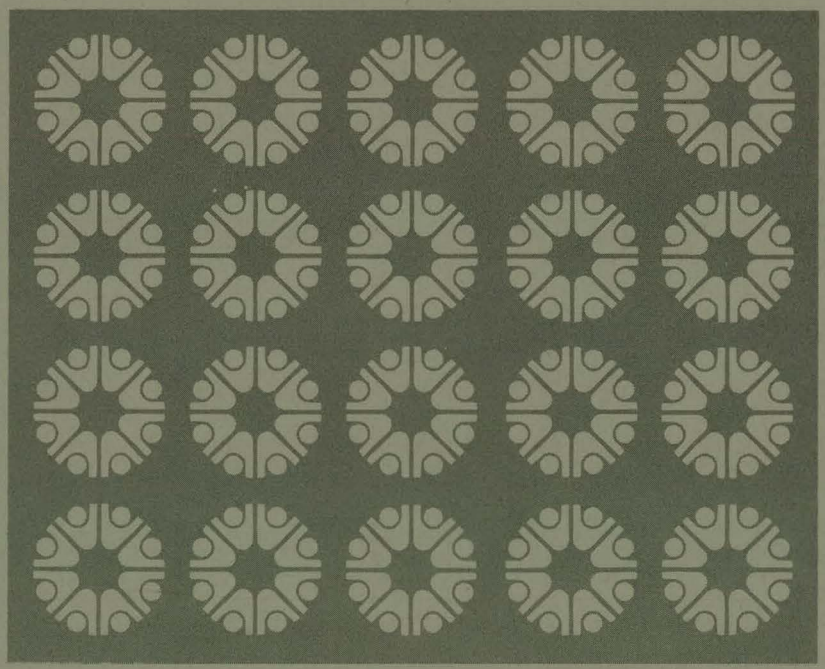
BNWL-B-196

Battelle
Pacific Northwest Laboratories
Richland, Washington 99352

This report is intended primarily for internal use by the sponsoring organization and Battelle.

ANALYSIS OF THORIUM-URANIUM CARBIDE COATED FUEL BEADS



BNWL-B-196

DISCLAIMER

INFORMATION CONCERNING USE OF THIS REPORT

PATENT STATUS

This document copy, since it is transmitted in advance of patent clearance, is made available in confidence solely for use in performance of work under contracts with the U. S. Atomic Energy Commission. This document is not to be published nor its contents otherwise disseminated or used for purposes other than specified above before patent approval for such release or use has been secured, upon request, from the Chief, Chicago Patent Group, U. S. Atomic Energy Commission. 9800 So. Cass Ave., Argonne, Illinois.

PRELIMINARY REPORT

This report contains information of a preliminary nature prepared in the course of work under Atomic Energy Commission Contract AT(45-1)-1830. This information is subject to correction or modification upon the collection and evaluation of additional data.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

54-1100-057 (5-67)
AEC-RL RICHLAND WASH

BNWL-B-196
UC-4

ANALYSIS OF THORIUM-URANIUM CARBIDE COATED FUEL BEADS*

D. M. Robertson

Battelle
Pacific Northwest Laboratories
Richland, Washington 99352

July 12, 1972

*This report is based on work performed under United States Atomic Energy Commission Contract AT(45-1)-1830.

TABLE OF CONTENTS

[redacted]

LIST OF FIGURES

LIST OF TABLES

BNWL-B-196

ANALYSIS OF THORIUM-URANIUM CARBIDE COATED FUEL BEADS

D. M. Robertson

ABSTRACT

Thorium-uranium fuel spheres are coated with pyrolytic carbon and silicon carbide (SiC) for fuel containment purposes. Most methods of fuel assay involved grinding the beads followed by acid dissolution of fuel and leaching of the residue. The present work involved gas ignition (volatilization) of coating material followed by acid dissolution. This process converts a five-gram bead sample to a clear solution (no residue) in less than 1 hour. Subsequent ^{235}U assays agreed well with other methods.

ANALYSIS OF THORIUM-URANIUM CARBIDE COATED FUEL BEADS

I. Introduction

Thorium-uranium carbide fuel spheres are coated with pyrolytic carbon and silicon carbide (SiC). The fuel has a nominal 200 micrometers (μm) diameter and the coated sphere or bead is 500 μm. The coatings, particularly the SiC, produce a rather inert and impregnable barrier around the fuel. This results in good containment during irradiation. It also presents a problem of assay involving complete recovery and measurement of fuel material.

Some preliminary studies of coating removal using single beads indicated the possibility of ignition de-coating and an alternative procedure to grind and leach techniques[1] for fuel assay. That preliminary work has been reported[2].

The present work was undertaken to study the feasibility of scale-up from the single bead to a few grams that would constitute an analytical sample representative of the bulk fuel material.

II. Experimental

A. Weighing a Sample Aliquot

Some tests were made to determine the conditions necessary for accurately and reproducibly weighing an aliquot of beads. Silica boats were ignited repeatedly up to 1100C, cooled in a dessicator and weighed[a] to 0.0001 g. The range in boat weights over several ignition cycles was insignificant at the representative sample size. Data are summarized in Appendix A.

(a) Balance was adjusted for accuracy using NBS certified weights.

[redacted]

Next an aliquot of beads was placed in an ignited boat, weighed, heated at 200°C for one hour and re-weighed. The heating and weighing were repeated several times. There was no change in the "as received" bead weights during these tests. The data are summarized in Appendix B.

The practice used in the remainder of the work was to heat 200°C for one hour and weigh in case the moisture content of the bulk sample possibly changed with time.

Two kinds of atypical beads were found in most samples. There were so few of the atypical kind that they would not significantly alter the fuel assay of a 5 g sample. Examples of atypical beads are shown in Figure 1.

The reweighing experiments indicate that weight aliquots of sample will have an uncertainty of less than ±0.1 percent.

B. Ignition in Oxygen

The ignition of the beads in oxygen removes the outer carbon layer and stops at the second layer, the silicon carbide coat, see Figure 2.

Samples 1 and 2 were ignited in silica boats at about 800°C in a stream of oxygen. Sample 1 lost 32.2 percent of the original sample weight after 1-hour of ignition. A second 1-hour ignition produced no weight change. Sample 2 lost 32.3 percent of the original sample weight. A second 1-hour ignition of this sample produced no weight change.

Subsequently 32 aliquots of beads were ignited in oxygen. The average weight loss was 32.259 percent. The standard deviation

of a single value was ±0.052 percent. The data are tabulated in Appendix C. An assay of fuel content (of a 5 gram sample of beads) may be expected to reflect this uncertainty due to outer carbon coat variation. There may be some compensation due to correlation of fuel and outer carbon coat of individual beads.

The oxidation results in a size reduction and a change in surface characteristics from dull to shiny and glassy, see Figure 3. The ignition was accompanied by light emission which stopped abruptly upon completion of reaction (about 10 minutes for a 5 gram sample).

No problems were encountered in volatilization removal of the outer carbon coat in silica boats or other ignition vessels used in later experiments.

C. Ignition in Chlorine

The ignition in chlorine gas is carried out to remove the second coat, the SiC layer. Quantitative reaction of SiC in Cl_2 at 1000-1050°C in 1-2 hours was reported for powder and crystals[3] and at 1200°C for 2 hours on scrap.[4] This work indicated that the carbide was chlorinated and volatilized and that elemental carbon was not affected by the process. Previous single bead ignitions were conducted at 1100°C.[2]

Three ignition vessels (see Appendix D) and two furnaces, a Fisher Micro Combustion and a Lindberg Hevi-Duty, each capable of producing a temperature of 1200°C, were used. Experimentation with the 3 systems will be described below. The outer carbon coat was removed with oxygen prior to the experimentation described.

[redacted]

1. Ignition in Silica Boats

Sample one (1.5 g of beads) was ignited for 2 hours at ~950°C in Cl_2. The weight loss was 20.8 percent of original weight. The beads were still shiny as shown in Figure 4a. A second 2-hour ignition in Cl_2 was made. There were both dull and shiny beads following this ignition. The top layer of beads in the boat appeared to have been stripped of SiC. Most obvious was white spots on the top most beads. These appearances are shown in Figure 4b. The white areas were found to be high in thorium indicating some beads had ruptured during this process.

Sample 2 (~5 g) was ignited in a larger boat. However the beads were still more than one bead deep. A 2.5 hour chlorination at ~950°C produced a loss of 16.4 percent of original weight.

2. Ignition In Flattened Quartz Tube

In an attempt to get better Cl_2 contact with sample during ignition, a flattened quartz tube was used. Sample 2 was transferred to this tube. Two more ignitions were carried out totaling 2 hours. The SiC appeared to be removed from an estimated three-fourths of the beads. This estimate is based on the reaction of the beads during a second oxygen contact (see Figure 5).

3. Ignition In Quartz Frit Tube

A third ignition system was tested. The tube with quartz frit to hold the sample was placed in a vertical position. Gas flow in this system from the bottom produced a very mobile bed of beads, essentially a fluidized bed, and could be expected to result in improved gas-solid contact and a more nearly uniform exposure of the beads.

Several aliquots of beads were ignited in chlorine at 1100-1200°C in the frit tube. Visual examination of the beads indicated removal of all SiC. A few beads from each sample were assayed with an electron microprobe for silicon. The assays verified that the silicon had been removed and that 5 gram samples could be successfully processed.

The adequacy of the chlorine ignition was further tested by making a second oxygen ignition, i.e., ignite the fuel beads in oxygen, ignite them in chlorine,and then ignite them again in oxygen. The second oxygen ignition will volatilize the inner carbon coat and convert the fuel to oxides if the SiC has been removed. The residue from the second oxygen ignition was heated with 8M HNO_3-0.05M HF which produced complete dissolution and a clear solution, indicating complete removal of SiC. Further along in the work some dissolved samples were found to contain a few black specks which electron microprobe assay indicated were carbon. These are probably pieces of inner carbon coat that broke away and remained in a cooler portion of the second oxygen ignition vessel.

Samples 12 through 16 were ignited with the frit tube with chlorine for 1.5 hours. At that point a test (electron microprobe) was made on beads (samples 17 through 43) ignited for only 0.5 hour. The SiC was found to have been removed from the latter samples. It is possible the ignition time could be further reduced. Weighing to determine weight loss from chlorine ignition was attempted but unsuccessful. The ignited samples continually increased in weight in the balance atmosphere. The nominal weight loss was 15 percent.

D. Second Oxygen Ignition

Both oxygen ignition[1] and wet oxidation[5] could be used on the beads following outer carbon coat and SiC coat removal. The dry oxidation is much faster and was the choice in this work.

Good containment and dissolution of the residue in the ignition vessel are required. The beads react like popcorn during conversion of the fuel core to oxide and the oxide (powder) sticks to the vessel surface. The oxidation vessel was a 100 ml platinium dish covered by a 1/4 inch quartz plate with a grove to admit the oxygen delivery tube (also quartz). The ignition accompanied by light emission converted the black colored beads to a grey powder (somewhat agglomerated).

Final preparation for ^{235}U analysis was dissolution of the powder with 8M HNO_3-0.05M HF.

E. Determination of Uranium-235 Content

The uranium-235 content was determined by isotopic dilution with a mass spectrometer, certified and calibrated volumetric equipment, and ^{233}U standardized against the NBS 950 uranium weight standard.

The usual practice was to dilute the dissolved sample to volume, V_1, and make 2 equivalent dilutions of V_1 to which ^{233}U spike was added. Then two mass spectrometer filaments were loaded from each of the 2 equivalent dilutions making 4 assays of each bead sample. It will be noted in the table of results that often more than 2 dilutions and/or 4 assays were made. More assays were made to better assess experimental

errors in this development work.

Samples of mixed ^{233}U-NBS 950 and samples of NBS U930 isotopic standard (~93% ^{235}U) were interspersed with bead samples to correct for measurement biases.

Two 5 gram samples of beads (#44 and #45) were ground in a mortar and pestle. Except for filtration and leaching steps they were treated and assayed by the same procedure used on the gas ignition oxide residue.

A final sample (#46) was placed in a mortar and pestle, spiked with 5 milligrams of ^{233}U in solution, ground, leached and directly assayed. The only measurement uncertainties involved in this assay are the weight of sample, the (5 ml) volume of ^{233}U spike and the concentration of spike. These are estimated to be $\leq \pm 0.01$, ± 0.05 and ± 0.07 percent respectively.

III. Analytical Results

The data obtained from the three ground-up samples are compared to the gas ignition data in Table I.

The isotopic data are contained in Table II. Data on samples #43 and #46 are reported. Sample 43 was processed through an ion exchange procedure to isolate the uranium which should result in better mass spectrometer data than straight dissolved sample. Sample #46 (as noted above) has the least processing, i.e., should have received the least contamination due to processing.

TABLE I

RESULTS OF ASSAY OF FUEL BEADS FOR ^{235}U

Sample No.	Sample Size grams	Weight Percent ^{235}U average(1)
12	5.0366	4.244
13	5.0368	4.240
16	5.0578	4.264
18	5.1864	4.234
20	5.4342	4.256
24	5.1328	4.244
33	5.0386	4.233
37	5.0369	4.272
40	5.2367	4.236
42	7.7038	4.283
43	7.6224	4.229
		Avg. 4.249 ± 0.005
44	5.1104	4.243
45	5.0106	4.246
46	5.0547	4.250

(1) Table of detailed data in Appendix E.

TABLE II

URANIUM ISOTOPIC COMPOSITION OF FUEL BEADS

Sample No.	Atom Percent[1]			
	234	235	236	238
43	0.727 ± 1	93.205 ± 8	0.279 ± 1	5.788 ± 8
46	0.727 ± 1	93.198 ± 8	0.279 ± 1	5.796 ± 8

[1] Errors are at the 95 percent confidence limit.

IV. Method Evaluation

The data (of Table I) show good agreement among methods. The choice of method for bead processing and methods for final ^{235}U assay probably depend heavily on the number of samples to be analyzed and to a smaller extent on available equipment.

The gas ignition system can be established to handle a large number of samples per operator, i.e., processing time is relatively short and manipulation of sample is minimal. These features are also advantageous in processing irradiated material. Hot (irradiated) samples may require special off-gas trapping, depending on existing facilities, which could be a disadvantage.

Isotopic dilution assay is expensive if a mass spectrometer facility has to be established for that purpose. However if the equipment is available, that measurement system is as simple and inexpensive to calibrate and apply for accurate work as any other. The preparation method produces a clean solution of fuel adequate for various assay methods.

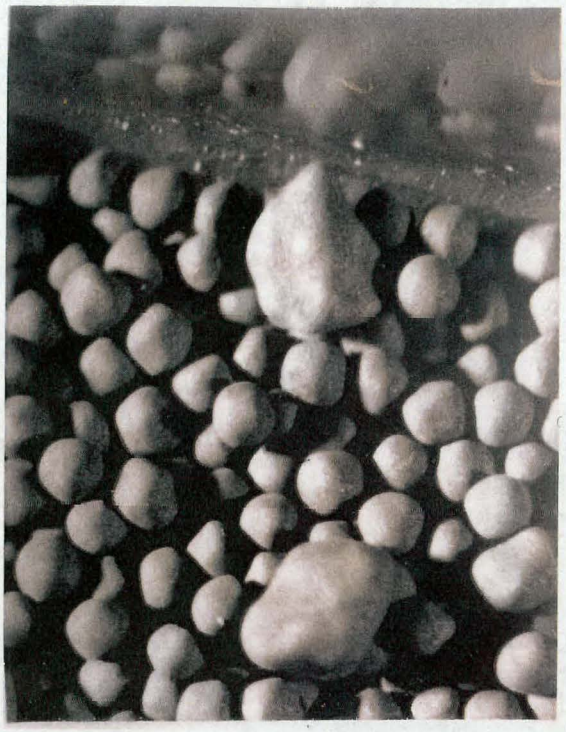


Fig. 1a. Atypical bead agglomerates. Oblique incident light X15.

Fig. 1b. Atypical white bead coat. Oblique incident light X45

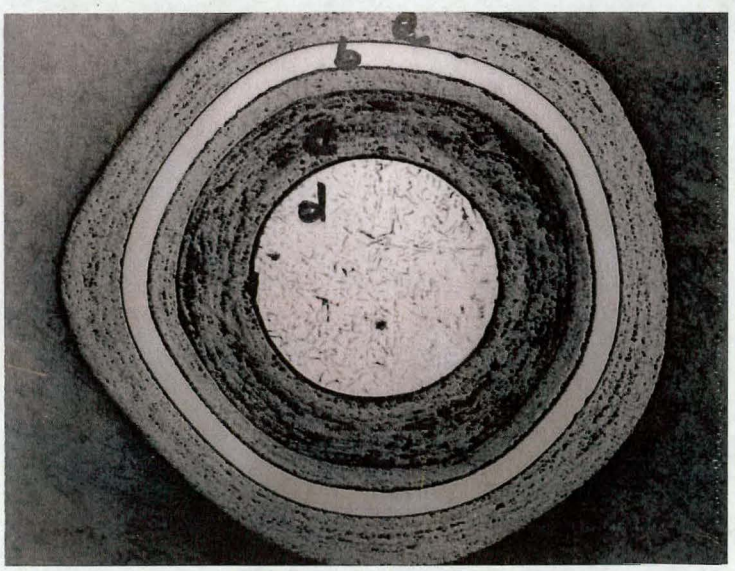


Fig. 2 Cross section of fuel bead. (a) outer carbon coat, (b) SiC coat, (c) inner carbon coat, (d) fuel kernel, X150.

Fig. 3a. Fully coated fuel beads. Oblique incident light at X15.

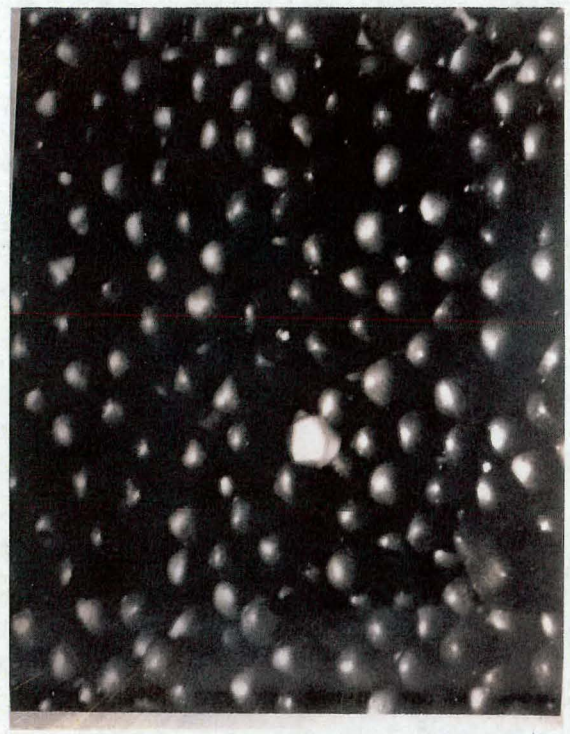


Fig. 3b. Same beads as in Fig. 3a but with the first or outer coat removed Oblique incident light X15.

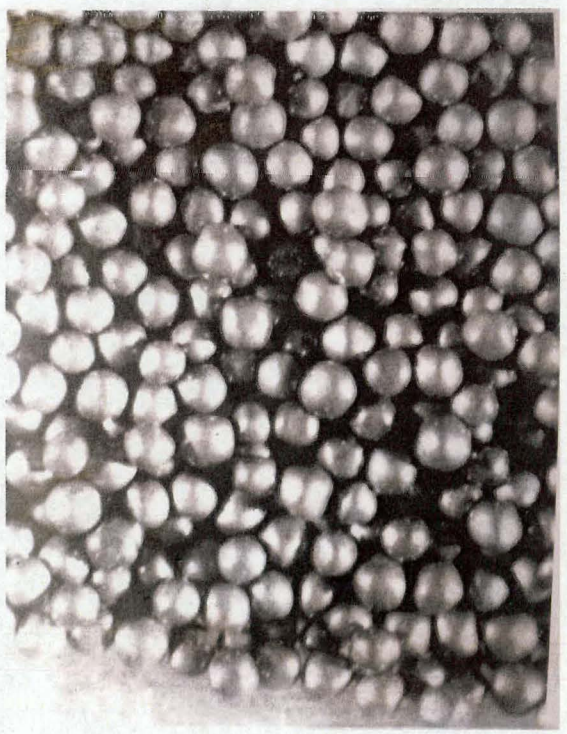


Fig. 4a. Beads showing shiny coat after 2 hrs. in chlorine at 950C. Oblique incident light X15.

Fig. 4b. Beads after 4 hrs. in Cl_2 at 950C. Both dull and shiny beads can be seen as well as white spots. Oblique incident light X20.

Fig. 5. Oxidized beads after having been stripped of SiC coat. A significant number were unreacted. Oblique incident light X20.

V. References

1. R. Lingjaerde, L. Podo,"Chemical Analysis of Fuel Particles," DP-Report-264, April 1964.

2. D. M. Robertson, et al.,"Investigations of Thorium-Uranium Carbide Coated Fuel Spheres," BNWL-B-97, May 1971.

3. J. Nickle and C. V. Braunmuhl," Chlorierung and Analyse Hochschmelzender Carbide," Z. Anal. Chem. 221, 223-228 (1966).

4. A. V. Serebryakova, et al., "Production of Silicon Tetrachloride from Wastes of Abrasives Plants," Kim. Prom. 41, 1965.

5. A. W. Mosen and G. Buzelli, "The Use of Perchloric Acid for Dissolution of Graphite and Other Carbonaceous Material," GAMD-567, Sec. 1, March 1971.

VI. Appendix

A. Reproducibility of Weighing Ignited Silica Sample Boats

Boat #1 Weight (grams)	Date	Boat #2 Weight (grams)	Date
21.6860	3-31-72	21.8012	4-26-72
21.6858	3-31-72	21.8012	5-5-72
21.6859	4-3-72	21.8012	5-8-72
21.6858	5-1-72		
21.6864	5-4-72		

B. Drying and Weighing Fuel Sample

Test Sample 1

Weight of"as received"beads	1.5036g
Heat 1 hour at 200C	
Reweight of beads	1.5035g

Test Sample 2

Weight of boat and beads	26.5030
Weight of (ignited) boat	21.6859
Bead Weight	4.8171
Heat 1 hour at 200C	
Reweight of beads and boat	26.5031
Repeat heating and weighing	26.5032
Repeat heating and weighing	26.5032

Appendix

C. Weight Loss From Oxygen Ignition of Outer Carbon Coat

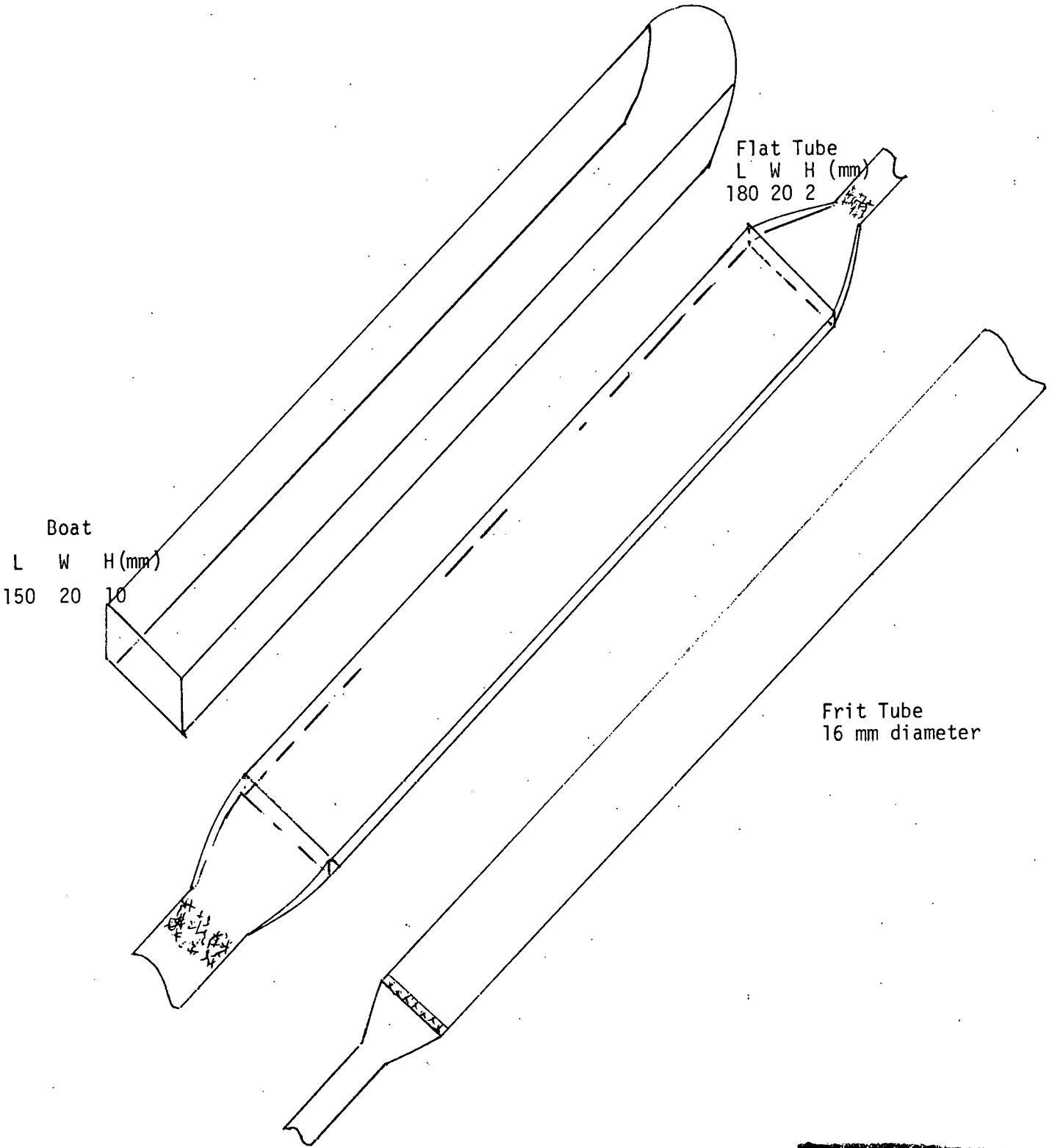
Sample No.	Sample Weight (grams)	Weight Loss (grams)	Weight Loss Percent
12	5.0366	1.6224	32.212
13	5.0368	1.6276	32.314
14	5.0989	1.6471	32.303
15	5.0226	1.6205	32.264
16	5.0578	1.6311	32.249
17	5.0209	1.6170	32.205
18	5.1864	1.6726	32.250
19	5.0211	1.6202	32.268
20	5.4342	1.7541	32.279
21	5.0345	1.6206	32.190
22	5.1338	1.6550	32.237
23	5.0032	1.6119	32.217
24	5.1328	1.6545	32.234
25	5.0156	1.6175	32.249
26	5.0025	1.6147	32.279
27	5.0413	1.6242	32.391
28	5.0685	1.6363	32.284
29	5.0727	1.6355	32.241
30	5.0610	1.6328	32.262
31	5.1109	1.6494	32.272
32	5.0336	1.6222	32.227
33	5.0386	1.6242	32.235
34	5.0169	1.6189	32.269
35	5.0329	1.6231	32.250
36	5.0861	1.6412	32.268
37	5.0369	1.6261	32.284
38	5.0911	1.6453	32.317
39	5.1259	1.6491	32.172
40	5.2367	1.6897	32.266
41	4.9883	1.6092	32.260
42	7.7038	2.4865	32.276
43	7.6224	2.4603	32.277

Average 32.259
± 0.052

[redacted]

Appendix

D. Quartz Ignition Vessels Used



Appendix

E. TABLE OF INDIVIDUAL ANALYSIS RESULTS

Sample No.	Sample Weight	Weight Percent ^{235}U Sample Average	Dilution No.	Mass Spectrometer Sample Analysis Wt.% ^{235}U
12	5.0366	4.244	12-1	4.246 4.239 4.242 4.244 4.227 4.243
			12-2	4.253 4.242
13	5.0368	4.240	13-1	4.252 4.250 4.249 4.234 4.234 4.248
			13-2	4.234 4.231
			13-3	4-244 4.237
16	5.0578	4.264	16-1	4.258 4.270
			16-2	4.266 4.263
18	5.1864	4.234	18-1	4.248 4.236 4.218
			18-2	4.231 4.235
20	5.4342	4.256	20-1	4.260 4.252
			20-2	4.262 4.249

[redacted]

Appendix

E. (continued)

Sample No.	Sample Weight	Weight Percent ^{235}U Sample Average	Dilution No.	Mass Spectrometer Sample Analysis Wt. % ^{235}U
24	5.1328	4.244	24-1	4.251 4.241
			24-2	4.243 4.244 4.236
33	5.0386	4.233	33-1	4.221 4.225
			33-2	4.252 4.246
			33-3	4.236 4.233
			33-4	4.225 4.221
37	5.0369	4.272	37-1	4.271 4.276
			37-2	4.276 4.285 4.296 4.293
			37-3	4.262 4.266
			37-4	4.261 4.267
40	5.2367	4.236	40-1	4.231 4.226
			40-2	4.241 4.239 4.249
42	7.7038	4.283	42-1	4.281 4.273
			42-2	4.283 4.292

[redacted]

Appendix

E. (continued)

Sample No.	Samples Weight	Weight Percent ^{235}U Sample Average	Dilution No.	Mass Spectrometer Sample Analysis Wt. % ^{235}U
43	7.6224	4.229		
			43-1	4.236
				4.233
			43-2	4.225
				4.221
44	5.1104	4.243		
			44-1	4.222
				4.246
				4.233
				4.232
			44-2	4.276
				4.269
			44-3	4.223
				4.228
			44-4	4.248
				4.235
45	5.0106	4.246		
			45-1	4.263
				4.257
			45-2	4.240
				4.240
46	5.0547	4.250		
				4.271
				4.236
				4.252
				4.250
				4.249
				4.256
				4.246
				4.247
				4.249
				4.240
				4.246
				4.258

[redacted]

Appendix

F. Determination of ^{235}U Content of Fuel Beads by Gas Ignition-Isotopic Dilution Method

Stepwise Procedure

1. Heat a sample of beads in an oven at 200°C for 1 hour.

2. Cool beads in dessicator, weigh out 5 grams of beads to ±0.0001 grams.

3. Place beads in quartz frit tube, place the tube in a tube furnace, raise the temperature to 800°C, adjust oxygen flow to 500 milliliters per minute and ignite for 10 minutes (see note 1).

4. Stop oxygen flow, open furnace and cool tube to around 600°C. Admit Cl_2 at 500 ml per minute for 1 minute. Close furnace and raise temperature to 1100-1200°C. Admit Cl_2 at 500 ml per minute and ignite for 30 minutes. Stop Cl_2 flow, remove tube from furnace and cool.

5. Remove beads from tube into a 100 ml platinum dish (see note 2). Cover dish with quartz plate, admit oxygen to dish through quartz delivery tube at 200-500 ml per minute. Raise temperature to ~800°C (light red color of platinum dish). Continue until reaction appears to cease and residue is grey powder. Cool.

6. Add 10 ml of 8N HNO_3-0.05N HF to residue. Heat to 80-90°C until sample dissolves (about 15 minutes). Evaporate to remove HF and reduce acid volume.

7. Transfer solution to a certified 100 ml vol. flask and make to volume with water.

8. Using calibrated pipets transfer 100 microliters (µℓ) of sample and 100 µℓ of 1 g/ℓ ^{233}U spike to a 25 ml vol. flask and dilute to volume with water. Prepare a duplicate dilution in the same manner

9. Load 2 mass spectrometer filaments from each of the 25 ml vol. flasks. Use about 0.1 µℓ to load the filament (see note 3).

10. Calculate the ^{235}U content (see Appendix G).

Note 1. In beginning work one should watch the sample during ignition and recognize the rather abrupt end of light emission indicating complete oxidation rather than using an arbitrary ignition time.

Note 2. The sample often becomes charged and sticks to the tube. Xylene or other inert liquid may be needed to wash the sample from the tube

Note 3. The optimum load for the mass spectrometers used in this work is about 2 nanograms of uranium. Dilution volumes may be adjusted to accommodate other instrument requirements. At the 2 nanogram level reagents and equipment must be particularly free of uranium contamination.

Appendix

G. Calculation of ^{235}U Content of Fuel Beads from Mass Spectrometer Isotopic Dilution Data

Let: R be the atom ratio $^{233}U/^{238}U$
N be number of atoms
and subscripts:

3 = ^{233}U

8 = ^{238}U

5 = ^{235}U

s = spike solution (quite pure ^{233}U)

w = U weight standard solution (NBS 950)

m = mixed spike and weight standard

Then,

$$(1)\quad R_m = \frac{N_{3s} + N_{3w}}{N_{8s} + N_{8w}} \qquad (2)\quad Rs = \frac{N_{3s}}{N_{8s}}$$

substituting Eq. (2) into Eq (1)

$$(3)\quad R_m = \frac{N_{3s} + N_{3w}}{\frac{N_{3s}}{R_s} + N_{8w}} \qquad (4)\quad Rw = \frac{N_{3w}}{N_{8w}}$$

substituting Eq. (4) into Eq. (3)

$$(5)\quad R_m = \frac{N_{3s} + R_w N_{8w}}{\frac{N_{3s} + R_s N_{8w}}{R_s}}$$

$$(6)\quad N_{8w} (R_m R_s - R_w R_s) = N_{3s} (R_s - R_m)$$

$$(7)\quad N_{8w} = \frac{N_{3s} (R_s - R_m)}{(R_s) (R_m - R_w)}$$

from Eq. (2), Eq's (8) and (9) are equivalent to Eq. (7)

$$(8)\quad N_{3s} = N_{8w}\ \frac{(R_s)(R_m - R_w)}{(R_s - R_m)}$$

$$(9)\quad N_{8s} = N_{8w}\ \frac{(R_m - R_w)}{(R_s - R_m)}$$

Through the measured R's the atoms in the spike are known in terms of the NBS weight standard

Now let:

V - volume

C - Concentration

M - Mass of an atom

and subscripts

A - sample A

m_2 - Mix of spike and sample A

from parallel development to Eq. (7)

$$(10)\quad N_{8A} = N^*_{3s}\ \frac{(R_s - R_{m_2})}{R_s\,(R_{m_2} - R_A)}$$

$$N_{3s} = \frac{C_3 V_{3s}}{M_3}$$

$$N_{3s}{}^* = \frac{C_3\, V^*_{3s}}{M_3}$$

$$N_{3s}{}^* = N_{3s}\ \frac{V^*_{3s}}{V_{3s}}$$

that is, the volume of spike used in the weight standard mix, V_{3s}, and the volume of sample mix, V^*_{3s}, are likely to be different.

$$(11)\quad N_{8A} = N_{3s}\ \frac{V^*_{3s}}{V_{3s}}\ \frac{(R_s - R_{m_2})}{(R_s)(R_{m_2} - R_A)}$$

substituting for N_{3s} from Eq. (8)

$$(12)\quad N_{8A} = N_{8w}\ \frac{V^*_{3s}}{V_{3s}}\ \frac{(R_s - R_{m_2})}{(R_s - R_m)}\ \frac{(R_m - R_w)}{(R_{m_2} - R_A)}$$

In the present work

$$R_s \simeq 10^6$$

$$R_A \simeq 10^{-6}$$

$$R_w \simeq 10^{-6} \qquad \text{and } N_{8A} \sim N_{8w} \frac{R_m}{R_{m_2}}$$

Thus the atoms of ^{238}U in the sample are known in terms of the NBS weight standard. By interspersing measurements of Rm and Rm_2 instrumental bias is removed. This scheme requires particular care to protect the spike - weight standard mix (Rm) from contamination.

At this point the sample is known in terms of number of atoms and a weight is needed.

Let

W = weight

Subscript T = total weight (in sample)

(13) $W = NM$, or $N = W/M$, and $N_{8A} = \frac{W_{8A}}{M_8}$

substituting Eq. (13) into Eq. (12)

(14) $$\frac{W_{8A}}{M_8} = \frac{W_{8w}}{M_8} \frac{V^*_{3s}}{V_{3s}} \frac{(R_s - R_{m_2})}{(R_s - R_m)} \frac{(R_m - R_w)}{(R_{m_2} - R_A)}$$

(15) and $W_{8T} = W_{8A} \frac{V_{8T}}{V_{8A}}$ where W_{8T} is the total weight of ^{238}U in the sample.

(16) $$W_{8T} = \frac{V_{8T}}{V_{8A}} \frac{V^*_{3s}}{V_{3s}} (W_{8w}) \frac{(R_{m_2} - R_s)(R_m - R_w)}{(R_m - R_s)(R_{m_2} - R_A)}$$

[redacted]

This can be converted as follows to total weight of ^{235}U (W_{5T}) in the sample, which is the number required:

Let

$R' = {}^{235}U/{}^{238}U$ atom ratio

$R'' = {}^{235}U/{}^{238}U$ atom ratio corrected for mass spectrometer bias

A = atomic weight

then

$$(17)\quad \frac{W_5}{W_8} = \frac{N_5 A_5}{N_8 A_8}$$

$$(18)\quad W_{5T} = R'_A \frac{A_5}{A_8} W_{8T}$$

By interspersing NBS U930 isotopic standard with sample a correction for instrumental bias can be made. NBS 930 is 93 percent ^{235}U, very close to the sample isotopic composition.

$$\frac{\text{NBS certified R' for NBS U930}}{\text{measured R' for NBS U930}} = \text{bias correction factor}$$

measured R'_A x correction factor = R''_A

and

$$(19)\quad W_{8T} = \frac{W_{5T}}{R''_A \frac{A_5}{A_8}}$$

substituting Eq. (19) in Eq. (16)

$$(20)\quad W_{5T} = R''_A \frac{A_5}{A_8} \frac{V_{8T}}{V_{8A}} \frac{V^*_{3s}}{V_{3s}} W_{8w} \frac{(R_s - R_{m_2})(R_m - R_w)}{(R_s - R_m)(R_{m_2} - R_A)}$$

and the percent ^{235}U in sample A is:

$$(21)\quad W\%\ ^{235}U = \frac{W_{5T} \times 100}{W_A}$$

$$(22)\quad W\%\ ^{235}U = \frac{(100)(R''_A)(A_5)(V_{8T})(V^*_{3s})(W_{8w})}{(W_A)(A_8)(V_{8A})(V_{3s})} \frac{(R_{m_2} - R_s)(R_m - R_w)}{(R_m - R_s)(R_{m_2} - R_A)}$$

A sample calculation is shown below

Sample 37

R''_A =	16.0754	R_w =	0
A_5 =	235.0439	R_A =	0
V_{8T} =	100 ml	R_s =	10^6
V_{3s}* =	0.10023 ml	Rm =	0.48763 (on 6-29-72)
W_{8w} =	0.0010535 g	Rm_2 =	7.6156 (on 6-29-72)
W_A =	5.0369 g		
A_8 =	238.0508		
V_{8A} =	0.10006 ml		
V_{3s} =	0.49975 ml		

$$W\%\ ^{235}U = \frac{(100)(16.0754)(235.0439)(100)(0.10023)(0.0010535)}{(5.0369)(238.0508)(0.10006)(0.49975)} \times$$

$$\frac{(10^6 - 7.6)\ (0.48763)}{(10^6 - 0.5)\ (7.6156)}$$

$$= (66.5419)\ (0.06403)$$

$$= 4.2607$$

DISTRIBUTION

		Number of Copies
S. C. T. McDowell	AEC Washington	6
H. V. Werner	AEC Washington	1
W. E. Lotz	AEC ROO	1
E. L. Alpen	BNW	1
N. E. Ballou	BNW	1
J. M. Batch	BNW	1
J. J. Fuquay	BNW	1
J. M. Nielsen	BNW	1
R. A. Schneider	BNW	1
D. M. Robertson	BNW	1
H. H. Van Tuyl	BNW	1