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Graphite Isotope Ratio Method Development Report: Irradiation Test Demonstration of Uranium as a Low Fluence Indicator

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Introduction

This report describes an irradiation test designed to investigate the suitability of uranium as a graphite isotope ratio method (GIRM) low fluence indicator. GIRM is a demonstrated concept that gives a graphite-moderated reactor's lifetime production based on measuring changes in the isotopic ratio of elements known to exist in trace quantities within reactor-grade graphite. Appendix I of this report provides a tutorial on the GIRM concept.

Previous reports in the GIRM development program have identified suitable indicator elements (elements composed of two or more isotopes known to have different neutron absorption properties) and the range of reactor fluences over which these indicator elements provide accurate results. A full-scale experiment was conducted on a decommissioned MAGNOX reactor where titanium was used as the indicator element (an element identified as suitable for high fluence reactors). That demonstration showed that GIRM gives a total lifetime production estimate that is accurate within the uncertainty of the known production. The research effort described in this report extends the GIRM range by demonstrating the applicability of uranium as an indicator in low power reactors or reactors that have operated for only a short period of time.

That uranium should be a reliable fluence indicator comes as no surprise. Uranium has long been used for such purposes in irradiation experiments. Small uranium (or uranium alloy) wires ("flux wires") are commonly inserted into irradiation capsules. Measurements performed on the wires after irradiation provide an accurate measure of the cumulative neutron flux (fluence) in the irradiation specimen. The objectives of this test, therefore, are not to test the suitability of uranium as a fluence indicator, rather to test the ability to use the uranium present in reactor-grade graphite as an indicator. The issues involved in establishing the usefulness of uranium in the GIRM technology are:

- Does reactor-grade graphite contain sufficient amounts of uranium?
- Can the uranium be separated from the graphite in measurable quantities?
- What analytical techniques are best for separating the uranium and performing the isotopic ratio measurements?

For the GIRM application, the interest is in the isotope ratios that are affected by neutron irradiation. In the case of uranium there are several that include not only uranium isotopes but isotopes of plutonium produced from neutron absorption in U-238. The ratios of interest are: U-235/U-238, U-236/U-235, Pu-240/Pu-239, Pu-241/Pu-239, and Pu-242/Pu-239. The fact that 5 different ratios are available to provide estimates of fluence make uranium a very attractive indicator element. Thus, another issue for investigation is the number of ratios that can be measured. There may be so little plutonium that the higher isotopes such as Pu-241 and Pu-242 are not present or extractable in measurable quantities.

The following sections of this report describe the irradiation experiment and give the results obtained from the isotope ratio measurements.

Irradiation Facility

The irradiation was performed in the University of Missouri research reactor, MURR - a 10 MW light water cooled pool type reactor. The small (30 cm) diameter core is surrounded by two reflectors – a 7-cm thick beryllium inner reflector and a 23-cm thick graphite outer reflector. An irradiation location in the outer graphite reflector was selected for the 10 samples used in this experiment. A schematic diagram of the reactor core is shown in figure 1.

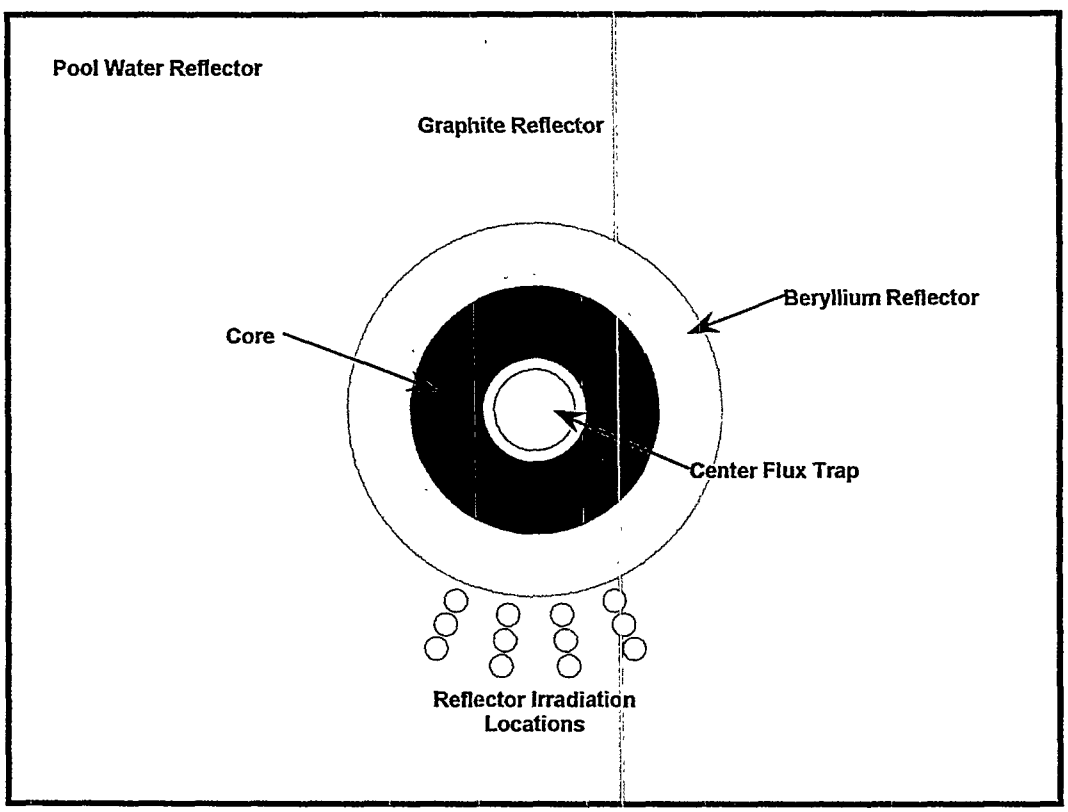

Figure 1 – Schematic Diagram of MURR Reactor Core

The samples were provided as five sealed capsules with instructions to irradiate each to different fluence levels of 2, 4, 6, 8, and $10x10^{19}$ n/cm^2 (thermal). It was left to the operator to determine the residence time necessary to achieve the requested fluences. Following irradiation, the capsules were returned to PNNL where they were disassembled and handled in a clean environment.

Sample Selection and Preparation

The samples selected for irradiation were taken from excess reactor-grade graphite remaining in Hanford storage. Initially, two types of graphite were selected – AGOT and SGBF. AGOT was made from coke produced from Gulf of Mexico oil by the Continental Oil Co. of Lake Charles, La. This graphite was purified in an air atmosphere at 2800 degrees C. SGBF graphite was made from coke produced with Texas oil. This graphite was purified using a halogen gas atmosphere at 2450 degrees C.

Prior to irradiation, samples of both graphite types were characterized to determine if uranium was present in extractable and measurable quantities. The results showed both to contain sufficient quantities of uranium; however, some of the SGBF graphite samples appeared to have been contaminated with depleted or irradiated uranium (lower than natural U-235 with U-236 present). Therefore, the SGBF samples were rejected and replaced with another similar graphite, TSGBF. TSGBF used the same raw materials and purification process, but was produced by a different company. Due to time constraints, it was not possible to characterize the TSGBF samples prior to irradiation.

The initial assumption was that the SGBF had been contaminated in the production process. Because the TSGBF graphite had been manufactured by a different company than the SGBF, it was expected to be free of the depleted uranium contamination. Such proved not to be the case. During the irradiation, samples of the left over TSGBF were characterized and found to also show signs of contamination. Further investigation identified the contamination as coming from the building in which the SGBF and TSGBF had been stored (the AGOT had not been stored in the same location). As a result of the contamination, it was expected that the TSGBF samples would show skewed U-235/U-238 and U-236/U-235 ratios.

Five small cylindrical samples of each graphite type were prepared for irradiation. The surfaces were machined to remove any potential contamination and the final capsule assembly was performed in a clean environment. Two samples, one each of AGOT and TSGBF, were placed inside a graphite sleeve and sealed inside an aluminum can as shown in figure 2. The cans were ultrasonically cleaned prior to filling and sealing. Small cobalt and silver flux wires were placed at the top and bottom of the samples in each can. The cans were numbered 1, 3, 4, 5, and 6.

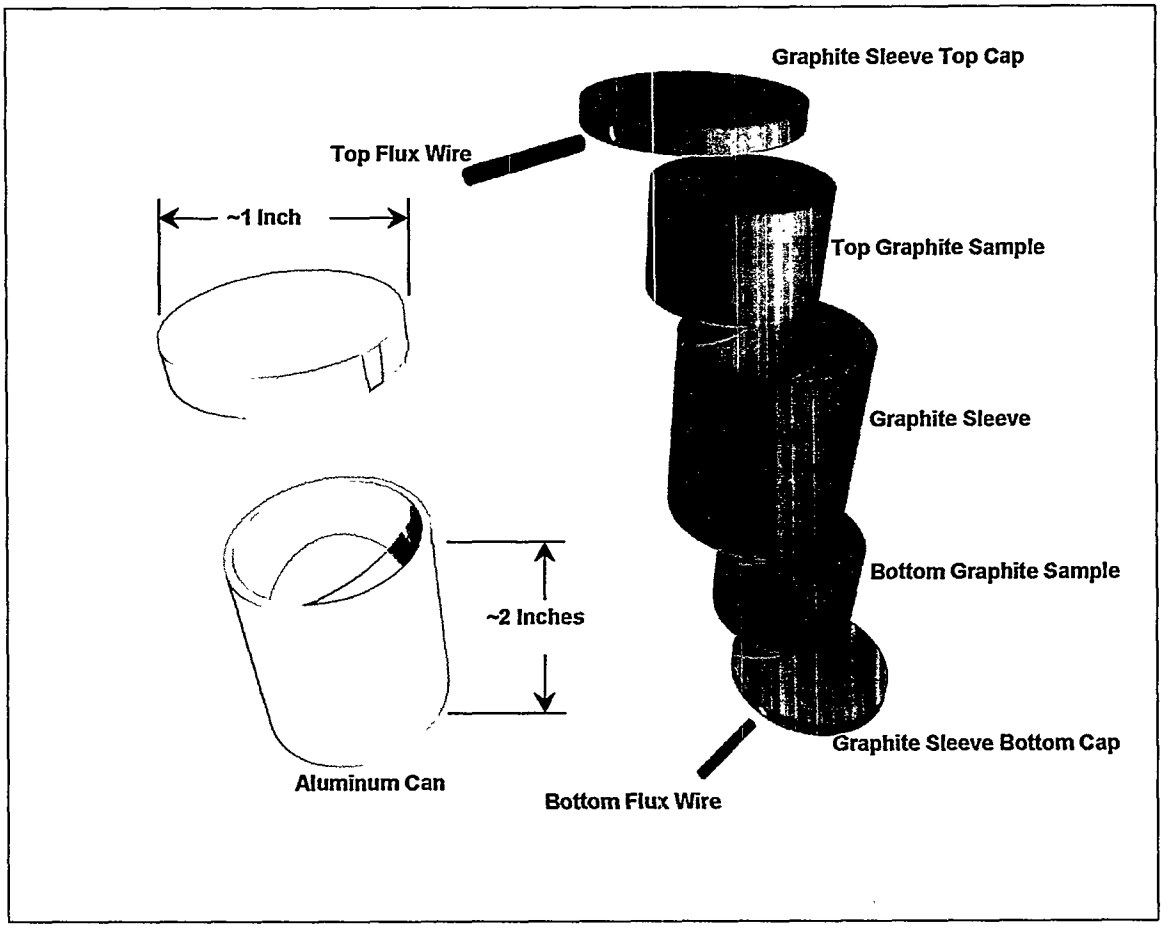

Figure 2 – Drawing of Samples and Container

Sample Irradiation

All five capsules were placed in a single reflector irradiation location of the MURR core. Due to the small size of the MURR core, a steep axial flux gradient existed along the length of the 5 capsules as shown in figure 3. Also, as the figure shows, there is a significant axial gradient along the length of a single capsule. The reactor operator shuffled the five capsules at some period during the irradiation in an effort to minimize the flux gradient.

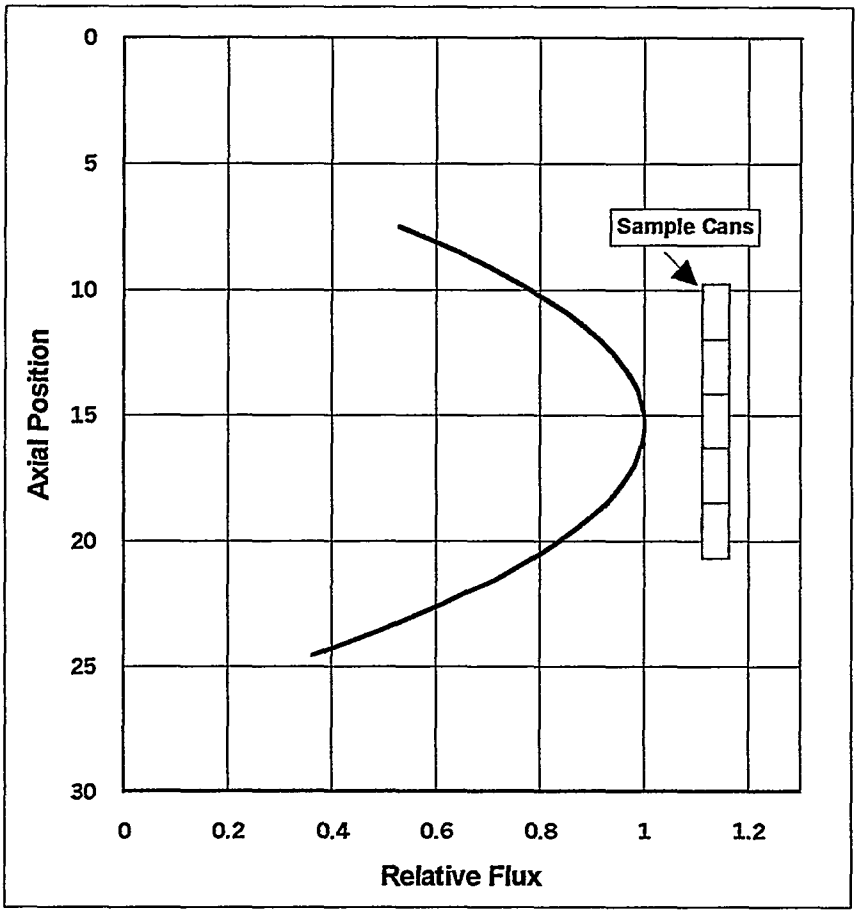

Figure 3 – MURR Axial Flux Profile

A comparison between the reported fluences and the fluences based on the flux wire measurements are given in table 1.

Table 1 – Comparison Between Reported Fluences and Flux Wire Measurements (Fluences in units of 10^{19} n/cm^2)

Sample ID*	Requested Fluence	Reported Fluence	Flux Wire Fluence	Ratio of Flux Wire to Reported Fluence
S-6-B	2	2.54	4.77	1.88
S-6-T	2	2.78	5.38	1.94
A-4-B	4	3.72	6.55	1.76
A-4-T	4	3.81	5.43	1.42
A-3-B	6	6.04	9.92	1.64
A-3-T	6	6.30	10.8	1.72
S-1-B	8	7.99	12.1	1.51
S-1-T	8	7.98	14.1	1.77
S-5-B	10	9.76	15.8	1.62
S-5-T	10	9.89	16.1	1.63
				Mean= 1.69
				St.Dev.=0.16

* The T and B denote top and bottom sample in the can.

The differences between the reported and measured fluences are due to the approximate nature of the operator-reported values (+/-15%) and the definition of the thermal cutoff energy. This difference does not adversely affect the experiment. The fluence range is still well within the range defined as "low fluence" and the relative differences between the 5 capsules are close to the requested values.

Sample Measurement

Sample Preparation

Ashing the graphite by slow, controlled combustion was chosen as the method to prepare the samples for isotopic measurement. This was accomplished by machining the samples to size and placing each on a high purity platinum foil in a pure quartz/silica glass tube inserted into a horizontal furnace. Ashing was expedited under a flow of pure, filtered oxygen. The ash from each sample was removed by rinsing with dilute nitric acid. A process "blank" was prepared by heating and rinsing an empty foil.

The ash residue rinsed from the platinum foil was evaporated down and redissolved in hydrochloric acid, and "spiked" by adding small amounts of U-233 and Pu-244 solutions. The isotopically enriched spikes are of sufficiently high purity that corrections performed on the resulting measurements are minor for the small amounts of other isotopes, (e.g., U-238 and Pu-239) contained in the spikes. The resulting mixture was treated to ensure equilibration of the U and Pu and spike and subjected to a standard ion exchange separation procedure using anion exchange resin and hydrochloric acid. While the uranium bearing elution fraction from this procedure was suitable for measurement, it was subjected to further clean-up separation to improve measurement quality. Elution fractions containing plutonium were subjected to ion exchange separation procedures. All procedures were conducted using the highest purity reagent available. All sample vials and containers used in the procedures were made of chemically inert Teflon.

The U and Pu from each graphite sample was redissolved in a small volume of hydrochloric acid and prepared for isotopic measurement by successive equilibration and rinsing of a single bead of ion exchange resin. This "microchemistry" procedure is effectively an additional ion exchange separation that is performed over 3 days. The single bead containing U and Pu was placed onto a high purity rhenium filament for measurement by thermal ionization mass spectrometry (TIMS). Measurements were conducted on a 3-stage magnetic section mass spectrometer with ion pulse counting detection capability and a 3rd stage consisting of an electrostatic analyzer. Counting times were carefully chosen for each isotope to improve precision. Small corrections for instrument bias were made by measuring certified U and Pu standards.

The above described procedure was used for the unirradiated graphite samples taken to characterize the three types of graphite available (AGOT, SGBF, and TSGBF) as well as the irradiated samples (AGOT and TSGBF). The analytic results are provided in the following sections.

Analytic Results: U and Pu in Unirradiated Graphite Samples

Several aliquots of AGOT graphite varied in uranium content from 6.9 to 10.4 ppb (10^{-9}g/g). The uranium isotopic measurement showed only natural uranium.

Three aliquots of SGBF graphite showed uranium content in the pptr (10^{-12} g/g). The uranium isotopic composition showed various contents of U-235 and U-236, indicating contamination with irradiated uranium (both irradiated natural and irradiated slightly enriched uranium). For this reason, the SGBF was disqualified as a candidate for the irradiation experiment. Samples of a similar graphite, TSGBF, were substituted without prior characterization.

While the irradiation was underway, samples of unirradiated TSGBF graphite were characterized. The uranium contents ranged from 1.7 to 11.5 ppb (10^{-9} g/g) - equivalent to that in the AGOT graphite. However, the uranium isotopic measurement showed results similar to those for the SGBF, namely, apparent contamination by irradiated uranium.

Table 2 summarizes the measurement results for the unirradiated graphite samples.

Table 2 – Summary of Uranium Measurements for Unirradiated Graphite

Sample #	Type	U-238 ng/g	U-234/U238	U-235/U-238	U-236/U-238
1	AGOT	10.36	0.00006064	0.007255	<2E-8
2	AGOT	6.91	0.00006393	0.007294	<4E-7
3	AGOT	8.83	0.00006271	0.007237	<5E-7
4	AGOT	6.26	0.0001108	0.007253	<8E-8
5	AGOT	3.07	0.00007472	0.007249	<5E-7
6	SGBF	0.020	0.0000643	0.008642	0.00005479
7	SGBF	0.022	0.0000671	0.009366	0.00005311
8	SGBF	0.040	<0.00007	0.00726	<4E-6
9	SGBF	0.0056	0.000053	0.006544	0.0000188
10	SGBF	0.0037	0.0000458	0.005746	0.0000160
11	SGBF	0.0032	0.0000477	0.006612	0.0000148
12	TSGBF	3.32	0.00009675	0.006509	0.00000387
13	TSGBF	1.65	0.00010075	0.002406	0.00002139
14	TSGBF	11.53	0.0001062	0.007011	0.00000088

Tables showing all measurement results including uncertainties and process blank values for the unirradiated graphite samples are given in Appendix II. Uncertainties in the measured isotopic ratios were typically on the order of 1% (1 sigma).

Analytic Results: U and Pu in Irradiated Graphite Samples

Uranium and plutonium isotopic measurements were performed on the four samples of AGOT and six samples of TSGBF graphite sent for irradiation. Based on the results from the measurements with the unirradiated TSGBF, some skewing of uranium isotopics were to be expected. The results show two samples with uranium isotopic ratios inconsistent with natural uranium – sample S-5-T (the top TSGBF graphite sample in can 5) and S-6-T (the top TSGBF graphite sample in can 6). In addition, both samples showed plutonium isotopic results inconsistent with the other samples. After much investigation, including a remeasurement, the only logical conclusion was that these samples had been contaminated.

The uranium measurement results are summarized in table 3 and plutonium results in table 4.

Table 3 – Summary of Uranium Measurements for Irradiated Graphite

ID	Type	U-238 ng/g	U-234/U238	U-235/U-238	U-236/U-238
A-3-T	AGOT	1.03	0.0001153	0.006608	0.0000828
A-3-B	AGOT	6.16	0.0000693	0.006736	0.00007912
A-4-T	AGOT	6.47	0.0001117	0.006981	0.00004533
A-4-B	AGOT	4.46	0.0000663	0.006982	0.0000493
S-1-T	TSGBF	4.98	0.0001096	0.006547	0.00010461
S-1-B	TSGBF	1.92	0.0000893	0.006615	0.00009965
S-5-T	TSGBF	0.133	0.0000545	0.002848*	0.0000533
S-5-B	TSGBF	1.45	0.0001116	0.006492	0.00011703
S-6-T	TSGBF	1.33	0.0000892	0.006222*	0.00006926
S-6-B	TSGBF	3.70	0.0000668	0.006999	0.00003927

*Uranium isotopics indicates possible contamination

Table 4 – Summary of Plutonium Measurements for Irradiated Graphite

ID	Type	Pu-239 pg/g	Pu-240/Pu-239	Pu-241/Pu-239	Pu-242/Pu-239
A-3-T	AGOT	2.12	0.019395	0.0005198	0.00000675
A-3-B	AGOT	40.87	0.018994	0.0004964	0.00000546
A-4-T	AGOT	8.00	0.010121	0.0001496	0.000001272
A-4-B	AGOT	7.03	0.010797	0.00017049	0.00000139
S-1-T	TSGBF	14.83	0.02528	0.0008661	0.00001286
S-1-B	TSGBF	8.76	0.02416	0.0007947	0.00001105
S-5-T	TSGBF	0.343	0.02941	0.0011354	0.00002381*
S-5-B	TSGBF	20.40	0.02946	0.001140	0.00001889
S-6-T	TSGBF	1.68	0.019131	0.0003279	0.00005162*
S-6-B	TSGBF	3.92	0.008408	0.00010026	0.00000107

*Plutonium isotopics inconsistent with other samples

More detailed tables of results showing uncertainties and process blank data for the irradiated graphite are given in Appendix II. Uncertainties in the measured isotopic ratios were less than 3% (1 sigma).

Evaluation of Experiment Results

Combining the fluence results from the flux wires and the measured isotopic ratios from the eight samples that did not appear to have been contaminated, provides a set of values that can be examined to determine the success of the irradiation experiment. Tables 5 and 6 show the summarized results used in the evaluation.

Table 5 – Summary of Uranium Measurements Used in Evaluation (Fluence in units of 10^{19} n/cm^2)

ID	Type	Fluence	U-235/U238	U-236/U-238	U-236/U-235
S-6-B	TSGBF	4.77	0.006999	0.00003927	.005611
A-4-T	AGOT	5.43	0.006981	0.00004533	.006493
A-4-B	AGOT	6.55	0.006982	0.0000493	.007061
A-3-B	AGOT	9.92	0.006736	0.00007912	.011746
A-3-T	AGOT	10.8	0.006608	0.0000828	.01253
S-1-B	TSGBF	12.1	0.006615	0.00009965	.015064
S-1-T	TSGBF	14.1	0.006547	0.00010461	.015978
S-5-B	TSGBF	15.8	0.006492	0.00011703	.018027

Table 6 – Summary of Plutonium Measurements Used in Evaluation (Fluence in units of 10^{19} n/cm^2)

ID	Type	Fluence	Pu-240/Pu-239	Pu-241/Pu-239	Pu-242/Pu-239
S-6-B	TSGBF	4.77	0.008408	0.00010026	0.00000107
A-4-T	AGOT	5.43	0.010121	0.0001496	0.000001272
A-4-B	AGOT	6.55	0.010797	0.00017049	0.00000139
A-3-B	AGOT	9.92	0.018994	0.0004964	0.00000546
A-3-T	AGOT	10.8	0.019395	0.0005198	0.00000675
S-1-B	TSGBF	12.1	0.02416	0.0007947	0.00001105
S-1-T	TSGBF	14.1	0.02528	0.0008661	0.00001286
S-5-B	TSGBF	15.8	0.02946	0.001140	0.00001889

A simple one-dimensional computer model of the MURR core was developed to test the reasonableness of the measured isotopic ratios. The model was developed using the unit-cell burn up code WIMS. This is a code widely used throughout the nuclear industry for modeling all types of reactor cores. No attempt was made to model the MURR core precisely. It was found during the modeling effort that the shape of the plutonium isotopic ratios is strongly affected by the choices made within the known parameters of the MURR core (dimensions, material densities and temperatures). The following graphs compare the measured and calculated isotopic ratios.

Figure 4 shows the uranium ratios. The measured U-235/U-238, U-236/U-238 and U-236/U-235 ratios are all in good agreement with the expected values from the calculations.

Figure 5 shows the plutonium ratios. Again the measured ratios are in good agreement with the calculations, although the Pu-241 and Pu-242 ratios appear

somewhat poorer than the Pu-240/Pu-239 ratio. It was suspected that the flux wire fluence results may not be in as good agreement with the actual fluence due to the severe flux gradients in the samples. To demonstrate this, the plutonium ratios were plotted against the U-236/U-235 ratio in figure 6. These results show much better agreement between the measured and calculated results.

Conclusions

The results from this test show that the trace amounts of uranium found in nuclear-grade graphite can be used as an effective low fluence indicator for GIRM. Sufficient amounts of uranium are present in the graphite to form measurable amounts of both uranium and plutonium isotopes (using thermal ionization mass spectrometery methods). The analytic techniques were successful in separating the uranium and plutonium from the graphite matrix in large enough quantities that the measurement uncertainty was small – less than 3%. In total, six isotopic ratios were shown to be available as low fluence indicators from this single impurity – U-235/U-238, U-236/U-238, U-236/U-235, Pu-240/Pu-239, Pu-241/Pu-239, and Pu-242/Pu239. Having a large number of ratios produced from a single impurity greatly increases the value of the indicator. Multiple ratios improve confidence in the measured results and increase the difficulty of trying to "spoof" the GIRM process by adding extraneous material to the reactor core.

The results also showed that much care must be exercised in preventing contamination by environmental uranium. Contamination of the unirradiated graphite by uranium handling operations in buildings adjacent to the graphite storage area was shown in two of the three graphite varieties selected for the testing. Furthermore, the mechanical cleaning efforts used to reduce possible contamination proved to be unsuccessful. Further investigations into chemical cleaning methods are needed to assure that the samples are free from environmental uranium contamination.

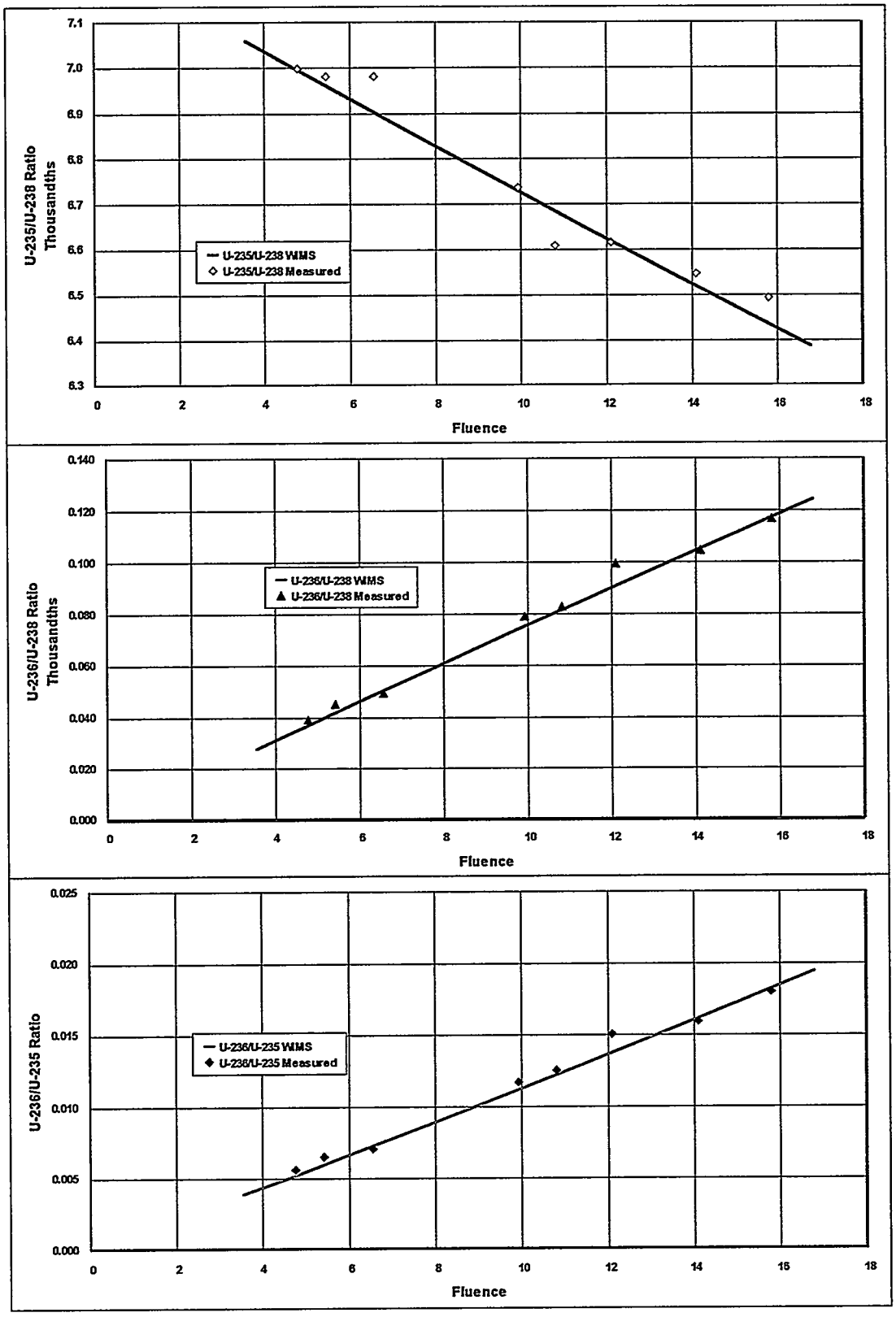

Figure 4 – Uranium Ratios vs Measured Fluence

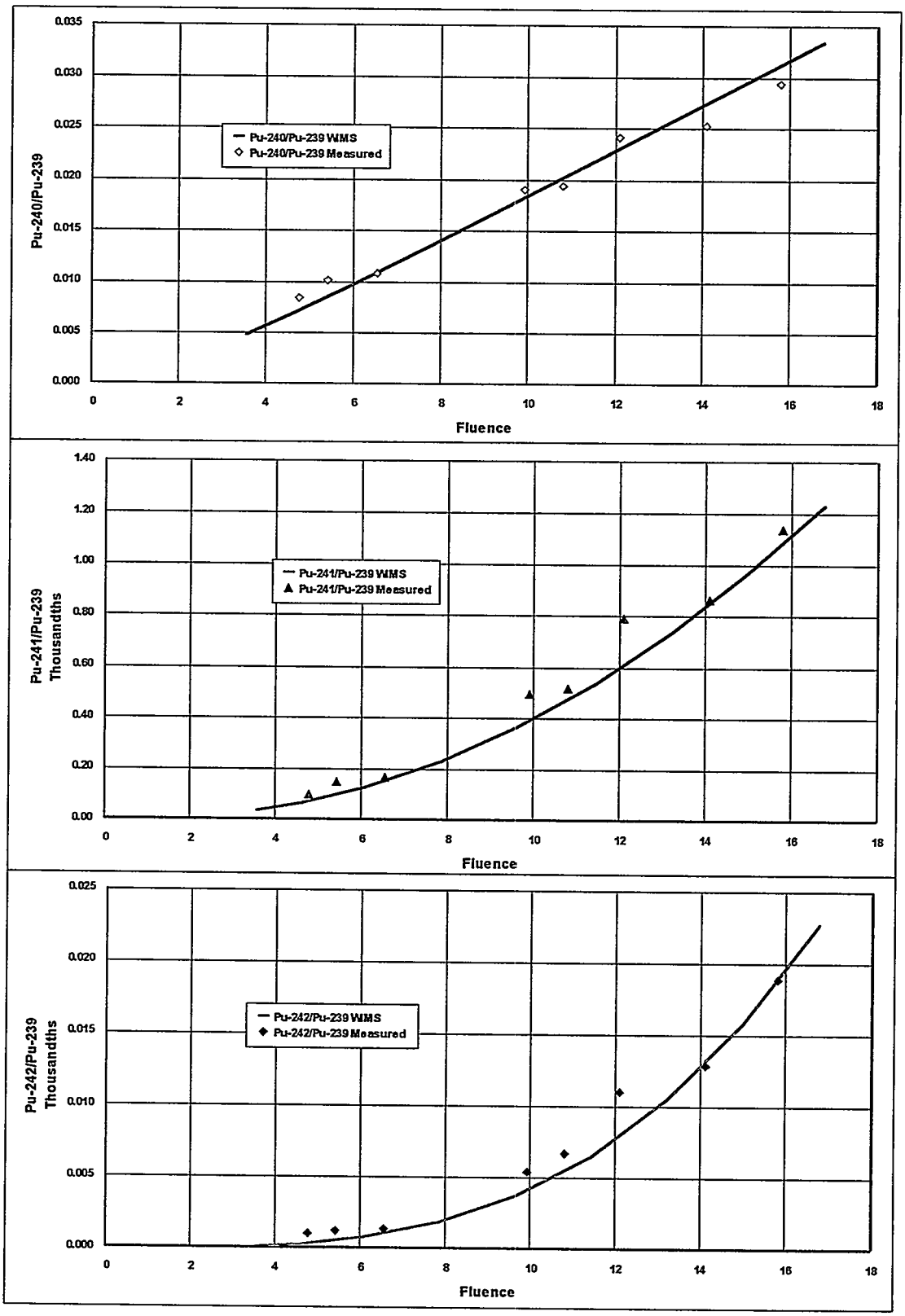

Figure 5 – Plutonium Ratios vs Measured Fluence

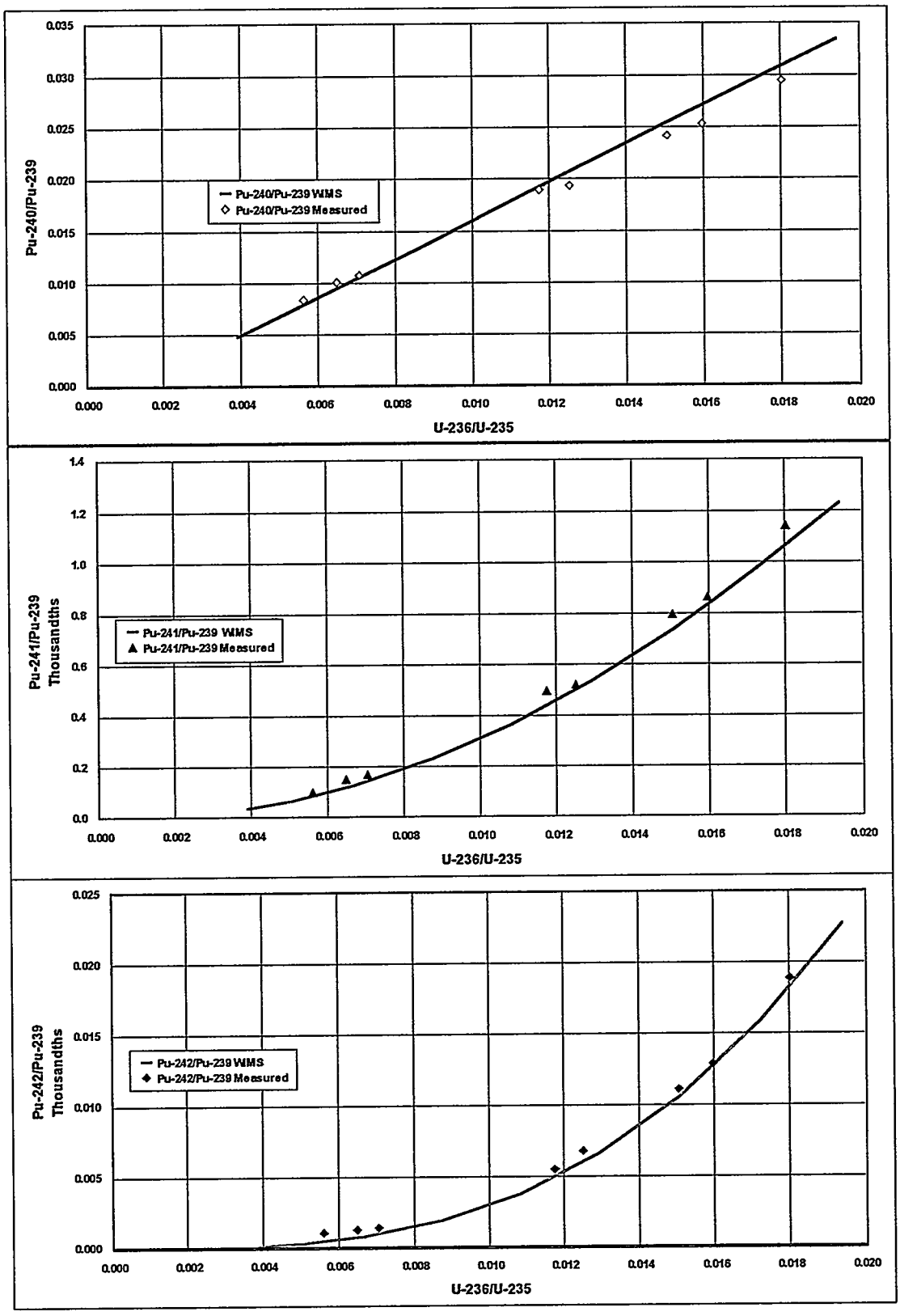

Figure 6 – Plutonium Ratios vs U-236/U-235 Ratio

Appendix I – GIRM Tutorial

The Graphite Isotope Ratio Method (GIRM):

A Plutonium Production Verification Tool

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The purpose of this document is to provide a simple, concise description of the graphite isotope ratio method (GIRM) for use as a verification tool in estimating a graphite-moderated reactor's total plutonium production. The description covers the theory behind the technique and how the method is actually applied.

Background

Over the lifetime of a production reactor, neutrons from the fission process not only convert U-238 into plutonium but also bring about changes in the elements of the reactor's core components. Components such as shielding, pressure vessels, coolant piping, control rods, structural supports, and, in the case of graphite moderated reactors, the solid graphite moderator are all affected. Because a reactor's total plutonium production is directly related to total neutron fluence, and, likewise, changes in the elements and isotopes of a reactor's core components are directly related to fluence; it was argued that measuring these changes could provide an accurate estimate of a reactor's total plutonium production. The U.S. Department of Energy funds a project at Pacific Northwest National Laboratory (PNNL) to develop this concept into a practical plutonium production verification tool for graphite moderated reactors. The following sections describe the GIRM project development process.

Identification of Useable Core Components

The first step was to identify those core components containing the most reliable sources of information about the reactor's operating history. Clearly, only items that remain in place throughout the reactor's lifetime would be useful. Components that have been replaced only provide information about the reactor's production since the time of replacement. Control rods and coolant pipes were routinely replaced, so they were eliminated early on. Shielding materials around the core, while remaining in place, were disqualified due to large spatial variations in the neutron flux (based on measurements from the French G-2 reactor).

It was soon obvious that the most reasonable candidate was the graphite moderator and the impurities known to exist in even the most highly purified reactor-grade graphite. In the known operating experiences of the U.S., U.K., France, and Russia no significant portions (if any) of the graphite moderator were replaced in their large production reactors.

Identification of Suitable Indicator Elements

The next step was to identify elements in the graphite that could be used as "indicator" elements, that is, elements that undergo transmutation in a predictable manner due to neutron bombardment. Carbon was ruled out because other sources of carbon are present in the reactor core (nitrogen is converted to carbon when it absorbs a neutron and some reactors use carbon dioxide as a coolant). This left only the graphite impurities as candidate indicator elements. The literature reports a long list of impurities in reactor grade graphite. Examples for several types of reactor grade graphite are given in table 1 (based on early, 1960 era, measurements).

Table 1 – Concentrations of Selected Impurities in Various Hanford Reactor-Grade Graphites (ppm)

Element	Detection Limit	KSO	KCF	CSO	CSF	GBF	SGBF
Al	0.007	0.59	0.06	0.36	0.09	0.15	0.83
B	0.005	3.0	0.08	2.8	0.13	0.04	0.10
Ba	0.0005	2.6	0.02	2.6	0.03	0.04	0.007
Ca	0.002	210.0	0.13	135.0	0.27	0.59	0.22
Cr	0.003	1.1	—	0.34	—	0.005	—
Cu	0.001	0.68	0.15	0.19	0.28	0.06	0.68
Fe	0.001	5.6	0.33	2.8	0.28	3.1	0.19
Li	0.001	0.37	0.002	0.21	0.003	0.003	0.003
Ni	0.005	0.31	0.02	2.5	0.06	0.2	0.05
S	0.02	31.0	0.04	33.0	0.07	0.07	0.05
Si	0.005	1.3	0.67	6.0	1.3	0.07	1.25
Sr	0.0005	4.0	0.003	3.1	0.002	0.008	—
Ti	0.001	7.5	0.001	8.2	0.01	0.02	0.001
V	0.001	11.0	—	12.0	0.004	0.12	0.015
Zn	0.001	5.4	0.06	160.0	0.16	0.08	0.43

In addition to the elements listed in table 1, other elements have been recently measured using more sensitive techniques. These additional elements include uranium, chlorine, cobalt, niobium, neodymium, hafnium, tungsten, and rhenium.

A first concept, simply measuring the change in concentration of the impurity elements, was rejected because of the wide variation in the initial concentrations of these impurities. Impurity concentrations in graphite vary from location to location within a single piece of graphite, from one piece to another within a single batch of graphite, from batch to batch for a given manufacturer, and from manufacturer to manufacturer. Therefore, no reliable initial concentration could be established against which to compare the final measured concentration. It became obvious that only by measuring the change in the isotopic ratio of certain impurity elements, could an accurate measure of total lifetime neutron fluence be obtained. The use of ratios eliminates the need to know initial concentrations – it is only important to know that the element is present in measurable quantities.

Using isotopic ratios is possible because the initial ratios are fixed by nature (they are not changed by the manufacturing processes except in the case of very light elements such as lithium) and because of differences in the neutron absorption

cross section of the various isotopes. For example, consider the element boron. As shown in table 1, boron is a common impurity in graphite (albeit very small). Natural boron consists of two isotopes – B-10 and B-11. In nature, the B-10/B-11 isotopic ratio is 0.25. Only one of these isotopes, B-10, has a significant neutron absorption cross section. Therefore, as boron is subjected to neutron irradiation, B-10 is transmuted at a much faster rate than B-11 (B-10 is converted to Li-6 in a neutron-alpha reaction). Figure 1 below illustrates how the B-10/B-11 ratio would change as a function of neutron fluence.

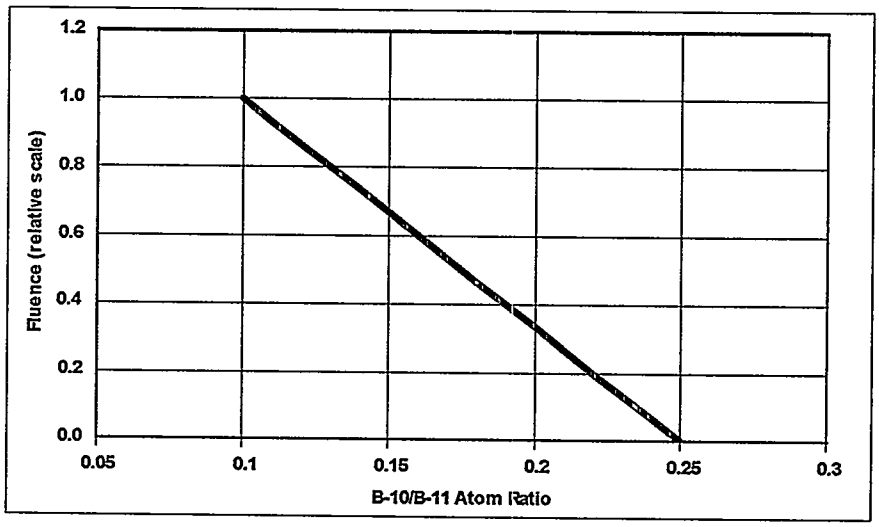

Figure 1 – Change in Boron Isotope Ratios

Therefore, measuring the B-10/B-11 isotopic ratio in a sample of graphite that had been subjected to an unknown neutron fluence and applying the results in figure 1 would give a measure of the actual fluence. There are many other elements that behave in a similar manner. Some are given in table 2. Graphs similar to figure 1 can be generated for all of these.

Table 2 – Isotopes of Indicator Elements

Element	Isotopes
Sulfur	S-32, S-33
Chlorine	Cl-35,Cl-36,Cl-37
Calcium	Ca-40,Ca-41
Titanium	Ti-48,Ti-49
Chromium	Cr-50,Cr-52,Cr-53,Cr-54
Iron	Fe-54,F-56,Fe-57,Fe-58
Uranium	U-235,U-236,U-238,Pu-240,Pu-241,Pu-242
Cobalt	Co-59,Co-60
Niobium	Nb-93,Nb-94
Neodymium	Nd-142,Nd-143
Hafnium	Hf-174,Hf-176,Hf-177,Hf-178,Hf-179,Hf-180
Tungsten	W-180,W-182,W-183,W-184,W-186
Rhenium	Rh-185,Rh-187
Boron	B-10,B-11

Not all the indicator elements identified in table 2 are suitable for all applications. For high power reactors that have operated for many years, isotopes with large neutron absorption cross sections will be completely consumed. Such is the case with boron. Boron-10, with its very large absorption cross section, is reduced below measurable amounts in only a few years in a high power reactor like those at the U.S. Hanford site. Boron, therefore, is more useful for low power reactors, or other reactors that have operated for only a short time. Choosing a suitable indicator element, therefore, requires a rough idea of the reactor's power level and operating time. Figure 2 shows the effect of reactor operation on the uncertainty of the production estimate for several potential indicator elements.

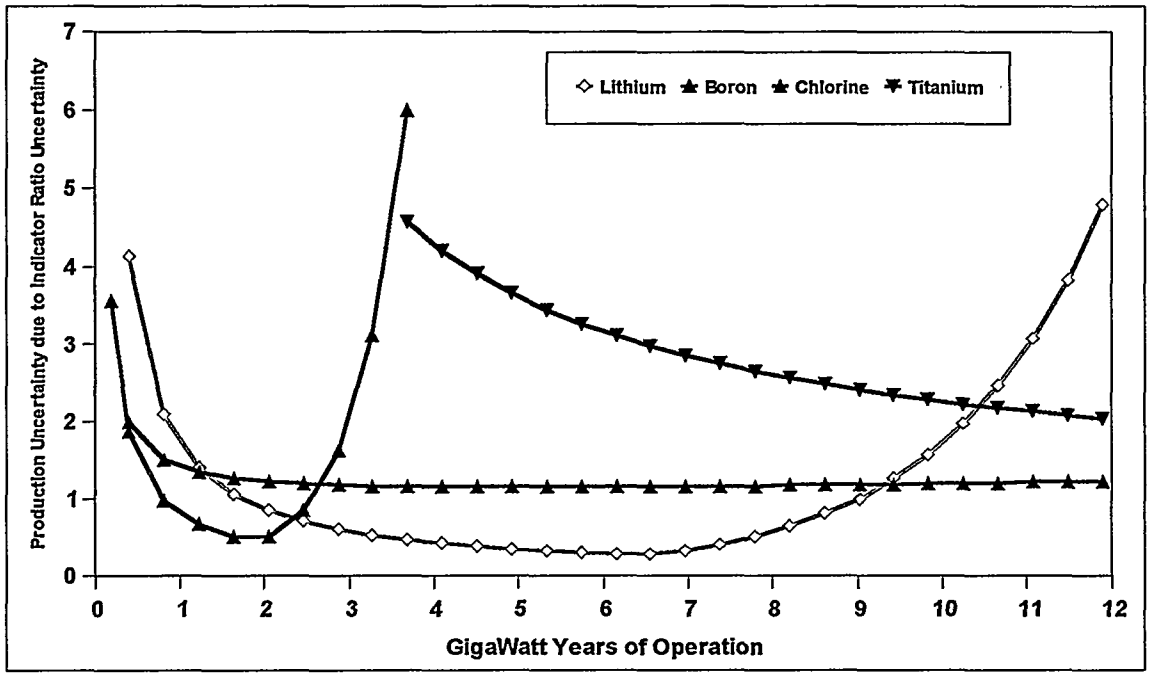

Figure 2 – Production Uncertainty as Affected by Reactor Operation

There are additional, more subtle factors that come into play when selecting a suitable indicator element. Consider the uranium impurity. The major isotopes are U-238 and U-235, both of which undergo transmutation at different rates. In addition, U-236 is produced in about 20% of the neutron captures in U-235 giving rise to a U-236/U-235 ratio that is initially zero and increases with increasing neutron fluence. (Uranium has long been used as a sensitive neutron fluence indicator. Experimentors place tiny uranium "flux wires" in with their irradiation samples. After the irradiation the flux wires are measured to provide an accurate measurement of the fluence.) Furthermore, U-238 gives rise to plutonium which has four isotopes (Pu-239, Pu-240, Pu-241, and Pu-242) all of which can be measured to give additional estimates of the neutron fluence. Therefore, this one element provides five different isotopic ratios, U-235/U-238, U-236/U-235, Pu-240/Pu-239, Pu-241/Pu-239, and Pu-242/Pu-239, from which to make a fluence estimate.

Experiments have been conducted to demonstrate that analytical techniques are available to perform the measurements described above. In some cases the separation and measurement process is relatively straightforward. In others, most notably boron, the process has yet to be fully demonstrated (separating boron from graphite has proven to be difficult). Work continues on improving the analytical methods.

Full Scale Reactor Application

With the theory confirmed by experiment, the next step was a full-scale reactor application. An opportunity to apply GIRM was provided by the British who were in the process of decommissioning the Trawsfynydd MAGNOX reactor in Wales. This is a graphite-moderated, CO_2 cooled power reactor fueled with natural uranium. They offered to provide graphite samples from the core for demonstration of the GIRM technique. In addition, they provided information on core and fuel design along with fuel cycle data. Information on total plutonium production was withheld until after the application of the graphite isotope ratio had determined the total production. The following discussion describes how the method was applied.

Selecting a suitable indicator element was the first step. Because the reactor operated at relatively high power for a number of years, the most suitable indicator was determined to be titanium. Ninety small graphite samples were taken from known locations throughout the core. All samples were approximately 1/2 cm. in diameter by 1 cm. long and were taken in areas adjacent to the fuel as shown in figure 3.

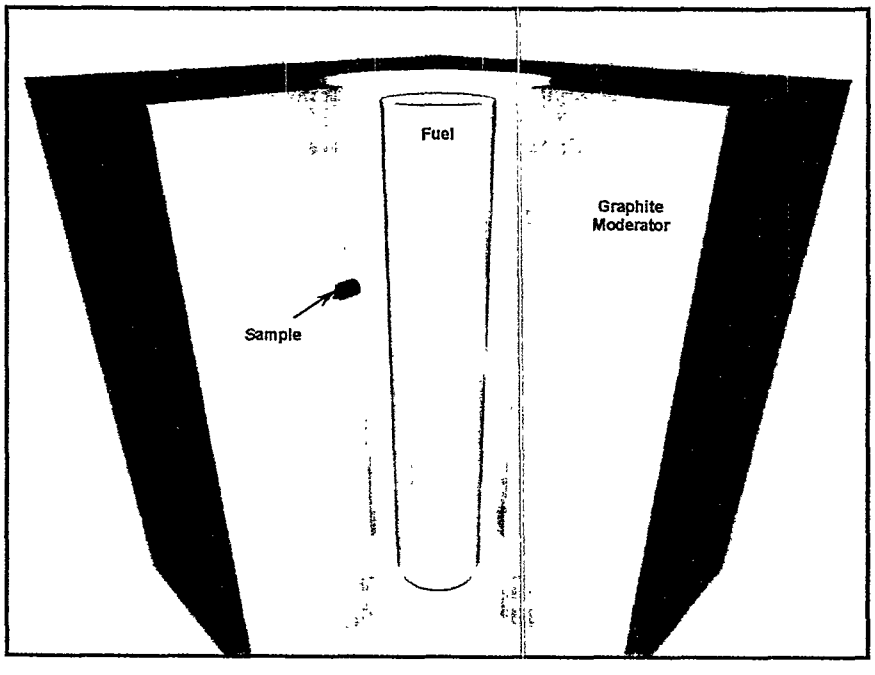

Figure 3 – Sampling Location in MAGNOX Reactor

The samples were shipped to PNNL where the titanium was separated from the graphite and measurements made of the titanium isotopic ratios. While a number of isotopes are available, the Ti-49/Ti-48 ratio was deemed the most useful over the fluence range expected in this reactor. (The details of the analytical procedures for separating and measuring the isotopic ratios will not be discussed. It is sufficient to state that the process is well developed and resulted in measured ratios with small errors. Other documents are available that discuss the measurement techniques in detail.)

In the foregoing discussion, the emphasis was on using the isotopic ratio to give an estimate of the neutron fluence from which an estimate of plutonium production could be made. In applying the method to a full-scale reactor where details of fuel and core design are known, a more direct correlation can be made between changes in isotopic ratio and plutonium production. Using reactor physics models of the fuel and moderator geometry, calculations can be made that relate changes in isotope ratio to plutonium production in fuel located adjacent to the sample location. So, instead of having a correlation like that shown in figure 1 which relates isotope ratio to fluence, the result is a correlation like that shown in figure 4 which relates isotope ratio to plutonium production (in terms of grams of plutonium/unit length of fuel).

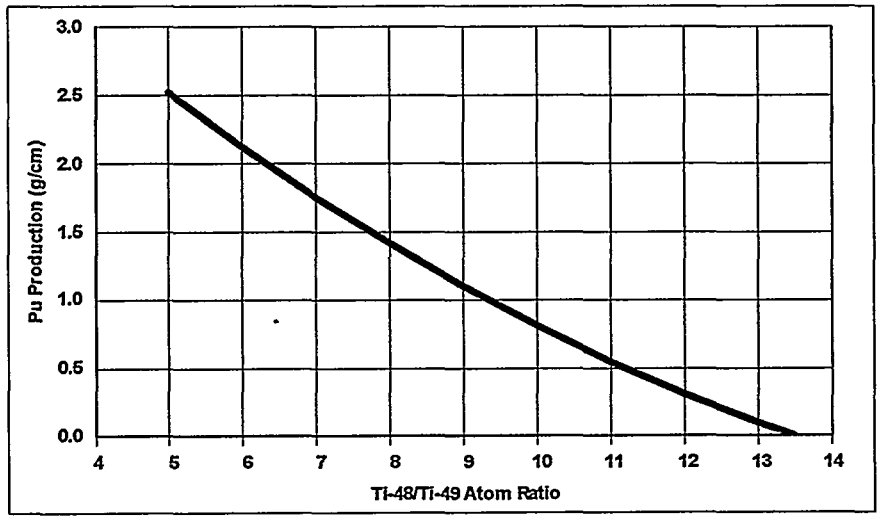

Figure 4 – Plutonium Production Correlation for Trawsfynydd Reactor

The final step in computing the total production was to use the results from the 90 sampling locations to produce a reactor volume weighted average plutonium production per cm of fuel length which, when multiplied by the total fuel length, gives the total plutonium production. Computing an average value from a number of samples taken over the reactor volume is necessary due to the spatial variation of the neutron flux (and, thus, plutonium production). Due to neutron leakage from all the reactor surfaces, the flux profile is peaked in center and falls off in a roughly cosine shape to the reactor edges (it is not zero at the edge but it is roughly a factor of four lower than at the center).

Aggregating the 90 local plutonium/cm values into a reactor average value was accomplished by performing a regression analysis of the values (complete with error propagation). The regression analysis utilized a functional fit to a set of cosine functions. (The details of the regression analysis are not included in this discussion. It is sufficient to state that the method is based on sound statistical principles and the results provide an accurate measure of the total reactor production rate in grams of plutonium/cm of fuel length. Other documents are available that describe the regression method in detail.)

Comparing the result of multiplying the total fuel length by the average linear production gave a total reactor plutonium production for Trawsfynydd that agreed within the uncertainty range of the value provided by the operator (based on records of fuel reprocessing for this reactor).

This full-scale reactor experiment provided proof that GIRM is a viable tool for use in validating plutonium production in graphite moderated reactors.

Future Directions

GIRM development is not fully completed. While the full-scale reactor test demonstrated the method's applicability to high fluence reactors, more work is needed to make the method useable over a broader range. Analytical techniques have been developed for only a small suite of the potential indicator elements. For application over a broader range of reactors, analytical techniques will need to be developed for additional indicators. To date, no single technique is applicable for more than one indicator element. Each will require its own unique separations and measurement process.

Improvements can be made in the analytical techniques required to obtain the isotope ratio values. Presently, the technique involves laborious wet chemistry techniques to separate the indicator element from the graphite matrix. The separated material is then loaded into a high sensitivity mass spectrometer for the ratio measurement. New state-of-the-art mass spectrometers are becoming available that offer the promise of *in situ* measurement of the isotope ratios (that is, separating the indicator from the graphite matrix would not be required) which would eliminate much of the expense and effort required to make the ratio measurements. Further investigations using such instruments is planned.

Appendix II – Detailed Analytical Results

Table 1: Uranium Concentrations and Isotopics for Unirradiated Graphite

TIMS Analysis Number	TIMS Analysis Date	Customer Sample I.D.	Sample Size (g)	^{238}U Conc. [a] ± 1σ Error (ng/g graphite)	Uranium Atom Ratio ± 1σ Error [b] ^{234}U/^{238}U	^{235}U/^{238}U	^{236}U/^{238}U
81259	14Apr98	AGOT LS-152	5.42	10.36	0.00006064	0.007255	<2E-8
			0.01	0.12	0.00000062	0.000036	
81260	14Apr98	AGOT LS-152	5.30	6.914	0.00006393	0.007294	<4E-7
			0.01	0.081	0.00000064	0.000036	
81261	14Apr98	AGOT LS-152	3.60	8.83	0.00006271	0.007237	<5E-7
			0.01	0.11	0.00000063	0.000036	
81262	14Apr98	SGBF-1	8.26	0.02018	0.0000643	0.008642	0.00005479
			0.01	0.00023	0.0000010	0.000043	0.00000099
81263	14Apr98	SGBF-2	10.17	0.02278	0.0000671	0.009366	0.00005311
			0.01	0.00026	0.0000010	0.000047	0.00000093
81264	28Aug98	SGBF-3	8.24	0.03958	<7E-5	0.00726	<4E-6
			0.01	0.00053		0.00027	
81265	14Apr98	AGOT 282	17.85	6.263	0.0001108	0.007253	<8E-8
			0.01	0.072	0.0000010	0.000036	
81266	14Apr98	AGOT 864	30.59	3.074	0.00007472	0.007249	<5E-7
			0.01	0.035	0.00000073	0.000036	
81267	14Apr98	Process	—	0.05854	0.0000609	0.007216	~~0.0000052~~
		Blank #1		0.00067	0.0000016	0.000042	~~0.0000010~~
81269	14Apr98	Process	—	0.03260	0.0000610	0.007163	0.0000187
		Blank #4		0.00037	0.0000025	0.000046	0.0000015
81272	15Apr98	Process	—	0.06218	0.0000576	0.007253	0.00000509
		Blank #2		0.00071	0.0000015	0.000036	0.00000084
81273	28Aug98	Process	—	0.05719	0.0000604	0.007173	0.00000515
		Blank #3		0.00066	0.0000012	0.000036	0.00000077
81276	15Apr98	Microchemistry	—	0.00002021	<6E-3	~~0.00575~~	<9E-3
		Blank #U1		0.00000034		~~0.00077~~	
81277	28Aug98	Microchemistry	—	0.00002133	<4E-3	~~0.00444~~	<7E-3
		Blank #U2		0.00000036		~~0.00078~~	

[a] The U-238 concentrations for blanks are given as total mass.

[b] Values that have been struck through are based on <200 net counts of the minor isotope and are unreliable.

Table 2: Plutonium Concentrations and Isotopics for Unirradiated Graphite

TIMS Analysis Number	TIMS Analysis Date	Customer Sample I.D.	Sample Size (g)	Mass ^{239}Pu [a] ± 1σ Error (fg)	Plutonium Atom Ratio ± 1σ Error $^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$
81278	15Apr98	AGOT LS-152	5.42	0.1262	0.293	<0.2	<0.3
			0.01	0.0099	0.041		
81290	17Jul98	AGOT LS-152	5.30	0.1058	0.202	<0.4	<0.3
			0.01	0.0090	0.040		
81291	17Jul98	AGOT LS-152	3.60	0.0853	0.291	<0.2	0.143
			0.01	0.0046	0.030		0.030
81284	16Apr98	SGBF-1	8.26	0.0556	<0.5	<0.5	<0.5
			0.01	0.0082			
81292	17Jul98	SGBF-2	10.17	0.0519	0.385	<0.3	0.193
			0.01	0.0059	0.060		0.050
81293	17Jul98	SGBF-3	8.24	<0.03	—	—	—
			0.01				
81281	16Apr98	AGOT 282	17.85	1.072	0.1419	<0.04	<0.04
			0.01	0.026	0.0070		
81285	16Apr98	AGOT 864	30.59	0.501	0.184	<0.04	0.0265
			0.01	0.013	0.011		0.0053
81279	15Apr98	Process Blank #1	—	<0.07	—	—	—
81282	16Apr98	Process Blank #4	—	<0.03	—	—	—
81283	16Apr98	326 Glovebox Blank	—	0.201	<0.2	<0.2	0.250
				0.012			0.030
81294		Process Blank #2	—				
81286	16Apr98	Microchemistry Blank	—	<0.03	—	—	—
81296	17Jul98	Microchemistry Blank	—	<0.04	—	—	—

[a] Total mass Pu-239 in the sample.

Table 3: Uranium and Plutonium Measurements for Irradiated Graphite Samples

Customer Sample I.D.	TIMS Analysis Date [a]	Sample Size (g)	Conc. ± 1σ Error [b] (mass/g graphite)		Atom Ratio ± 1σ Error [c]							
			ng ^{238}U	pg ^{239}Pu	^{236}U/^{235}U	^{234}U/^{238}U	^{235}U/^{238}U	^{236}U/^{238}U	^{239}Pu/^{238}U	^{240}Pu/^{239}Pu	^{241}Pu/^{239}Pu	^{242}Pu/^{239}Pu
S-6-B	18Sep98	10.361	3.697	3.916	0.00561	0.00006679	0.006999	0.00003927	0.001055	0.008408	0.00010026	0.000001070
		0.002	0.042	0.051	0.00010	0.00000033	0.000035	0.00000027	0.000018	0.000042	0.00000066	0.000000064
A-4-B	17Sep98	9.967	4.461	7.026	0.00706	0.00006632	0.006982	0.00004930	0.001569	0.010797	0.00017049	0.000001390
		0.002	0.051	0.084	0.00013	0.00000037	0.000035	0.00000032	0.000026	0.000054	0.00000085	0.000000051
A-3-B	17Sep98	10.067	6.160	40.87	0.01175	0.00006930	0.006736	0.00007912	0.00661	0.018994	0.0004964	0.00000546
		0.002	0.071	0.94	0.00022	0.00000035	0.000034	0.00000058	0.00017	0.000095	0.0000025	0.00000011
S-1-B	17Sep98	10.059	1.916	8.76	0.01507	0.00008932	0.006615	0.00009965	0.004551	0.02416	0.0007947	0.00001105
		0.002	0.022	0.11	0.00029	0.00000072	0.000033	0.00000091	0.000076	0.00012	0.0000040	0.00000010
S-5-B	18Sep98	10.007	1.453	20.40	0.01803	0.00011157	0.006492	0.00011703	0.01398	0.02946	0.0011402	0.000018890
		0.002	0.017	0.24	0.00033	0.00000078	0.000032	0.00000082	0.00023	0.00015	0.0000057	0.000000094
S-6-T	18Sep98	10.833	1.329	1.675	0.01113	0.00008917	0.006222	0.00006926	0.001254	0.019131	0.0003279	0.00005162
		0.002	0.015	0.020	0.00022	0.00000064	0.000031	0.00000073	0.000021	0.000096	0.0000016	0.00000038
A-4-T	17Sep98	10.677	6.473	8.00	0.00649	0.0001117	0.006981	0.00004533	0.001231	0.010121	0.00014963	0.000001272
		0.002	0.075	0.10	0.00016	0.0000013	0.000035	0.00000081	0.000021	0.000051	0.00000075	0.000000036
A-3-T	17Sep98	10.745	1.030	2.122	0.01253	0.0001153	0.006608	0.0000828	0.002051	0.019395	0.0005198	0.00000675
		0.002	0.011	0.025	0.00030	0.0000016	0.000033	0.0000015	0.000033	0.000097	0.0000026	0.00000016
S-1-T	18Sep98	10.647	4.980	14.83	0.01598	0.00010961	0.006547	0.00010461	0.002966	0.02528	0.0008661	0.00001286
		0.002	0.057	0.19	0.00030	0.00000068	0.000033	0.00000076	0.000050	0.00013	0.0000043	0.00000010
S-5-T	18Sep98	10.551	0.1333	0.3429	0.01871	0.0000545	0.002848	0.0000533	0.002562	0.02941	0.0011354	0.00002381
		0.002	0.0015	0.0043	0.00049	0.0000011	0.000015	0.0000010	0.000044	0.00015	0.0000057	0.00000085
Chemical Process	17Sep98	—	0.03220	0.000917	—	0.0000660	0.007653	<0.00004	0.00002835	0.0280	<0.02	0.0206
Blank #1			0.00037	0.000026		0.0000044	0.000075		0.00000088	0.0049		0.0036
Chemical Process	18Sep98	—	0.02955	0.000830	—	0.0000510	0.007103	<0.00003	0.0000280	0.0483	<0.04	<0.05
Blank #2			0.00034	0.000028		0.0000031	0.000063		0.0000010	0.0072		
Microchemistry	23Sep98	—	0.005216	<0.00002	—	<0.00008	0.00682	<0.0002	—	—	—	—
Blank #4			0.000084				0.00014					

[a] nalysis date given is for Pu isotopes, for which no decay correction has been applied.

[b] oncentrations for blanks are given as total mass.

[c] ot decay corrected.