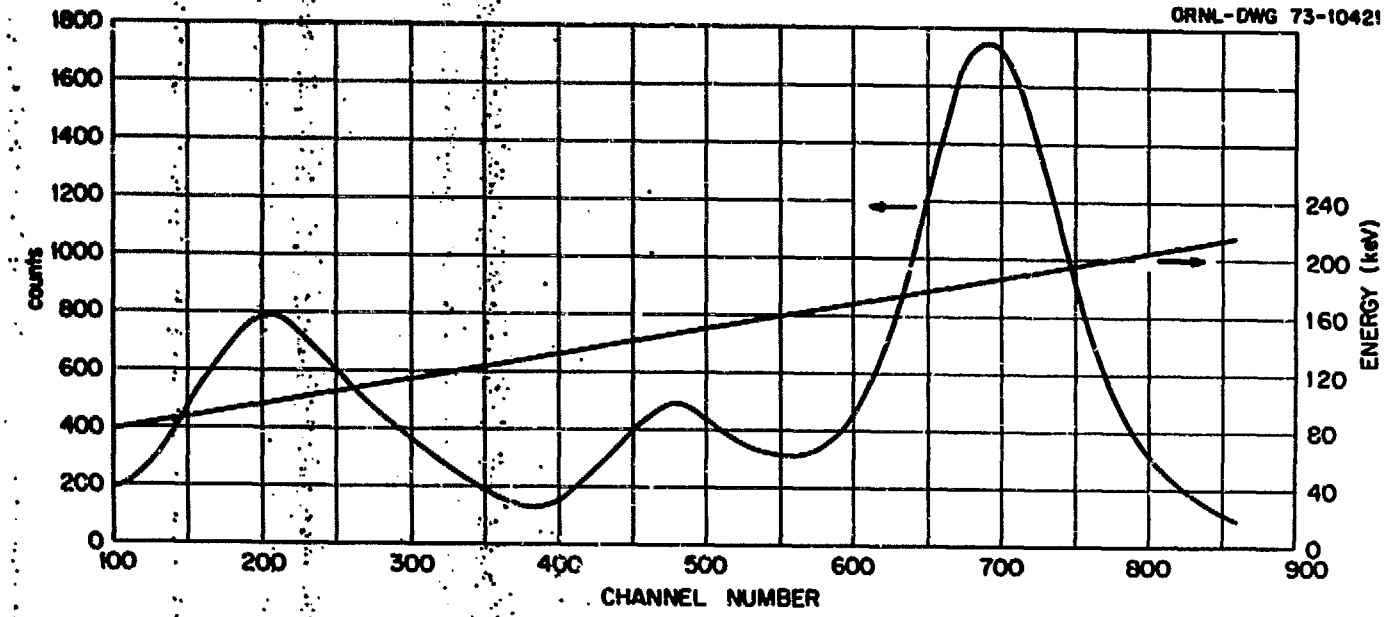
The vanadium capsules used to encapsulate the dosimeter materials are shown in Fig. 1. The capsules have a 1.27-mm diam and vary in length from 3.05 mm to 8.64 mm. The internal cavity is 0.76-mm diam and varies in depth from 2.28-mm to 7.87-mm. The amount of material loaded into each capsule varies from ~1-10 mg, depending upon the particular isotope. The material type is identified by the length of the capsule and each individual capsule is identified by a dot coding system.[2]

The procedure for loading the capsules is described in Ref. 2 and will not be described here.

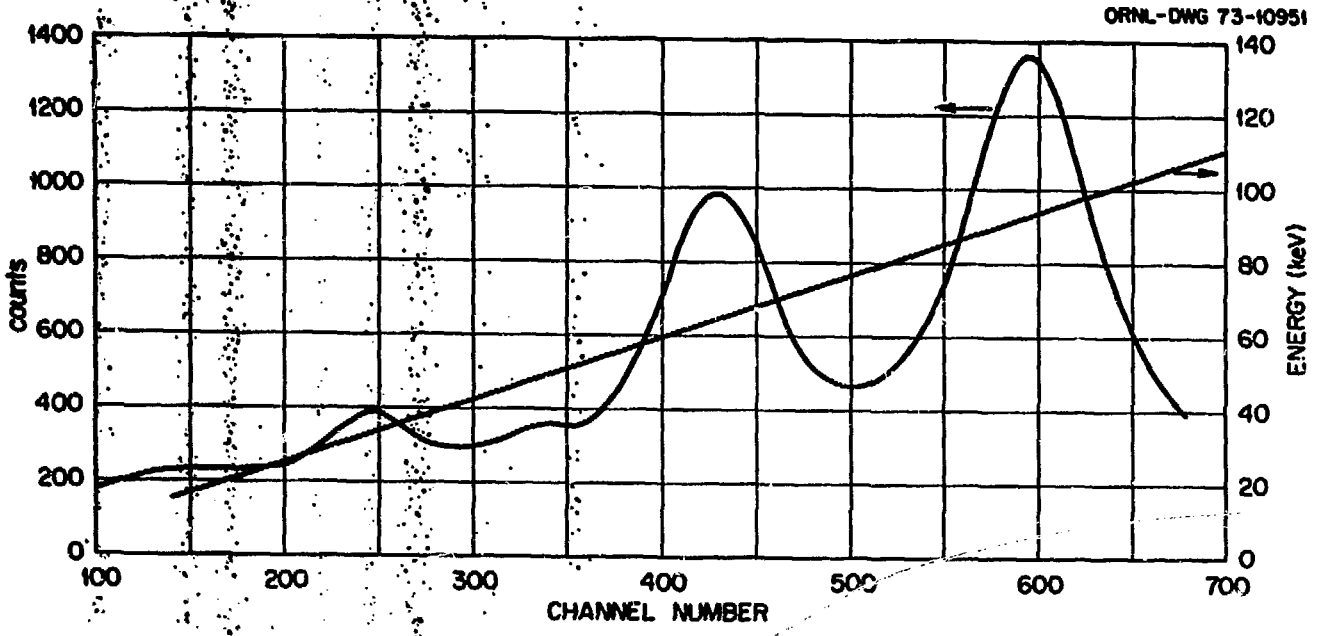
After the dosimeter materials have been encapsulated in a welded vanadium capsule and decontaminated, if they contain radioactive materials, the capsules are leak checked by using an ethylene glycol vacuum leak test procedure which will detect leaks as small as 10^{-4} cm^3/min. In addition, the dosimeters are heated to 800°C in argon for one hour and leak checked again. At this stage the stable materials are ready for shipment. However, the radioactive materials are given a one-week shelf test after which they are checked for contamination. At this stage, if the dosimeters contain any removable detectable contamination, they are rejected for shipment.

Characterization of Dosimeters

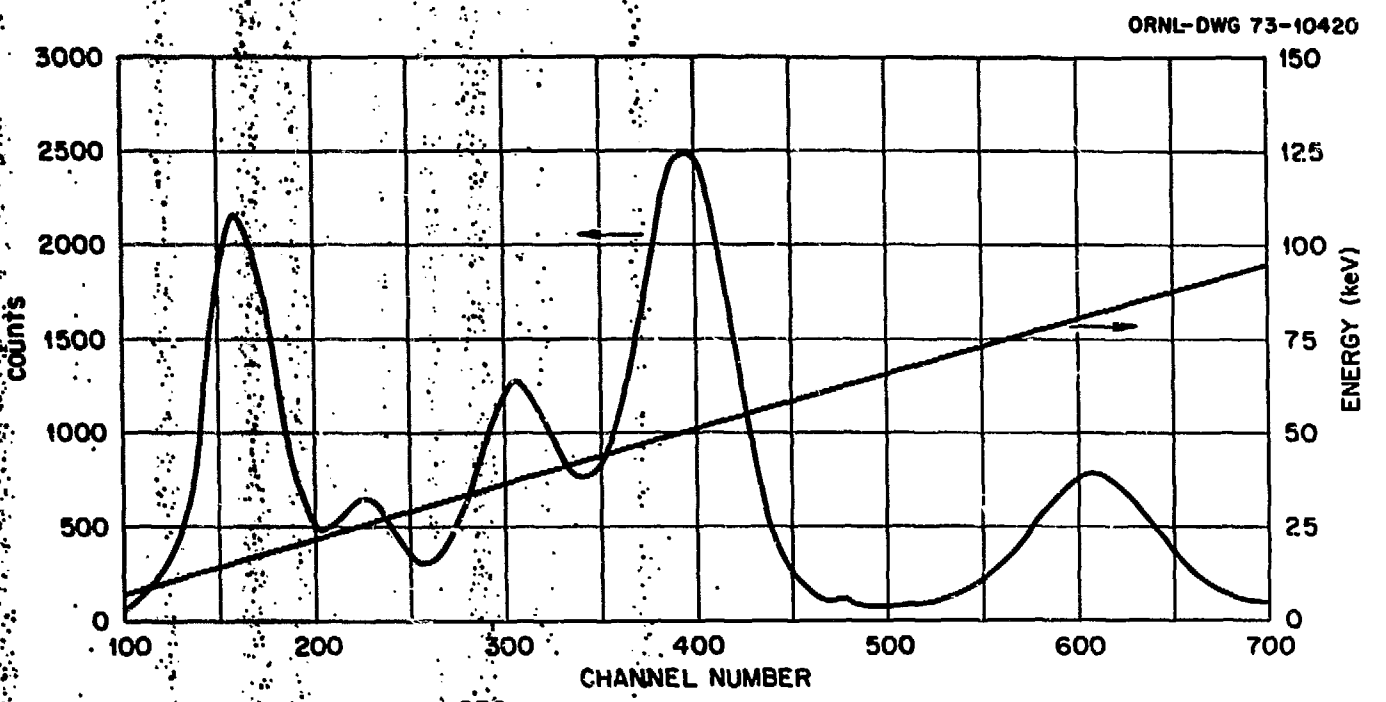
The amount of material contained in each dosimeter is determined initially by weight difference using a Mettler M5 microbalance. The accuracy of the weight of material in each monitor containing ≥1 mg of material is ±0.5% at the 95% C.I. For the radioactive samples of $^{235}U_3O_8$, $^{238}U_3O_8$, $^{239}PuO_2$, and $^{237}NpO_2$, gamma counting, using a 7.6 cm by 7.6 cm NaI(Tl) detector, is presently being used to verify the amount of encapsulated material after the capsules have been welded and decontaminated. Figures 2 through 5 show typical gamma-ray spectra obtained for ^{235}U, ^{238}U, ^{239}Pu, and ^{237}Np dosimeters. For the ^{235}U dosimeters, the number of gamma



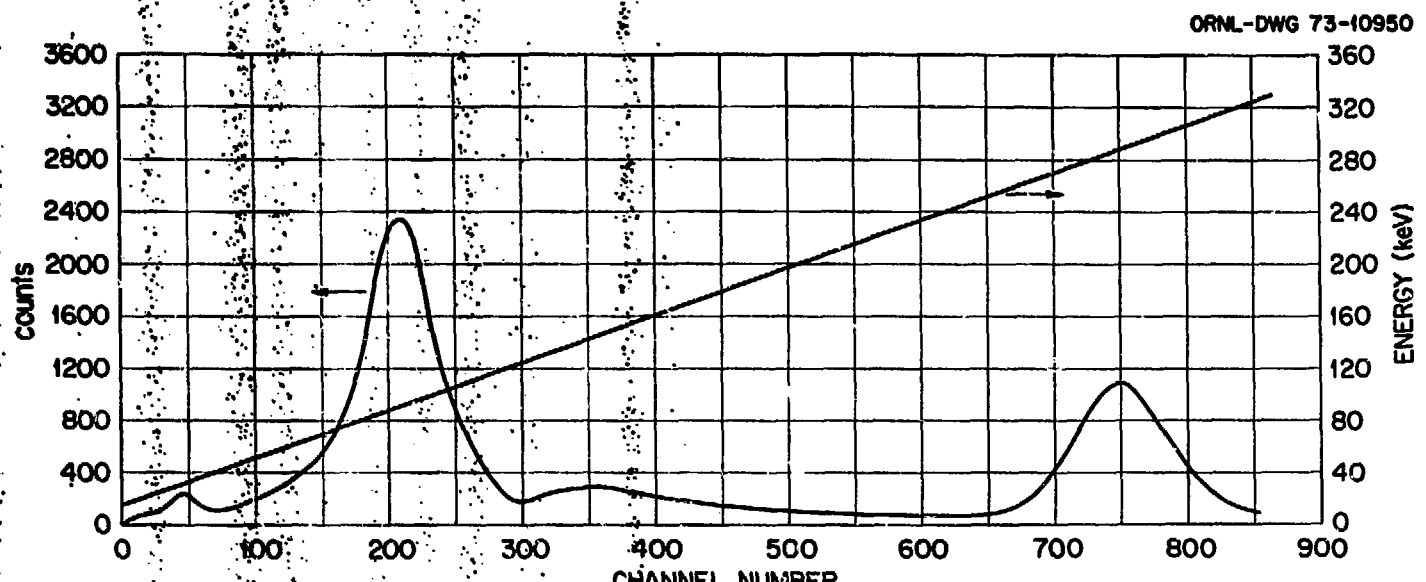
^{235}U Dosimeter Gamma Spectrum.



^{238}U Dosimeter Gamma Spectrum.



^{239}Pu Dosimeter Gamma Spectrum.



^{237}Np Dosimeter Gamma Spectrum.

counts obtained from the 164 and 185 keV peaks are obtained for each dosimeter and compared to the number of counts from the same peaks from a ^{235}U standard dosimeter. The ^{235}U dosimeter that is used as a standard has been standardized both by comparing gamma counts to a dosimeter that has been destructively analyzed and by comparing the gamma counts to the initial weighed material.

For the ^{238}U dosimeters, the gamma counts from the daughter products ^{234}Th-^{234}Pa, which are in equilibrium with the ^{238}U, are used to determine the amount of ^{238}U in the dosimeter capsule. For the ^{239}Pu and ^{237}Np dosimeters, the gamma counts from the 52 keV and 87 keV peaks, respectively, are used to compare with standard dosimeters to determine the amount of dosimeter material present. In the latter three cases, the standards are prepared from known weight samples and are not compared to samples that have been destructively analyzed. For each material the gamma counting results indicate an accuracy of $\sim\pm 1\%$. One possible explanation for the variation in gamma data, from the desired $\pm 0.5\%$ level, could be due to the absorption of gamma rays by the vanadium. A measurement of the mass absorption coefficient for the 164 and 185 keV gamma rays from ^{235}U indicated that a 0.008 cm thickness of vanadium could cause an $\sim 1\%$ difference in intensity. Thus, if the cavity containing the material is not directly in the center of the 1.27 mm diam vanadium capsule for each dosimeter, a variation in intensity for a particular amount of material could be obtained.

One of the reasons for gamma counting the dosimeters was to determine if material was being lost during the welding process because on some of the smaller capsules, for example ^{235}U, the material, when loaded, is very close to the weld zone. Table 2 shows the gamma counting results for ^{235}U dosimeters which were counted before and after welding. As can be seen from the table, no variations except those due possibly to capsule thicknesses were noted. Also, the number of gamma counts per minute per microgram shows a variation among the dosimeters of $\sim \pm 1.5\%$. The counting time for each dosimeter was 10,000 sec. In Table 3 the results obtained for ^{238}U dosimeters before and after welding are shown. Again, no material was lost in the welding process and the variation in gamma counts per minute per microgram among the dosimeters is $\sim \pm 1\%$.

Archive Samples

For further verification or reanalysis of the batches of isotopic materials used in the dosimeter program, archive samples of ^{235}U, ^{238}U, ^{237}Np, and ^{239}Pu have been prepared and encapsulated for storage at the Oak Ridge National Laboratory. Each isotope (oxide and metal) was characterized by the following analysis.

1. Mass spectrographic analysis,
2. Spark-source mass spectrographic analysis,
3. Amount of the major element per unit weight of material.

In addition, the moisture content of the oxide samples was determined. The results of these analyses are shown in Tables 4 through 7.

Table 2

^{235}U Dosimeters γ-Counted Before Welding

Dosimeter No.	Oxide Wt. (mg)	Elemental Wt. (mg)	Gamma Counts Minus Background	Count Rate per min.	Count Rate per min. per mg
Std. -1	2.671	2.259	291407	1748.40±2.23	773.97
Std. -5	0.973	0.823	108705	652.22 ±1.42	792.49
Std. -7	3.406	2.881	370947	2225.64±2.50	772.52
Std. -8	2.328	1.969	259893	1559.33 ±2.11	791.94
Std. -9	1.404	1.188	154198	925.17 ±1.66	778.76

^{235}U Dosimeters γ-Counted After Welding

Std. -1	2.671	2.259	288141	1728.81 ±2.22	765.30
Std. -5	0.973	0.823	108827	652.95 ±1.42	793.38
Std. -7	3.406	2.881	369986	2219.87 ±2.50	770.52
Std. -8	2.328	1.969	260414	1562.45 ±2.11	793.52
Std. -9	1.404	1.188	155151	930.89 ±1.66	783.58

Table 3

^{238}U Dosimeters γ-Counted Before Welding

Dosimeter No.	Oxide Wt. (mg)	Elemental Wt. (mg)	Gamma Counts Minus Background	Count Rate per min.	Count Rate per min. per mg
Std.-1	8.265	6.987	93062	186.12 ±0.52	26.64
Std.-3	8.526	7.208	96880	193.76 ±0.52	26.88
Std.-4	8.660	7.321	98494	196.99 ±0.53	26.91

^{238}U Dosimeters γ-Counted After Welding

Std.-1	8.265	6.987	95171	190.34 ±0.52	27.24
Std.-3	8.526	7.208	95622	191.24 ±0.52	26.53
Std.-4	8.660	7.321	98488	196.98 ±0.53	26.91

Table 4. Analyses for the Major Element (The Amount of the Major Element Per Unit Weight of Material)

Batch No.	U (mg/g) ±0.5%	Np (mg/g) ±0.5%	Pu (mg/g) ±0.5%
U-235-264-C	846.8		
U-235-264-CM	994.4		
U-238-ES-Z	845.4		
U-238-ES-ZM	994.8		
Pu-239-453-B-O			895.2
Pu-239-453-B-M			982.5
Np-237-NP-21		861.0	
Np-237-24HP		874.5	

Table 5. Isotopic Composition of the Major Element

Batch U-235-264-C

Isotope	Atom Percent
233	<0.0005
234	0.034 ±0.001
235	99.89 ±0.01
236	0.025 ±0.001
238	0.052 ±0.002

Batch U-235-264-CM

233	<0.0005
234	0.035 ±0.001
235	99.89 ±0.01
236	0.025 ±0.001
238	0.053 ±0.002

Batch U-238-ES-Z

233	<0.0001
234	<0.0001
235	0.0012 ±0.0001
236	<0.0001
238	99.998 ±0.001

Batch U-238-ES-ZM

233	<0.0001
234	<0.0001
235	0.0015 ±0.0001
236	<0.0001
238	99.998 ±0.001

Batch Pu-239-453-B-M

238	≤0.002
239	99.11 ±0.01
240	0.880 ±0.005
241	0.010 ±0.001
242	0.005 ±0.001
244	<0.0005

Table 5 (Cont'd)

Batch Pu-239-453-B-O

Isotope	Atom Percent
238	≤0.012
239	99.11 ±0.01
240	0.875 ±0.005
241	0.010 ±0.001
242	0.005 ±0.001
244	<0.0005

Batch Np-237-NP21

235	<0.0005
236	<0.0005
237	≥99.99 ±0.01
238	≤0.003
239	≤0.004

Batch Np-237-24HP

235	<0.0005
236	<0.0005
237	≥99.99 ±0.01
238	≤0.003
239	≤0.003

Table 6. Impurity Analysis

(Wt. ppm)

	^{235}U 264-C	^{235}U 264-CM	^{238}U ES-Z	^{238}U ES-ZM	^{239}Pu 453-B-M	^{239}Pu 453-B-O	^{237}Np NP21
Al	<1	30	5	30	1,000	15	1
As	<1	<1	1	<1		1	1
B	<0.5	<0.5	2	<0.5	0.5	0.2	<0.5
Ba	<1	<1	<1	<1	<1	<1	<1
Ca	2	2	15	2	40	8	8
Co	<1	<1	<1	<1	<1	<1	<1
Cr	<1	30	1	30	20	<1	<1
Cu	5	10	2	10	40	6	4
Fe	8	80	25	200	400	10	2
K	<1	<1	<1	<1	20	10	<1
Mg	<2	<1	2	1	100	1	<1
Mn	<1	7	<1	7	7	<1	<1
Na	<1	<1	<1	<1	<1	1	<1
Ni	<1	100	2	30	30	1	1
P	1	<1	10	<1	1	<1	<1
Pb	1	<1	<1			<1	<1
Si	<3	20	3	20	20	10	<1
Sn			5			1	
S	4	1	10	1	10	1,000	4
Ti	10	2	10	2	<1	<1	<1
^{238}U	100	100	M	M	10	5	1
V	100	20	100	200	<1	<1	<1
W	<1	<1	<1	<1			
Zn	<1	<1	<1	<1	10	2	2
Zr	1	<1	<1	2	2	<1	
^{235}U	M	M	4	3	10	1	<1
^{237}Np	<1	<1	<1	<1	1		M
^{239}Pu	<1	<1	≤10	3	M	M	1
^{244}Cm	<1	<1	<1	<1	<1	<1	<1

M - Major

Table 6. Impurity Analysis

(Wt. ppm)

	^{235}U 264-CM	^{238}U ES-Z	^{238}U ES-ZM	^{239}Pu 453-B-M	^{239}Pu 453-B-O	^{237}Np NP21	^{237}Np NP24HP
	30	5	30	1,000	15	1	2
	<1	1	<1		1	1	<1
	<0.5	2	<0.5	0.5	0.2	<0.5	<0.5
	<1	<1	<1	<1	<1	<1	<1
	2	15	2	40	8	8	2
	<1	<1	<1	<1	<1	<1	<1
	30	1	30	20	<1	<1	<1
	10	2	10	40	6	4	2
	80	25	200	400	10	2	4
	<1	<1	<1	20	10	<1	1
	<1	2	1	100	1	<1	<1
	7	<1	7	7	<1	<1	<1
	<1	<1	<1	<1	1	<1	<1
	100	2	30	30	1	1	1
	<1	10	<1	1	<1	<1	<1
	<1	<1			<1	<1	
	20	3	20	20	10	<1	3
		5			1		2
	1	10	1	10	1,000	4	4
	2	10	2	<1	<1	<1	<1
	100	M	M	10	5	1	10
	20	100	200	<1	<1	<1	<1
	<1	<1	<1				
	<1	<1	<1	10	2	2	<1
	<1	<1	2	2	<1		<1
	M	4	5	10	1	<1	<1
	<1	<1	<1	1		M	M
	<1	≤10	3	M	M	1	<1
	<1	<1	<1	<1	<1	<1	<1

Major

2

Table 7. Moisture Content of Oxides

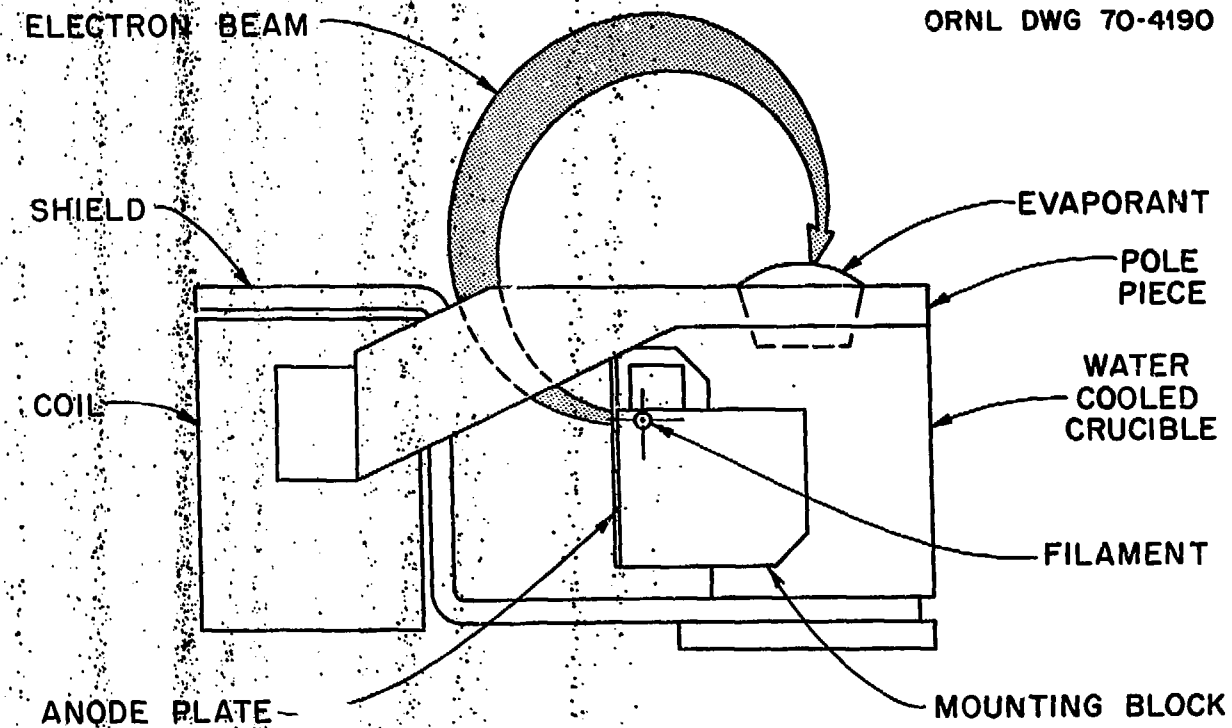
(Numbers given are ppm ±2.5%)

Batch No.	Room Temperature
U-235-264-C	574
U-238-ES-Z	698
Np-237-NP21	<10
Np-237-NP24HP	<10
Pu-239-453-B-O	1321

Preparation of Well-Defined Layers for Reaction Rate and Neutron Cross-Section Measurements

Thin films of $^{235}UO_2$ and $^{239}PuO_2$ were deposited by vacuum evaporation-condensation ($<10^{-6}$ torr) onto platinum and aluminum substrates for use in reaction rate and neutron cross-section determinations.

The material was deposited by the electron bombardment heating and vaporization of the oxide materials. A schematic of the 270°, 10 kW evaporation source used is shown in Fig. 6. Two $^{239}PuO_2$ and two $^{235}UO_2$ targets were prepared for the National Bureau of Standards to be used for obtaining reaction rates in support of the Interlaboratory LMFBR Reaction Rate Program and for reactor dosimetry in general.[3] The mass analyses of the ^{235}U and ^{239}Pu used are shown in Tables 8 and 9. The materials were deposited on 1.27-cm diam polished platinum substrates. The amount of material on each target was determined by alpha counting in a low geometry counting system. The difference in count rates among the samples made it necessary to count the targets at different positions in the low geometry counter. The ^{235}U targets were positioned 1.27-cm from the silicon detector and the ^{239}Pu targets were positioned at 15.24 or 38.10-cm depending on their thickness. The geometry factors for the ^{239}Pu analyses were determined by using a standard ^{241}Am source. The amount of ^{235}U contained on the targets was determined by destructively analyzing similar targets and comparing count rates between those prepared for NBS and those destructively analyzed. The geometry factor obtained by using the count rate and the actual ^{235}U material determined for the



270° 10KW EVAPORATION SOURCE

Table 8. ^{235}U, Batch 264C-1

Isotope	Atom Percent
234	0.0345 ±0.0009
235	99.699 ±0.002
236	0.0252 ±0.0005
238	0.241 ±0.002

Table 9. ^{239}Pu, Batch 277A

Isotope	Atom Percent
238	≤0.0002
239	99.978 ±0.002
240	0.021 ±0.002
241	0.0005 ±0.0003
242	0.0005 ±0.0003
244	<0.0002

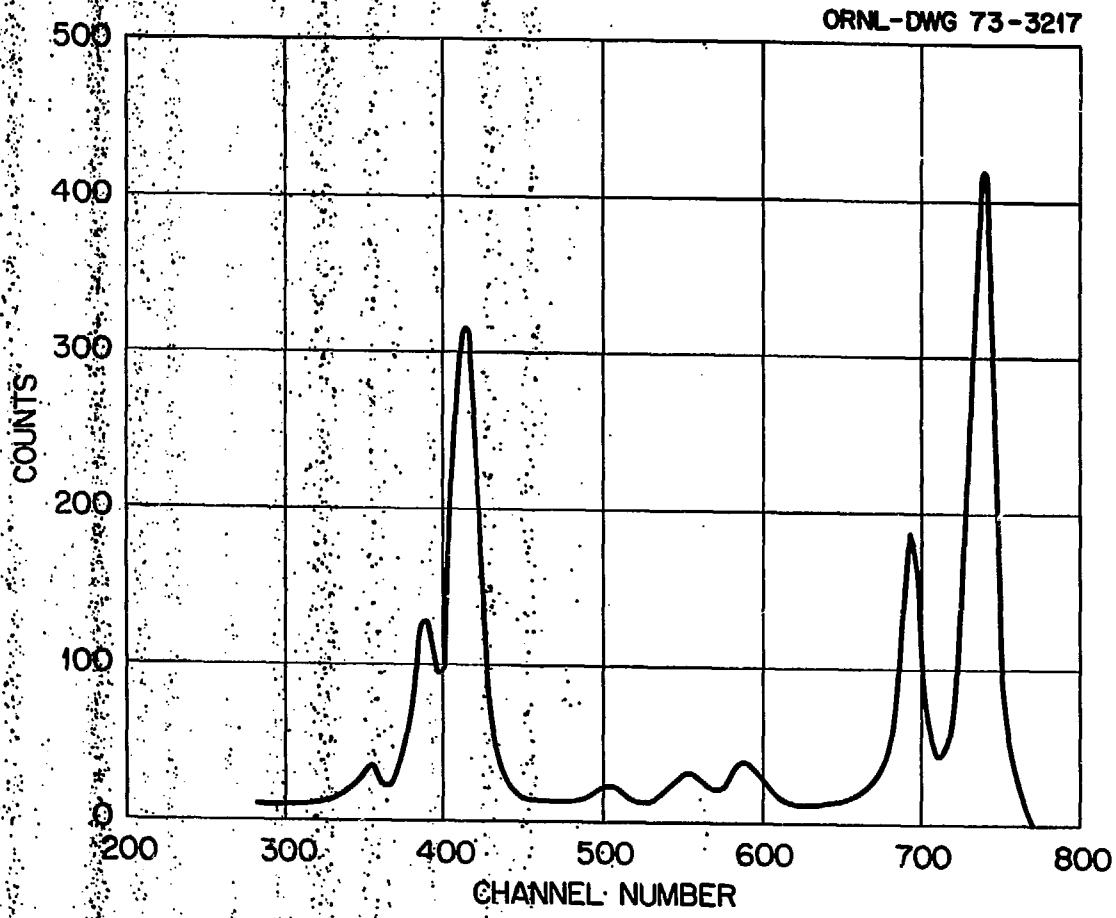
destructively analyzed ^{235}U targets was also used to calculate the amount of material contained on the NBS ^{235}U targets. As expected, the last two methods gave essentially the same results. The results for the ^{235}U and ^{239}Pu NBS targets is summarized in Table 10.

Similar procedures were used to prepare 15 $^{235}UO_2$ and 24 $^{239}PuO_2$ targets for use in fission chambers at ORNL to determine precision cross-section measurements. In each case the material was deposited by electron bombardment evaporation condensation onto a 5-cm diam spot centered on a 10-cm diam by 0.001-cm thick aluminum substrate. The substrates were located approximately 25 cm from the source material and were rotated to improve the uniformity of the deposited material.[4] Typical spectra for the ^{235}U and ^{239}Pu targets are shown in Figs. 7 and 8. In the U spectrum the two ^{234}U peaks (4.773 and 4.722 MeV) are the last two peaks shown in Fig. 7. The remainder of the peaks are due to ^{235}U and small contributions from ^{236}U and ^{238}U. The energy calibration is 1.2 keV per channel. The ^{239}Pu spectrum (Fig. 8) was obtained for a ^{239}Pu thickness of 60 $\mu g/cm^2$. It shows the 5.105 and unresolved 5.143 and 5.156 MeV alpha peaks. The mass analyses of the ^{239}Pu and ^{235}U materials is shown in Tables 9 and 11, respectively.

Although the ^{235}U targets were alpha counted to get approximate weights, gamma counting was used for the final determination because of the counting time involved. Alpha counting was used to determine the ^{239}Pu thickness. In each case a target was destructively analyzed to

Table 10. Isotope Content of NBS Targets

Target No.	^{235}U (μg)
25K-1-1	126.3 ±1.5%
25K-02-1	28.5 ±2%
	^{239}Pu (μg)
49K-01-2	13.3 ±1%
49K-4-1	472.2 ±1%



^{235}U Spectrum for a 28 $\mu g/cm^2$ Target.

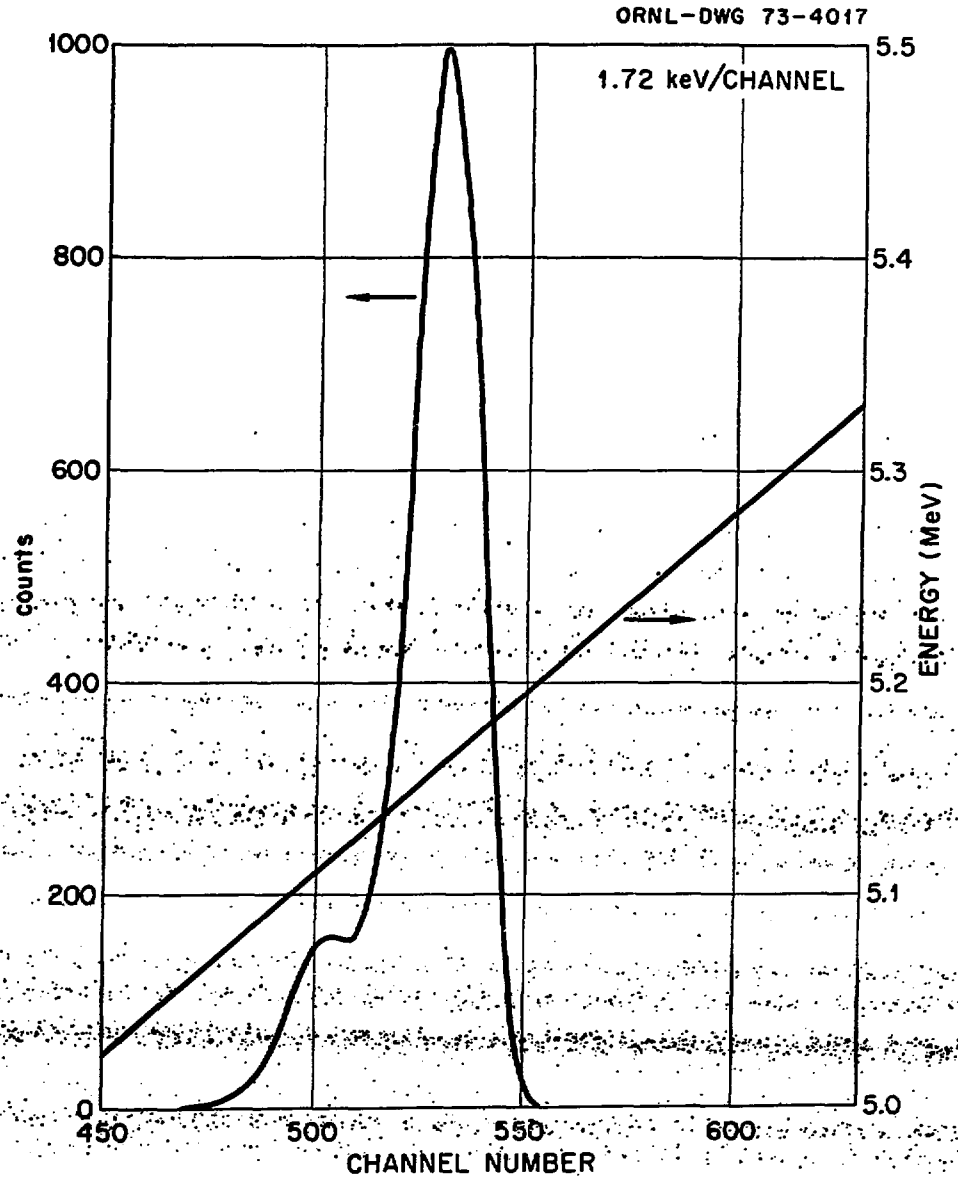

ORNL-DWG 73-4017
1.72 keV/CHANNEL
counts
ENERGY (MeV)
CHANNEL NUMBER
1000
800
600
400
200
0
5.5
5.4
5.3
5.2
5.1
5.0
450
500
550
600

Table 11. ^{235}U, Batch 264B

Isotope	Atom Percent
233	<0.0001
234	0.029
235	99.912
236	0.0165
238	0.0414

calibrate each counting system. The results are shown in Tables 12 and 13. The uniformity of the deposits was also checked by alpha counting several small areas of the foils. The foils were placed below a silicon detector which was collimated to detect only those alphas originating from a 3-mm diam spot. A schematic drawing of the system used to check the uniformity is shown in Fig. 9. The ^{235}U target was scanned in both the x and y directions and the results are shown in Fig. 10. The maximum deviation from the mean was ±5%. The uniformity of the ^{239}Pu deposit was determined around a circumference at various distances from the center of the target. The results are shown in Fig. 11. The numbers shown represent the number of counts (in thousands) obtained from a 3-mm diam spot in 100 sec. Except for the outer edge, the uniformity is well within a desired tolerance of ±5%. The outer edge variation is probably the result of a mask effect.

Preparation of Homogeneous Alloys

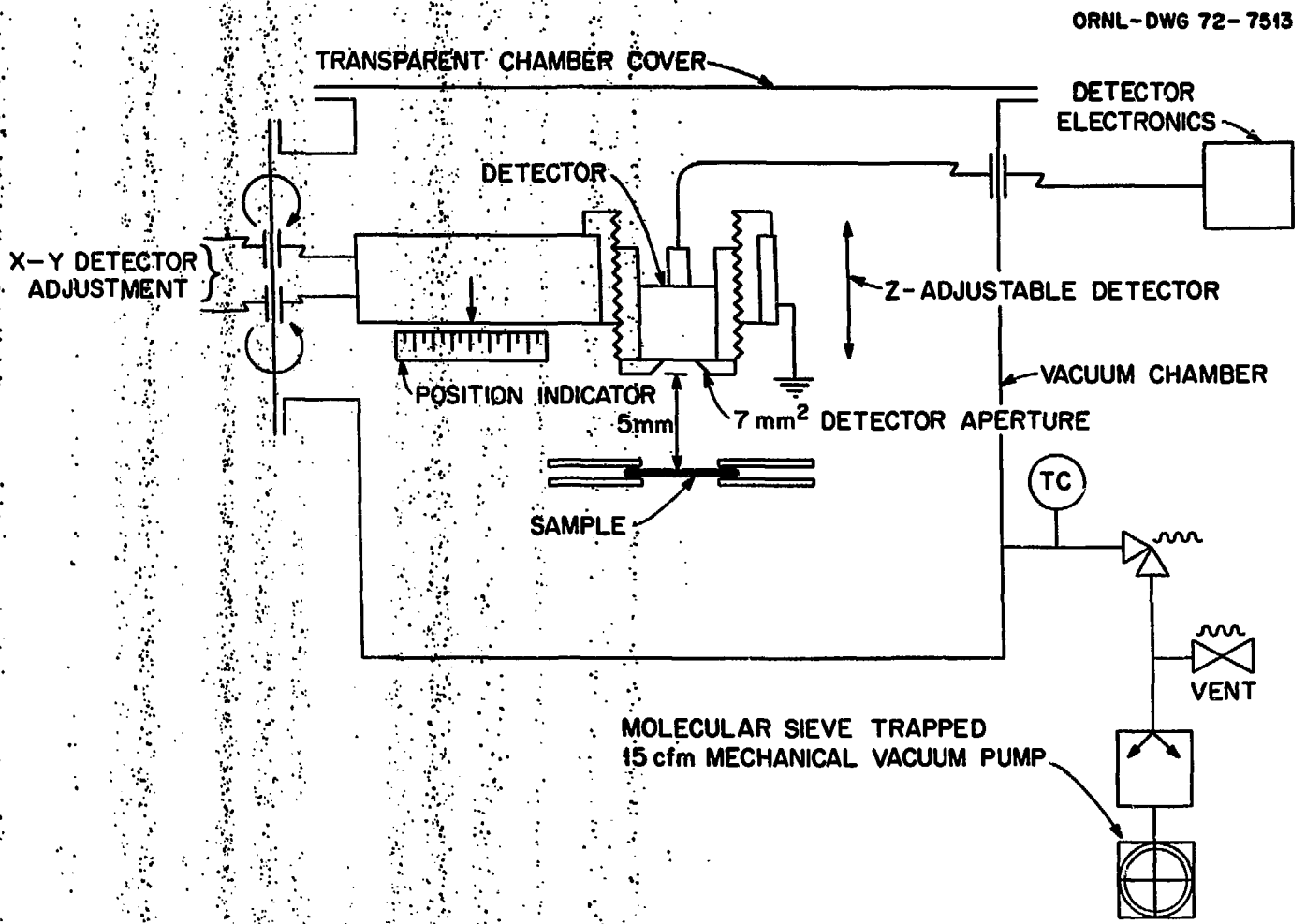
Homogeneous alloys of multigram quantities of various materials have been prepared using levitation and arc melting. These alloys have a normal concentration of ~1% of the minor component and a normal concentration variation of <±0.5%. Levitation melting is preferred over arc melting because it is easier to obtain homogenization and subsequent rapid quenching of the melt to produce the small grain size required for drawing wire (0.08-mm diam) whose concentration uniformity would be ~±0.5%

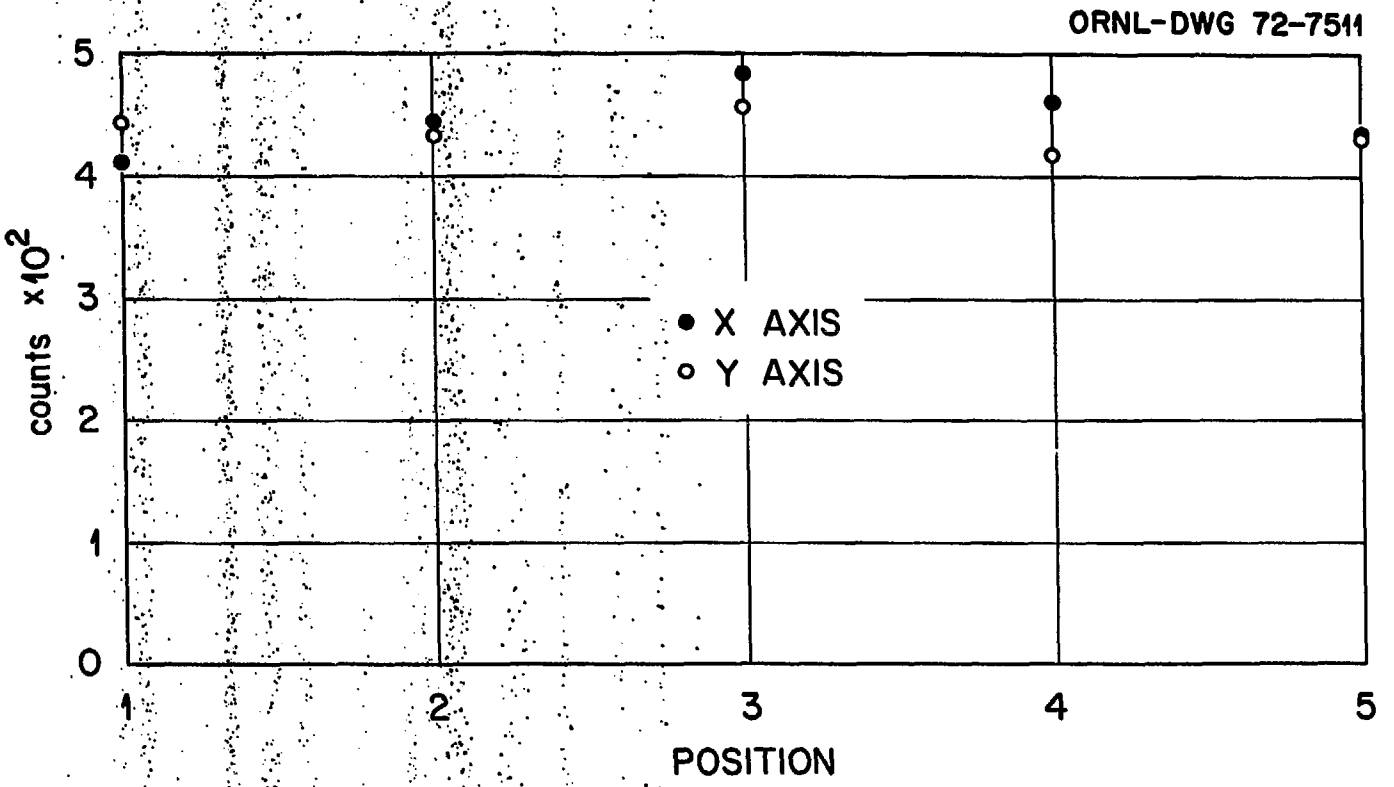
Table 12. ^{235}U Content of Fission Foils Determined by Gamma Counting

Target No.	$\mu g/cm^2$ (γ Counting) ± 0.5%
41	99
42	91.2
43	92
44	130
44A	105
45	140
46	116
46A	95
49	26.8
50	25
51	34
52	32.1
53	51.0
54	33.6
55	36

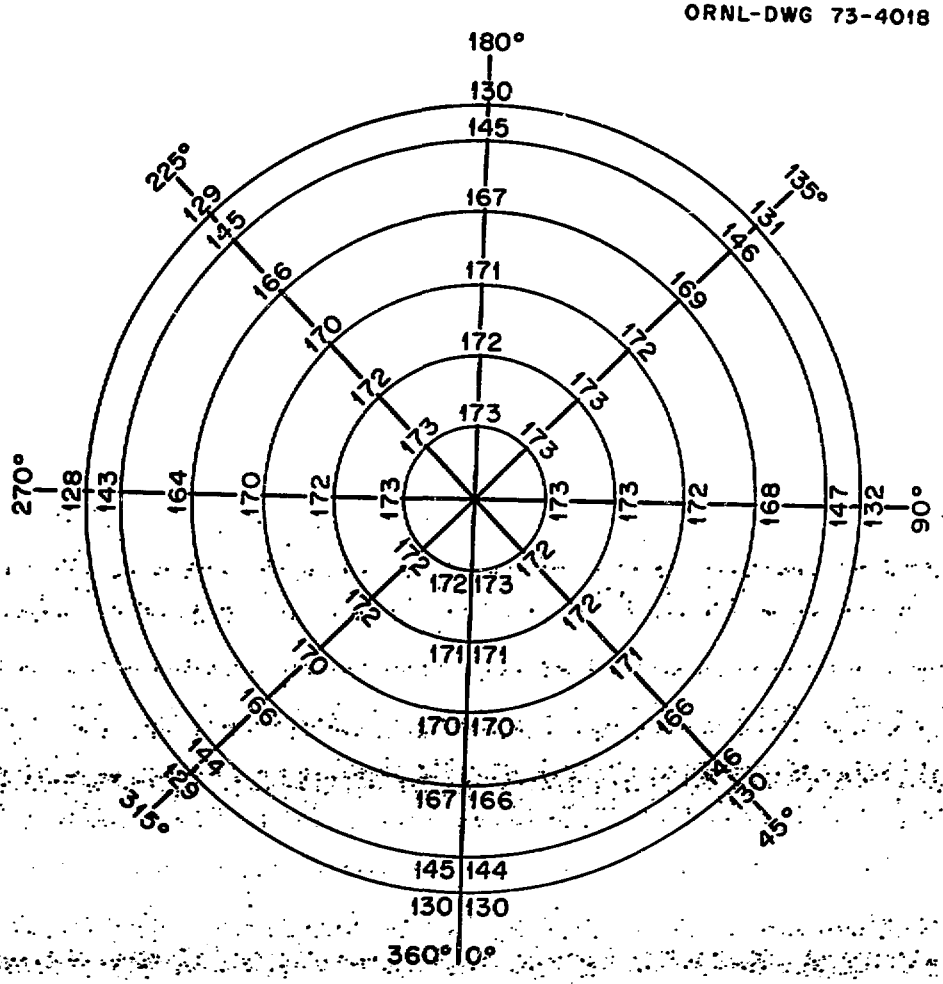
Table 13. ^{239}Pu Content of Fission Foils Determined by Low-Geometry Alpha Counting

Target No.	Thickness ($\mu g/cm^2$) ±1%
9	118.6
10	143.6
11	96.7
12	79.6
13	87.9
14	144.1
15	69.3
16	77.6
17	73.0
18	70.6
19	Destructively Analyzed
20	95.1
21	103.7
23	88.2
24	60.4
26	89.7
27	87.2
28	101.1
29	84.4
30	126.6
33	77.8
34	75.3
35	117.7
36	89.9


ORNL-DWG 72-7513
TRANSPARENT CHAMBER COVER
DETECTOR ELECTRONICS
DETECTOR
X-Y DETECTOR ADJUSTMENT
Z-ADJUSTABLE DETECTOR
VACUUM CHAMBER
POSITION INDICATOR
5mm
7 mm² DETECTOR APERTURE
TC
SAMPLE
VENT
MOLECULAR SIEVE TRAPPED
15 cfm MECHANICAL VACUUM PUMP


ORNL-DWG 72-7511
counts x10²
0
1
2
3
4
5
1
2
3
4
5
POSITION
X AXIS
Y AXIS

ORNL-DWG 73-4018



Uniformity Measurement of ^{239}Pu Target Number 29

per cm with regard to the minor component. Preliminary work has concentrated mainly on minor component alloys such as gold or cobalt with high purity vanadium for use in reactor dosimetry. Figure 12 shows a 10 g sample of vanadium containing 1.30 wt. % gold being levitated and melted using a 10 kW RF generator and a capacitor bank set at 0.06 μf to match the RF unit with the load coil. The RF coil and procedures used are described in Ref. 5. Although this work is in its early stages, it appears that very homogeneous, well-defined alloys can be prepared for use in reactor dosimetry.

Summary

The Isotopes Division of the Oak Ridge National Laboratory has established a program for providing well-defined samples to be used for reactor dosimetry and precision neutron cross-section measurements. The materials used, characterization of the materials, and procedures are described.

V-4
SERIES

References

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2. Research Materials for Nuclear Measurements, CONF-711002, p. 86, Oct. 5-8, 1971, Gatlinburg, Tenn.

3. LMFBR Reaction Rate and Dosimetry 7th Quarterly Progress Report, Dec. 1972, Jan.-Feb. 1973, W/FFTF 732556, Hanford Engineering Development Laboratory, Operated by Westinghouse Hanford Co.

4. H. L. Adair, Preparation of Well-Defined Deposits of $^{235}UO_2$. To be published in Nucl. Inst. and Methods.

5. ANL-7398.

Figure List