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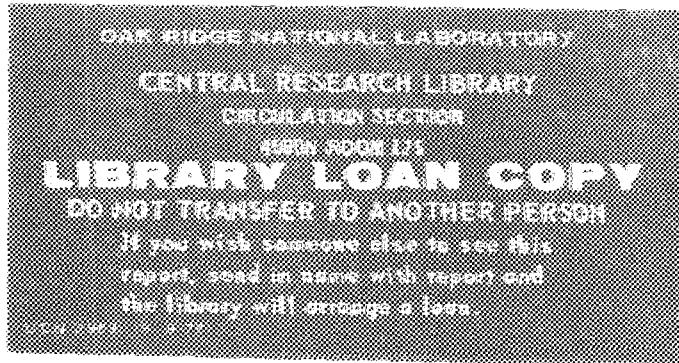
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OAK RIDGE NATIONAL LABORATORY

MARTIN MARIETTA

ISPO Task A-126: Application of Mixed Internal Standards to the Mass Spectrometric Analysis of Plutonium and Uranium in Spent Fuel Dissolver Solutions: ORNL Results

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Abstract

An experiment conducted jointly by the International Atomic Energy Agency, the COGEMA reprocessing facility at LaHague, France, the French Center for Nuclear Studies at Saclay, and ORNL is nearing completion. The aim of this experiment is to evaluate the use of internal standards when applied under field conditions to spent fuel dissolver solutions. Samples were taken at LaHague and shipped to Saclay, the IAEA in Vienna, and ORNL. Both resin beads and dried residues were shipped.

ORNL has analyzed plutonium and uranium from these samples with good results: external precisions for uranium concentrations were +0.06% and for plutonium +0.2%.

Copies of our report sheets are given in the appendices.

INTRODUCTION: Internal Standards

Use of internal standards (also called double spikes) significantly improves the precision and accuracy of isotope ratio measurements. This technique has long been used in geological applications, and the use of synthetic standards for uranium was first suggested by Dietz et al. in 1962.¹ In our experience, improvements in external precision by factors of five or more can be realized when such standards are applied to uranium and plutonium analyses.

Internal standards address one of the thorniest problems in thermal ionization: irreproducibility of ionization behavior from filament to filament. Mass spectrometrists in the field have long known that a different bias correction is needed for each filament, but, without internal standards, are unable to measure it. The universally applied technique is to calibrate the instrument using a certified isotopic standard (such as NBS-U500) and determine what we shall call an average bias correction. This average is derived from a number (5-10) of replicate analyses of different sample loadings on different filaments. The value thus determined is monitored by periodic analysis of certified isotopic standards whose compositions approximate that of typical samples. NBS-U010, NBS-U020, and NBS-U030, with about 1, 2, and 3 atom percent ^{235}U , respectively, are the most often used standards for heavy elements; NBS-Pu947 is also used.

There are many identifiable causes of bias in thermal ionization analysis. All elements will fractionate during the evaporation process, the lighter isotopes being slightly more volatile than the heavy ones. This is a well-known phenomenon, and volatility varies with the inverse square root of the mass. To obtain the best results using an average bias correction, one must take data for all samples at that point on the fractionation curve where this correction applies. This is not easy to do in practice, however. The exact shape of the fractionation curve is unknown for any given sample, being a function of the amount of sample loaded, the chemical form of the sample, what contaminants and how much of them are present, filament temperature, the work function of the

ionizing surface, and many more. The analyst tries to standardize his procedure so that sample size and chemical form are as nearly the same as possible and by following the same thermal conditioning schedule—in general, treating all samples as nearly identically as is possible.

Other factors that affect bias are variable extraction efficiency of the ion source, transmission through the spectrometer, and conversion of ions to electrons at the detector. These factors are not nearly as significant as vagaries in the ionization process and are addressed by internal standards only insofar as they are mass-dependent, as opposed to random, in origin.

To apply an internal standard, one must have a spike that has an isotope ratio that is known to a high degree of accuracy. By comparing the measured value of this ratio to the known, a bias correction applicable to the filament in question can be calculated. The most felicitous case of an internal standard is exemplified by strontium, where the $^{86}\text{Sr}/^{88}\text{Sr}$ ratio is invariant in nature and can be used as an internal standard to determine ^{87}Sr , a fission product used in geochronology. Mother Nature is not usually so cooperative, however, and it then becomes necessary to synthesize one's own internal standard.

For the cases of uranium and plutonium, available spike materials will have isobaric overlaps from sample isotopes, making it essential to have accurate knowledge of the complete isotopic composition of each to allow the necessary corrections to be made. For uranium, the obvious choices for isotopes are ^{233}U and ^{236}U because they are of low abundance in most samples. For plutonium, the choices are ^{242}Pu and ^{244}Pu . Both these isotopes have relatively long half-lives, making them safer to work with than the shorter-lived isotopes and yielding a ratio that is stable on a human time scale.

As an example of applying an internal standard, let us consider uranium. The two isotopes, ^{233}U and ^{236}U , are mixed to give a

ratio of about one. The isotopic composition of this mixture is measured, and an accurate value of the $^{233}\text{U}/^{236}\text{U}$ ratio determined using NBS-U500 ($^{235}\text{U}/^{238}\text{U} = 1.0$) as an internal standard. The concentration of the 233-236 mixture is determined using a gravimetric solution for a reference. Appropriate amounts of spike (also called tracer) are added to the target samples, and an isotopic analysis performed. Computer programs perform the necessary calculation of the bias, and a report sheet of the isotopic composition of the mixture of spike and sample and of the concentration of the sample is generated.

Thus, from the analyst's point of view, use of an internal standard is no different from that of a conventional, single-isotope spike for isotope dilution analysis. The additional work necessary has all been done beforehand by calibrating the internal standard and modifying computer programs.

The theory of internal standards has been discussed by Dodson.^{2,3} Among the elements to have been analyzed by this technique are U^{4,5}, Pb, Ca, Ba, and Mo.⁶ Previous work in this laboratory on uranium and plutonium has been reported.⁷

INTRODUCTION: Task A-126

There have been numerous laboratory experiments verifying the efficacy of internal standards as applied to uranium. Callis has been able to measure isotopic ratios to precisions and accuracies of better than $\pm 0.01\%$,⁸ and precisions of $\pm 0.15\%$ or better were obtained in our laboratory for $^{235}\text{U}/^{238}\text{U}$ ratios during a comprehensive survey of uranium isotopic standards.⁷ We also obtained $\pm 0.1\%$ or better for uranium and plutonium concentration measurements. This is the first reported application of a plutonium internal standard. The consensus is that improvements in precision and accuracy of about a factor of five can be realized by use of internal standards. This means that, for pulse-counting mass spectrometers that analyze nanogram-sized samples, precision improves from about $\pm 0.5\%$ to $\pm 0.1\%$ —a dramatic improvement. For instruments with Faraday cup detectors that analyze microgram-sized samples, precisions much better than $\pm 0.1\%$ should be routinely achievable; we have obtained $\pm 0.005\%$ for replicate analyses of a single sample using our multi-collector commercial instrument.

One area where such analytical improvement would be of great value is in nuclear safeguards. To evaluate the effect of internal standards in a safeguards application, an experiment was set up to be carried out under the administrative leadership of the International Atomic Energy Agency in Vienna. French participation and cooperation were the key to the experiment. Arrangements were made through P. Patigny to sample the French reprocessing plant operated by COGEMA near Cap LaHague. The mass spectrometry section under J. Cesario at the French nuclear center at Saclay synthesized and characterized the internal standards, creating mixtures of the spikes of the two elements in appropriate Pu/U ratios. ORNL participation was funded through ISPO as Task A-126.

The goals of the experiment may be summarized:

1. To compare results obtained using internal standards to those obtained without.

2. To compare results obtained from samples loaded on resin beads⁹ to those obtained from samples loaded conventionally as dried solutions.

Inter- and intra-laboratory comparisons would be made in both cases. The IAEA and Saclay were to analyze all samples by both loading techniques; COGEMA was to analyze only solution loadings, and ORNL was to analyze only resin beads.

To facilitate comparisons, each laboratory was to report its results as calculated in three different ways: 1) using the bias corrections derived from use of the internal standards; 2) applying the conventional average bias corrections; 3) with no bias correction applied.

This report thus contains only a relatively small fraction of the results generated in the experiment. Detailed evaluation of the entire experiment will require the services of a professional statistician.

EXPERIMENTAL OVERVIEW

Two samples were processed in parallel at the COGEMA facility: one taken from a spent-fuel dissolver solution and one provided by Saclay to serve as a reference to calibrate the tracer and in case questions should arise. Each of these two samples was in turn processed in parallel: each was divided into three samples, and all chemical and spiking operations were carried out individually on each subsample. Each of these samples was to be analyzed in duplicate at each laboratory using the loading techniques described above. Table 1 summarizes the samples analyzed at ORNL.

Table 1. Sample Summary

<u>Sample Name</u>	<u>Description</u>
T015	Pure tracers; isotopic analysis only
R015	Pure reference; isotopic analysis only
E015	Pure sample; isotopic analysis only
P215	Mixture of tracer and reference in triplicate; isotopic and isotope dilution analyses.
P315	
P415	
M115	Mixture of tracer and spent fuel sample in triplicate; isotopic and isotope dilution analyses.
M215	
M315	

Thus, since each of the nine samples was analyzed in duplicate for both plutonium and uranium, 36 mass spectrometric analyses were required. In addition, since it had been decided to report results three different ways to facilitate comparisons, 108 different passes through the data reduction computer programs were necessary.

The reference sample, whose characteristics were well-defined and which are summarized in Table 2, was to be used to determine the concentration of the internal standard for use in isotope dilution calculations of the spent fuel sample. The uranium was the natural element.

Table 2. Reference Sample

	238	239	240	241	242	244	
Pu	0.01	95.26	4.52	0.203	0.007	0.000	Saclay (5/15/75)
	0.009	95.32	4.54	0.130	0.007	0.000	Saclay (10/22/84)
	0.2	95.19	4.48	0.131	0.008	0.000	ORNL (10/22/84)
U	233	234	235	236	238		
	0.000	0.0054	0.7205	0.000	99.2741		Saclay
	0.0021	0.0053	0.7186	0.0009	99.2731		ORNL

SAMPLE ACQUISITION

D. H. Smith of ORNL visited the reprocessing facility at LaHague on October 24-26, 1984, to participate in collection of the samples and organize analytical details with staff members of the other laboratories involved. Sample collection proceeded fairly smoothly; the actual hot cell and glove box operations were performed by COGEMA technicians under the direction of S. Deron of IAEA. H. Swietly of IAEA participated in preparation of the resin-bead-loaded samples. Details of this technique for collecting and subsequently mass analyzing uranium and plutonium have been previously described.⁹

EXPERIMENTAL

The samples were received at ORNL via mail from the IAEA in undamaged condition. Samples were analyzed using ORNL's three-stage, high abundance sensitivity mass spectrometer.¹⁰ This instrument is equipped with a pulse-counting detection system to allow analysis of nanogram-sized samples. Data acquisition is effected through a locally designed control panel;¹¹ the software governing data acquisition and processing has been described.^{12,13} These programs automatically apply the bias correction called for, whether calculated from internal standard ratios or by use of an average value.

All samples ran quite well during mass spectrometric analysis, indicating that reasonable loading of the resin beads had been achieved. It was noted, however, that some samples required that two beads be loaded simultaneously on a mass spectrometer filament to obtain a sufficiently intense and stable Pu^+ signal, while others required fairly long times to burn off excess plutonium before starting acquisition of uranium data. This suggests that variable amounts of sample were loaded on the resin beads.

RESULTS AND DISCUSSION

Reference Sample

Our first task was to verify the isotopic composition of the reference sample provided by Saclay. Our results are included in Table 2. Agreement is generally good. The ORNL ^{238}Pu result is not valid because the low abundance of this isotope combined with the high abundance of ^{238}U united to make a good measurement impracticable; this is the cause of the occasional negative values in the appendices. We had only the Pu-U mixture and did not have samples of the pure elements. Because of this, we used Saclay's abundance values for our calculations. They were corrected to October 22, 1984 (the date of sampling) to adjust for radioactive decay. This is particularly significant for ^{241}Pu . On the other hand, we felt constrained to use our abundance values for uranium because we found small amounts of ^{233}U and ^{236}U indicating contamination of the sample. Since these are the internal standard isotopes, the value of the bias corrections calculated from their ratio will be very sensitive to any discrepancy in its value.

Tracer

The internal standard (or tracer) alone was analyzed two different ways. We first measured its isotopic composition from samples loaded on beads at LaHague; results are given in Table 3. We also analyzed some of the starting material obtained directly from Saclay using NBS-U500 and NBS-Pu947, both certified isotopic standards, as internal standards. Table 4 contains our results for uranium. Agreement with Saclay values is quite good, and no problems are anticipated from the slight disagreement between the two laboratories.

Table 3. Analysis of Internal Standard Tracer
from LaHague

	238	239	240	241	242	244	244/242	Conc. $\mu\text{g/g}$	Lab
Pu	0.3537	0.4801	1.7389	0.7582	66.6821	29.9870	0.44970	6.189	Saclay
	0.3499	0.4854	1.7354	0.7562	66.6853	29.9879	0.44969		ORNL
	233	234	235	236	238		236/233	Conc. $\mu\text{g/g}$	Lab
U	67.6520	0.3329	3.0226	28.5470	0.4456		2.36946	981.0	Saclay
	67.6531	0.3308	3.0176	28.5522	0.4464		2.36946		ORNL

Table 4: Uranium Results for Tracer from Saclay

	<u>233/236 (as received)</u>	<u>233/236 (after HC104)</u>
	2.37279	2.37088
	2.37306	2.37059
	2.37074	2.36793
	2.37090	2.37544
	2.37139	2.37374
	2.37056	2.37252
<u>Avg.</u>	2.37157	2.37185
<u>SD</u>	0.00109	0.00264
<u>RSD, %</u>	0.05	0.12
<u>ORNL/Saclay</u>	1.0007	1.0008

The two columns in Table 4 refer to two different sample preparations that were dictated by our experiences with plutonium described below. Each preparation gave an average within $\pm 0.1\%$ of Saclay's values, which is within expected experimental uncertainties.

It was found difficult to obtain comparable precision and agreement with Saclay's values for plutonium. Analysis of our results revealed that the problem was probably due to the fact that we did not have an appropriate reference for use as an internal standard. We used the $^{239}\text{Pu}/^{240}\text{Pu}$ ratio of the NBS-947 certified isotopic reference standard as the calibration ratio for our internal standard calculations. This standard has a $^{239}/^{240}$ ratio of 0.2414, with an isotopic abundance of ^{240}Pu of 18.8%. The abundance of ^{240}Pu in the Saclay internal standard was about 1.7%. Our mixture of the Saclay internal standard and NBS-947 was in an approximate 60/40 ratio with an abundance of ^{240}Pu of about 8.4%. The relatively high contribution of the internal standard

to this mass position resulted in a less-than-perfect situation with regard to correction of it prior to performing calibration calculations: about 12% of the total counts had to be subtracted before the bias correction per mass could be calculated. Although our precision and agreement with the Saclay value for the $^{244}\text{Pu}/^{242}\text{Pu}$ ratio were within the targeted range of $\pm 0.2\%$, previous experience had led us to hope for better results.⁷ To investigate the possibility of failure to attain isotopic equilibrium during mixing of the two components, we prepared a second set of samples that had been evaporated with HClO_4 to break up any polymers that might have formed. Results from the two preparations were comparable, thus eliminating this possibility. Another possible limitation to our precision was due to counting statistics. We therefore analyzed the samples from the original preparation a second time using a peak monitoring scheme devised to give approximately the same numbers of counts for each critical mass position (239, 240, 242, 244): the time spent on each isotope was in a 1:4:1:2 ratio. Results are given in Table 5a.

With a mixture of this sort, one can use either component as the internal standard; our goal was, of course, to verify the abundance values measured at Saclay for the material later used as the internal standard for the LaHague spent fuel sample, but using Saclay's reference value for the $^{244}\text{Pu}/^{242}\text{Pu}$ ratio as the internal standard calibration ratio provided a check on the results obtained using the NBS-947 as the internal standard. Results are presented in table 5. Table 5a lists values obtained for the $^{244}\text{Pu}/^{242}\text{Pu}$ using the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio as the internal standard for both sets of analyses; those in the first column were obtained for the first set of measurements which had relative factors of 1:2:1:1 for the times spent on mass positions 239, 240, 242, and 244, respectively; in the second column, the results for the second analyses, with relative times of 1:4:1:2 for the critical isotopes, are listed. Table 5b presents different results obtained from the same data; in this case, $^{240}\text{Pu}/^{239}\text{Pu}$ was calculated using the $^{244}\text{Pu}/^{242}\text{Pu}$ from the Saclay spike as the internal standard. This ratio should be the

Table. 5a. Calibration of Saclay Tracer using NBS-947 as Internal Standard

	244/242 (1)	SD		244/242 (2)	SD
1	0.45082	0.00217	7	0.44904	0.00213
2	0.44956	0.00274	8	0.44946	0.00273
3	0.44882	0.00266	9	0.44804	0.00184
4	0.44983	0.00261	10	0.45014	0.00215
5	0.44861	0.00156	11	0.44927	0.00160
6	<u>0.44860</u>	<u>0.00190</u>	12	<u>0.44985</u>	<u>0.00216</u>
X =	0.44937	0.00227		0.44930	0.00210
SD =	0.00087			0.00073	
RSD =	0.20%			0.16%	

Table. 5b. Calibration of NBS-947 using Saclay Tracer as Internal Standard

	240/239 (1)	SD		240/239 (2)	SD
1	0.24087	0.00045	7	0.24131	0.00044
2	0.24113	0.00058	8	0.24121	0.00056
3	0.24130	0.00056	9	0.24152	0.00039
4	0.24107	0.00054	10	0.24108	0.00045
5	0.24133	0.00033	11	0.24127	0.00034
6	<u>0.24134</u>	<u>0.00061</u>	12	<u>0.24115</u>	<u>0.00046</u>
X =	0.24117	0.00051		0.24126	0.00044
SD =	0.00019			0.00015	
RSD =	0.08%			0.06%	

(1) 1:2:1:1 Scanning scheme

(2) 1:4:1:2 Scanning scheme

certified value for NBS-947 at the date in question: 0.24136. Thus, our accuracy in Table 5b is better than 0.1%. The results show about a 25% improvement in precision when the optimized scanning scheme was used (i.e., comparing between the two columns); however, for the $^{244}\text{Pu}/^{242}\text{Pu}$ ratios listed in Table 5a, precision is still about $\pm 0.2\%$, which meets our goal but is not as good as we had hoped. On the other hand, when $^{244}\text{Pu}/^{242}\text{Pu}$ ratio is used for calibration purposes, internal precisions for the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio are improved by more than a factor of four. External precisions were improved by a factor of 2.5, to better than $\pm 0.1\%$, which is consistent with our previous experience. During an earlier calibration of a $^{244}\text{Pu}/^{242}\text{Pu}$ internal standard synthesized in our laboratory for ORNL use, we used enriched isotopes that yielded a much lower (0.07%) abundance of ^{240}Pu and thus required application of a much lower correction during data processing. Results of this calibration are summarized in Table 6.

Precision for the $^{244}\text{Pu}/^{242}\text{Pu}$ ratio for these measurements is $\pm 0.06\%$; thus, from Tables 5b and 6, it seems clear that our inability to duplicate this level of precision for the results in Table 5a is due to the combination of a relatively high concentration of ^{240}Pu in the proposed internal standard and a relatively low abundance of that isotope in the certified reference material used to calibrate it. What is needed is a reference material that has a $^{240}\text{Pu}/^{239}\text{Pu}$ reasonably close to 1.0 to reduce the statistical effects of the correction. Since enriched plutonium isotopes of sufficient purity for use in internal standard applications are in extremely short supply, it may be necessary to synthesize such a calibration sample solely to certify internal standards.

To keep results from the various laboratories consistent, we used the Saclay values for the critical isotopic ratios ($^{244}\text{Pu}/^{242}\text{Pu}$ and $^{233}\text{U}/^{238}\text{U}$). In neither case did our values differ significantly from theirs.

Table 6. Calibration of Local ORNL Pu Internal Standard

	<u>238/242</u>	<u>239/242</u>	<u>240/242</u>	<u>241/242</u>	<u>244/242</u>
	0.00000	0.00042	0.00133	0.00015	0.99682
	0.00001	0.00046	0.00137	0.00020	0.99587
	0.00001	0.00046	0.00136	0.00018	0.99681
	0.00002	0.00045	0.00136	0.00018	0.99720
	0.00001	0.00046	0.00138	0.00018	0.99586
<u>Avg</u>	0.0001	0.00045	0.00136	0.00018	0.99663
<u>SD</u>	0.0005	0.00001	0.00002	0.00002	0.00062

Unspiked Sample

Analyses of the unspiked sample are summarized in Table 7. It is unfortunate that insufficient high purity ^{236}U is available for isotope dilution work. This isotope, enriched to 99% or better, could be mixed with high purity ^{233}U (which is available) to yield an internal standard capable of refining $^{235}\text{U}/^{238}\text{U}$ values to give external precisions comparable to those for isotope dilution ratios. The ^{236}U used in this experiment was obtained from the U. S. and had an enrichment of about 89%. It also had about 10% ^{235}U and, when mixed 1:2 with ^{233}U , led to a tracer of about 3% ^{235}U (see Table 3). Since the sample was less than 1% ^{235}U , the adjustment necessary to apply to that mass position to correct for the contribution of the tracer in the mixture was too large to yield reliable results. There was no way of checking the results in Table 7 since the composition of the sample was unknown.

Table 7. Isotopic Analysis of Spent Fuel Sample

	238	239	240	241	242	244
Pu	1.312	60.484	23.719	9.872	4.613	0.000
	233	234	235	236	238	
U	0.000	0.0144	0.8856	0.3072	98.793	

Reference Plus Tracer

To obtain a concentration for the tracer, it was necessary to use the reference sample as a calibration standard. Since, in the mixture of tracer and reference sample, the calibration ratio was to be found in the sample rather than the spike, our computer programs¹³ were revised to accommodate this combination. Results for the same analyses calculated both with an average bias correction applied and with the specific bias corrections calculated through use of the internal standards are listed in Table 8. As can be seen, use of the internal standard substantially improved the precision for the six analyses of each element by factors of about 2 and 4 for plutonium and uranium, respectively.

Table 8. Tracer Calibration

Sample	Concentration, $\mu\text{g/g}$			
	Avg.	Int. Std.	Avg.	Int. Std.
P215	10.228	10.160	1420.20	1424.10
	10.227	10.134	1421.95	1423.38
P315	10.160	10.166	1426.23	1421.59
	10.195	10.151	1425.40	1423.45
P415	10.147	10.184	1428.52	1422.83
	10.175	10.139	1428.38	1422.85
Avg.	10.189	10.156	1425.11	1423.03
S.D.	0.034	0.018	3.4	0.84
RSD, %	0.33	0.18	0.24	0.06

Sample Plus Tracer

The concentrations of the tracer determined by application of average bias corrections were used to determine the concentration of the sample when average bias corrections were applied. For calculations using internal standards, the tracer concentrations supplied by Saclay were used. The results are summarized in Table 9. Precision for uranium concentration measurements was again improved by about a factor of four, but plutonium results yielded the same precision calculated either way.

Table 9. Sample Concentration Results

Sample	Concentrations, $\mu\text{g/g}$			
	Pu		U	
	Avg.	Int. Std.	Avg.	Int. Std.
M115	6.382	6.352	890.90	894.91
	6.370	6.365	894.69	894.11
M215	6.373	6.367	891.23	894.41
	6.357	6.364	890.27	895.45
M315	6.391	6.347	889.48	895.09
	6.370	6.337	888.38	895.24
Avg.	6.373	6.355	890.83	894.87
S.D.	0.012	0.012	2.15	0.51
RSD, %	0.19	0.19	0.24	0.06

Comments

The results presented in Tables 8 and 9 deserve some comment. First, the results obtained using our average bias correction are better than we usually obtain. A typical precision is in the range of 0.2-0.5%; except for plutonium in the reference-tracer mixture, we are in the lower portion of this range in Tables 8 and 9. Thus, the improvement in results obtained through use of an internal standard is not as dramatic as usual. Nonetheless, the consistent improvement of a factor of four in uranium concentration measurements is noteworthy.

To make comparisons as meaningful as possible, concentrations for uranium with average bias were calculated using 238/233 as the isotope dilution ratio. Any errors in the bias correction per mass is thus magnified by a factor of five by the difference in mass between the two isotopes. If 238/236 ratios had been used, more precise results could have been obtained, although it is possible that the relatively large contribution of the sample at the mass 236 positron might cause some loss in accuracy. In any case, since the goal of the experiment was to compare results obtained using internal standards to those obtained in a conventional manner, use of 238/233 for the isotope dilution ratio was indicated.

Another observation requiring comment is the inferior precision of plutonium concentration measurements in comparison to those for uranium. Because of the element's relatively benign behavior under thermal ionization conditions, plutonium analyses usually give better precision than uranium with application of an average bias correction; and we have always obtained $\pm 0.1\%$ or better on previous analyses using a plutonium internal standard.⁷ It appears that something is keeping our precision for plutonium concentrations using an internal standard at $\pm 0.2\%$. We collected about 4×10^6 counts of ^{244}Pu during a typical analysis, which imposes a lower limit of $\pm 0.05\%$ precision due to counting statistics; thus this approach does not explain our (relatively) poor results.

Any time one encounters erratic results in isotope dilution analyses of plutonium, the question of isotopic equilibration arises. For a valid isotope dilution analysis, sample and tracer must be brought to the same oxidation state at some point in the process. Uranium usually presents no problem, but plutonium can be very difficult. Plutonium assumes a multiplicity of oxidation states, and its various molecular anions tend to polymerize. Both these facts must be addressed in a successful equilibration procedure. Marsh et al. made a comparative study of ten reduction-oxidation equilibration procedures and found only one that reliably achieved its goal.¹⁴ This procedure involves reduction to Pu (III) with heated ferrous sulfamate followed by oxidation to Pu (IV) with heated sodium nitrite. This is the procedure followed by COGEMA at LaHague.

It is still possible that equilibrium was not attained. There are two points at which such an operation would be necessary: in synthesizing the internal standard from its enriched ^{242}Pu and ^{244}Pu components, and in mixing the tracer with the sample at LaHague. The fact that our analysis of the tracer supplied directly by Saclay (see Table 5b) gave results both accurate and precise indicates that equilibration was achieved in the former step. Use of an internal standard provides the potential of much higher precision than has previously been accessible, which in turn can lead to exposure of heretofore unsuspected problems. We would consider the precision of our plutonium results using an average bias correction as excellent ($\pm 0.2 - 0.35\%$), while those using the internal standard as mediocre.

The stated goal of the experiment, however, is to obtain a precision and accuracy of $\pm 0.2\%$ for isotope dilution analyses,¹⁵ and that goal has been met at ORNL.

An important point to keep in mind is that the results in Tables 8 and 9 are for three separate and independent sample preparations. This means that all chemical operations, including plutonium sample-tracer equilibration, were carried out individually for each of the three samples. Uranium concentration measurements of the precision we observed ($\pm 0.06\%$) are utterly impossible in our laboratory without using an internal standard.

It is instructive to investigate in more detail the operation of internal standards. Our average bias correction for uranium is 0.368% per mass and that for plutonium is 0.628% per mass. To apply it one selects a base mass (usually 238 for uranium and 242 for plutonium) that has a defined bias of 1.0. Multiplying the bias correction per mass by the difference in mass units between the isotope in question and the base mass and subtracting this from 1.0 yields the bias correction to apply to the intensity of the isotope in question. For example, for ^{235}U , the calculation would be $1.0 - 3(0.00368) = 0.9890$; for ^{244}Pu : $1.0 + 2(0.00628) = 1.0126$. Table 10 presents mean values of bias corrections

Table 10. Bias Corrections Calculated from Internal Standards

Sample	Pu		U	
	Bias Corr., %/Mass	Calc. Bias/ Avg. Bias*	Bias Corr., %/Mass	Calc. Bias/ Avg. Bias*
T015	0.601	0.957	0.575	1.563
	0.476	0.758	0.466	1.266
P215	0.408	0.650	0.320	0.870
	0.319	0.508	0.355	0.965
P315	0.647	1.030	0.433	1.177
	0.487	0.775	0.410	1.114
P415	0.723	1.151	0.465	1.234
	0.502	0.799	0.454	1.234
M115	0.681	1.084	0.423	1.149
	0.559	0.890	0.329	0.894
M215	0.564	0.898	0.418	1.136
	0.490	0.780	0.446	1.212
M315	0.690	1.099	0.465	1.264
	0.797	1.269	0.492	1.337
Avg.	0.567	0.903	0.432	1.175
S.D.	0.131	0.209	0.067	0.181
RSD%	23.2	23.2	15.4	15.4

*Avg. bias correction = 0.628%/mass (Pu); 0.368%/mass (U).

applied to the various mixtures of tracer with reference or sample. Each mean is taken from the individual values, one for each run, that comprised the analysis. Ten to twelve runs were taken for each sample. Also included in the table are the values of the ratios obtained when the bias corrections calculated from the internal standards were divided by the average bias correction of the element in question. These ratios should, when averaged over all samples, give a value of 1.0. Neither of our values is 1.0, but the limits of error overlap that figure. The evidence indicates that our average bias correction for uranium may be a bit low, but this may be due to similar chemical interaction of the samples with the filaments. We have noted before that samples of similar origin tend to require similar bias corrections.

It should be pointed out that, if the internal standards are properly calibrated, the bias corrections calculated from them will be the correct ones. We have had occasions where, for less well-behaved samples than those of this experiment, the bias correction per mass has been negative. Bias correction values during a single analysis often vary +20% from the average for that analysis.

CONCLUSIONS

It is clear from our results that use of internal standards more than justifies the additional cost and effort involved in synthesizing and calibrating them. Material balance calculations for safeguards require the highest possible precision, and it is only through use of internal standards that levels of $\pm 0.1\%$ or better can be approached using pulse-counting instruments, or $\pm 0.01\%$ using instruments with current-integrating detectors. An additional advantage that we hope will be made clear when results from all participants are correlated is that, with the internal standard, all laboratories will have calibrated to an identical ratio. Round robin experiments, such as IDA-80¹⁶ and that of the resin bead overseen by NBS and funded by the Office of Safeguards and Security,¹⁷ have usually shown more scatter in interlaboratory than in intralaboratory results; in other words, laboratories disagreed with each other more than they did with themselves. One reason for this variance lies in the vagaries of instrumental calibration, which vary between laboratories. It is hoped and expected that internal standards will largely eliminate this effect.

To have a viable internal standard program on an international (or even national) scale, enriched isotopes of sufficient purity must be available in sufficient quantity. Earlier in this report we described the benefits that would accrue if ^{236}U were available in 99% purity as opposed to the 89% now available. The problem is even worse for plutonium. With uranium, we can at least perform isotope dilution measurements with the present stock, although we cannot provide precise $^{235}\text{U}/^{238}\text{U}$ ratios; with plutonium, there is not enough ^{244}Pu of any purity to allow more than the most valuable of samples to be treated with internal standards. It is hoped that the results of this experiment will provide a cogent argument for production of the two isotopes in short supply.

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Appendix 1: Results with No Bias Correction

Laboratoire ORNL		Echantillon	R015		Methode GR			
Signature -----	Date 11- 9-85	Correction	WITHOUT		Element FU			
	Bloc	Intensite Principale	238/239	240/239	241/239	242/239	244/239	Element us/s
	1	1.6E-14	0.001583	0.046956	0.001338	0.000069	0.000002	
	2	1.4E-14	-0.001333	0.047110	0.001294	0.000064	0.000000	
	3	1.1E-14	-0.002450	0.046587	0.001292	0.000093	0.000004	
Filament	4	1.9E-14	-0.001314	0.046745	0.001441*	0.000070	0.000000	
	5	1.8E-14	-0.001180	0.046797	0.001355	0.000078	0.000002	
	6	1.6E-14	-0.000035	0.046772	0.001352	0.000075	0.000000	
Date de	7	1.5E-14	-0.001791	0.046922	0.001337	0.000088	0.000004	
Mesure	8	1.6E-14	0.000604	0.047029	0.001385	0.000075	0.000000	
22-10-84	9	1.3E-14	-0.001415	0.047015	0.001349	0.000078	0.000000	
	10	1.5E-14	-0.000753	0.047215	0.001344	0.000080	0.000004	
Valeurs moyennes			-0.000808	0.046915	0.001339	0.000077	0.000002	
SD			0.001203	0.000190	0.000029	0.000009	0.000002	
	1	2.5E-16	-0.015793	0.046845	0.001585*	0.000158*	0.000067*	
	2	3.0E-16	-0.010190	0.047035	0.001520	0.000128	0.000050*	
	3	6.6E-16	-0.002037	0.047072	0.001312	0.000106	0.000026	
Filament	4	6.8E-16	-0.006572	0.046635	0.001384	0.000082	0.000011	
	5	1.7E-15	0.002136	0.046752	0.001357	0.000066	0.000001	
	6	1.6E-15	0.006381	0.047143	0.001318	0.000079	0.000004	
Date de	7	5.5E-15	-0.007401	0.046509	0.001325	0.000078	0.000003	
Mesure	8	4.8E-15	0.010592	0.046860	0.001317	0.000070	0.000000	
22-10-84	9	1.3E-14	-0.008051	0.046193	0.001291	0.000072	0.000001	
	10	1.1E-14	-0.002789	0.046223	0.001343	0.000079	0.000000	
	11	1.7E-14	0.036418	0.046421*	0.001307	0.000064	0.000000	
	12	1.2E-14	0.015059	0.046852	0.001368	0.000064	0.000002	
Valeurs moyennes			0.001479	0.046738	0.001349	0.000081	0.000005	
SD			0.014181	0.000321	0.000063	0.000020	0.000008	
	1	1.6E-14	-0.000176	0.046479	0.001339	0.000065	0.000007	
	2	1.5E-14	-0.000007	0.046785	0.001318	0.000083	0.000006	
	3	1.4E-14	-0.000000	0.046628	0.001350	0.000085	0.000003	
Filament	4	1.3E-14	0.000088	0.046871	0.001331	0.000084	0.000000	
	5	1.7E-14	0.000026	0.046861	0.001314	0.000078	0.000004	
	6	1.6E-14	-0.000236	0.046263	0.001380	0.000073	0.000002	
Date de	7	1.7E-14	0.000149	0.046368	0.001396	0.000079	0.000000	
Mesure	8	1.7E-14	-0.000433	0.046691	0.001389	0.000097*	0.000003	
22-10-84	9	1.6E-14	-0.000299	0.046424	0.001338	0.000077	0.000000	
	10	1.6E-14	0.000059	0.046417	0.001309	0.000074	0.000001	
Valeurs moyennes			-0.000013	0.046579	0.001347	0.000078	0.000003	
SD			0.000335	0.000218	0.000032	0.000006	0.000003	

Laboratoire ORNL		Echantillon E015		Methode GR	
Signature	Date 11-9-85	Correction	WITHOUT	Element Pb	Element us/s
		Intensite			
Bloc	Principal	238/239	240/239	241/239	242/239
1	1.6E-14	0.022042	0.389519	0.161480	0.075027
2	1.3E-14	0.021772	0.389895	0.161090	0.075679*
3	1.6E-14	0.022130	0.389242	0.160864	0.074702
Filament	4	1.2E-14	0.021117	0.388432	0.160536
1	5	1.5E-14	0.021922	0.388189	0.161083
6	1.1E-14	0.022095	0.389734	0.160368	0.074432
Date de	7	1.6E-14	0.022607	0.388868	0.161232
Mesure	8	1.2E-14	0.022464	0.389394	0.161248
22-10-84	9	1.5E-14	0.021849	0.390201	0.161076
	10	1.1E-14	0.021452	0.390105	0.162243*
Valeurs moyennes		0.021945	0.389358	0.160997	0.074671
SD		0.000440	0.000683	0.000354	0.000384
1	1.6E-14	0.021433	0.389017	0.161392	0.074520
2	1.4E-14	0.021475	0.390595	0.161842	0.074785
3	1.2E-14	0.021379	0.388759	0.160898	0.074707
Filament	4	1.1E-14	0.021526	0.390961	0.162286
2	5	1.6E-14	0.021749	0.390651	0.161278
6	1.5E-14	0.021647	0.390461	0.161790	0.075204
Date de	7	1.4E-14	0.021819	0.390430	0.161556
Mesure	8	1.6E-14	0.021958	0.390496	0.161896
22-10-84	9	1.5E-14	0.021466	0.390241	0.161042
	10	1.4E-14	0.021968	0.389496	0.161424
	11	1.6E-14	0.020957	0.391404	0.161172
Valeurs moyennes		0.021580	0.390228	0.161507	0.074929
SD		0.000293	0.000810	0.000415	0.000363
1	1.6E-14	0.020894	0.388454	0.160272	0.074545
2	1.5E-14	0.021596	0.389302	0.160408	0.074930
3	1.3E-14	0.021930	0.389122	0.160710	0.074148
Filament	4	1.8E-14	0.022472	0.388638	0.160812
3	5	1.9E-14	0.021442	0.388871	0.161162
6	1.9E-14	0.021466	0.388906	0.160041	0.074180
Date de	7	1.9E-14	0.021740	0.390254	0.162141*
Mesure	8	2.1E-14	0.021591	0.390132	0.161150
22-10-84	9	2.2E-14	0.022301	0.390402	0.161276
	10	1.7E-14	0.022321	0.389709	0.160207
Valeurs moyennes		0.021775	0.389379	0.160671	0.0746B6
SD		0.000487	0.000703	0.000461	0.000347

Laboratoire ORNL	Echantillon P415				Methode GR
Signature -----	Date 11-9-85	Correction	WITHOUT	Element PU	Element us/s
Bloc	Intensite	238/239	240/239	241/239	242/239
1	Principal	0.005582	0.073646	0.013636*	1.037244
2	1.5E-14	0.005791	0.073937	0.012979	1.040786
3	1.2E-14	0.005572	0.073567	0.013000	1.033171
Filament	4	1.6E-14	0.005602	0.073659	0.013239
1	1.4E-14	0.005893	0.074157	0.013064	1.038228
6	1.3E-14	0.005746	0.073397	0.012942	1.035936
Date de	7	1.8E-14	0.005765	0.073710	0.012922
Mesure	8	1.7E-14	0.005725	0.073997	0.012980
22-10-84	9	1.7E-14	0.005827	0.073917	0.012905
10	1.7E-14	0.00571	0.073577	0.013019	1.036482
11	1.7E-14	0.005728	0.073805	0.013063	1.036155
12	1.6E-14	0.005750	0.073721	0.012936	1.039764
Valeurs moyennes		0.005713	0.073758	0.013004	1.036792
SD		0.000107	0.000213	0.000094	0.002469
					9.9544
1	2.0E-14	0.005621	0.074062	0.012909	1.039571
2	2.1E-14	0.005739	0.073873	0.012966	1.038721
3	2.2E-14	0.005416	0.073757	0.013042	1.038543
Filament	4	1.7E-14	0.005321	0.073797	0.013025
2	5	1.7E-14	0.005556	0.074106	0.013033
6	1.7E-14	0.005550	0.073891	0.012846	1.040017
Date de	7	1.7E-14	0.005570	0.073455	0.012949
Mesure	8	1.6E-14	0.005497	0.073876	0.013097
22-10-84	9	1.6E-14	0.006112	0.073606	0.013021
10	1.6E-14	0.005766	0.074283	0.013185	1.042746*
Valeurs moyennes		0.005617	0.073871	0.013007	1.039422
SD		0.000221	0.000241	0.000096	0.001015
					9.9817

Laboratoire ORNL		Echantillon		M115		Methode GR	
Signature	Date 11- 9-85	Correction	WITHOUT			Element PU	
		Intensite				Element us/s	
	Bloc	Principal	238/239	240/239	241/239	242/239	244/239
	1	1.7E-14	0.028660	0.421353	0.175973*	1.465722	0.615988
	2	1.3E-14	0.028962	0.422742	0.175456	1.469781	0.616396
	3	1.6E-14	0.028096	0.422096	0.174959	1.471388	0.621010
Filament	4	1.3E-14	0.027817	0.422670	0.175730	1.476381	0.621123
	1	1.1E-14	0.028010	0.426324*	0.175946	1.477191	0.623324
	6	1.8E-14	0.029172	0.423233	0.175106	1.471942	0.620184
Date de	7	1.5E-14	0.028838	0.422463	0.175443	1.474239	0.621153
Measure	8	1.3E-14	0.029334	0.420545	0.175704	1.472770	0.619949
22-10-84	9	1.7E-14	0.029182	0.425243	0.176436	1.484780	0.627373
	10	1.4E-14	0.027553	0.422218	0.176159	1.481749	0.628009
Valeurs moyennes			0.028562	0.422507	0.175660	1.474594	0.621451
SD			0.000641	0.001301	0.000478	0.005652	0.003961
							6.4918
	1	1.6E-14	0.028983	0.423545	0.175851	1.477374	0.624606
	2	1.5E-14	0.028549	0.423377	0.175966	1.474179	0.621818
	3	1.3E-14	0.028887	0.423003	0.176092	1.477117	0.621987
Filament	4	1.7E-14	0.029049	0.422637	0.175619	1.473635	0.624014
	2	1.6E-14	0.028908	0.422774	0.175791	1.476534	0.622553
	6	1.5E-14	0.028848	0.423334	0.175739	1.476777	0.6222841
Date de	7	1.4E-14	0.029247	0.425137*	0.175966	1.480603	0.624191
Measure	8	1.7E-14	0.029126	0.423881	0.175808	1.478736	0.626536
22-10-84	9	1.5E-14	0.028609	0.422826	0.175773	1.481297	0.626308
	10	1.4E-14	0.029209	0.422663	0.175879	1.474862	0.624511
Valeurs moyennes			0.028942	0.423116	0.175848	1.477111	0.623937
SD			0.000233	0.000438	0.000135	0.002552	0.001654
							6.4800

Laboratoire ORNL	Date	Echantillon	M215	Methode GR			
Signature -----	11-9-85	Correction	WITHOUT	Element PU			
Bloc	Intensite Principale	238/239	240/239	241/239	242/239	244/239	Element us/d
1	1.8E-14	0.029233	0.423174	0.175155	1.533962	0.646418*	
2	1.8E-14	0.029575	0.424587	0.175831	1.540682	0.651733	
3	1.8E-14	0.029026	0.424478	0.176120	1.538914	0.652197	
Filament	4	1.7E-14	0.029078	0.424420	0.176561	1.538848	0.652647
1	5	1.6E-14	0.028921	0.424649	0.176336	1.544706	0.652442
6	1.7E-14	0.029098	0.424687	0.175983	1.538332	0.652160	
Date de	7	1.5E-14	0.029094	0.424527	0.176109	1.543082	0.652383
Meure	8	1.4E-14	0.028946	0.422989*	0.177158	1.540952	0.653721
22-10-84	9	1.7E-14	0.029657	0.426127	0.178318*	1.547936	0.655262
	10	1.5E-14	0.029367	0.426110	0.176625	1.544197	0.654816
Valeurs moyennes		0.029199	0.424751	0.176209	1.541161	0.653040	6.4817
SD		0.000255	0.000901	0.000563	0.003970	0.001260	
	1	1.4E-14	0.029158	0.423745	0.179892*	1.542311	0.651469
	2	1.4E-14	0.029144	0.424649	0.176903	1.543974	0.651555
	3	1.1E-14	0.028851	0.425415	0.176716	1.543858	0.652581
Filament	4	1.2E-14	0.029368	0.423752	0.177366	1.545188	0.656884
2	5	8.7E-15	0.029201	0.425768	0.176172	1.543617	0.654070
	6	1.8E-14	0.028955	0.424002	0.176536	1.545889	0.654503
Date de	7	1.9E-14	0.028852	0.425690	0.176409	1.547000	0.655946
Meure	8	1.7E-14	0.029339	0.425174	0.176143	1.544782	0.656413
22-10-84	9	1.7E-14	0.029224	0.425640	0.175856	1.544344	0.654949
	10	1.7E-14	0.029069	0.423737	0.176582	1.546348	0.655984
	11	1.7E-14	0.029410	0.424164	0.175992	1.546462	0.657575
	12	1.6E-14	0.029191	0.424393	0.176835	1.546664	0.654582
Valeurs moyennes		0.029147	0.424677	0.176501	1.545036	0.654709	6.4644
SD		0.000187	0.000817	0.000447	0.001462	0.002011	

Laboratoire ORNL	Date	Echantillon	T015	Methode GR
Signature -----	11- 9-85	Correction	WITHOUT	Element U
Intensite				
Bloc	Principal	233/238	234/238	235/238
1	5.8E-14	156.951355	0.754622	6.933789
2	6.2E-14	154.275833	0.742473	6.811355
3	5.3E-14	158.233536	0.774981	6.972669
Filament	4	4.6E-14	157.865799	0.758396
1	5	3.9E-14	153.988556	0.744380
	6	5.1E-14	155.485535	0.758256
Date de	7	4.1E-14	155.833282	0.761189
Mesure	8	4.8E-14	156.957092	0.760887
24- 1-85	9	3.6E-14	154.551559	0.757937
	10	5.4E-14	157.219086*	0.771332
Valeurs moyennes		156.015839	0.758445	6.886503
SD		1.569149	0.010115	0.073854
Element us/d				
	1	5.6E-14	153.968414	0.760672
	2	5.5E-14	154.493954	0.748375
	3	4.9E-14	153.824615	0.746358
Filament	4	4.6E-14	156.584137	0.768190
2	5	4.4E-14	154.643127	0.757203
	6	4.1E-14	153.735504	0.746217
Date de	7	5.4E-14	156.148880	0.766590
Mesure	8	4.8E-14	153.148956	0.752167
28- 1-85	9	4.7E-14	153.531128	0.743461
	10	5.4E-14	156.669098	0.754485
	11	4.9E-14	156.020035	0.759649
Valeurs moyennes		154.997086	0.754851	6.845465
SD		1.318293	0.008390	0.058389
				0.511450

Laboratoire ORNL		Echantillon R015			Methode BR
Signature	Date 11- 9-85	Correction	WITHOUT	Element U	
		Intensite			Element us/g
	Bloc Principal	233/238	234/238	235/238	236/238
	1 4.9E-14	0.000020	0.000056	0.007324	0.000005
	2 4.7E-14	0.000019	0.000052	0.007240	0.000009
	3 4.4E-14	0.000020	0.000051	0.007278	0.000010
Filament	4 5.3E-14	0.000021	0.000051	0.007389	0.000010
1	5 4.8E-14	0.000018	0.000058	0.007273	0.000011
	6 4.1E-14	0.000015	0.000055	0.007329	0.000010
Date de	7 3.4E-14	0.000020	0.000058	0.007223	0.000014
Measure	8 4.7E-14	0.000016	0.000050	0.007229	0.000010
24- 1-85	9 3.1E-14	0.000024	0.000060	0.007197	0.000007
	10 4.1E-14	0.000027*	0.000058	0.007300	0.000008
Valeurs moyennes		0.000019	0.000055	0.007278	0.000009
SD		0.000003	0.000004	0.000059	0.000002
	1 5.8E-14	0.000026	0.000048*	0.007234	0.000010
	2 6.1E-14	0.000019	0.000056	0.007277	0.000011
	3 6.6E-14	0.000023	0.000051	0.007339	0.000011
Filament	4 5.4E-14	0.000022	0.000052	0.007312	0.000013
2	5 5.4E-14	0.000016	0.000054	0.007432	0.000007
	6 5.4E-14	0.000016	0.000055	0.007414	0.000011
Date de	7 5.4E-14	0.000023	0.000056	0.007313	0.000007
Measure	8 5.3E-14	0.000019	0.000055	0.007309	0.000010
24- 1-85	9 5.2E-14	0.000021	0.000056	0.007317	0.000010
	10 5.3E-14	0.000023	0.000056	0.007378	0.000008
Valeurs moyennes		0.000021	0.000055	0.007332	0.000010
SD		0.000003	0.000002	0.000060	0.000002
	1 5.0E-14	0.000022	0.000051	0.007332	0.000009
	2 4.7E-14	0.000019	0.000052	0.007420	0.000008
	3 4.5E-14	0.000021	0.000058	0.007409	0.000013
Filament	4 5.2E-14	0.000022	0.000055	0.007345	0.000009
3	5 5.0E-14	0.000023	0.000063*	0.007349	0.000007
	6 4.7E-14	0.000020	0.000055	0.007304	0.000008
Date de	7 4.5E-14	0.000016*	0.000052	0.007315	0.000011
Measure	8 5.6E-14	0.000023	0.000048	0.007359	0.000012
4- 2-85	9 5.6E-14	0.000022	0.000051	0.007310	0.000008
	10 5.3E-14	0.000026	0.000053	0.007312	0.000009
Valeurs moyennes		0.000022	0.000053	0.007346	0.000009
SD		0.000002	0.000003	0.000041	0.000002

Laboratoire	ORNL	Date	Echantillon	E015	Methode	GR
Signature	-----	11- 9-85	Correction	WITHOUT	Element	U
			Intensite			Element us/s
Bloc	Principal	233/238	234/238	235/238	236/238	
1	5.2E-14	0.000000	0.000138	0.009061	0.003076	
2	4.8E-14	0.000000	0.000144	0.008952	0.003068	
3	4.4E-14	0.000000	0.000157	0.008995	0.003115	
Filament	4	5.0E-14	0.000000	0.000142	0.008935	0.003104
1	5	4.3E-14	0.000000	0.000139	0.008998	0.003129
	6	3.8E-14	0.000000	0.000152	0.009049	0.003129
Date de	7	5.0E-14	0.000000	0.000159	0.008973	0.003116
Mesure	8	4.2E-14	0.000001	0.000145	0.009008	0.003085
25- 1-85	9	4.5E-14	0.000000	0.000149	0.008976	0.003089
	10	3.7E-14	0.000000	0.000140	0.008983	0.003176*
Valeurs moyennes		0.000000	0.000146	0.008993	0.003101	
SD		0.000000	0.000008	0.000039	0.000023	
1	5.2E-14	0.000000	0.000162*	0.009071	0.003170	
2	4.9E-14	0.000000	0.000145	0.009192*	0.003172	
3	4.6E-14	0.000000	0.000150	0.009068	0.003111	
Filament	4	5.2E-14	0.000001	0.000143	0.009046	0.003087
2	5	4.9E-14	0.000000	0.000148	0.009024	0.003138
	6	4.7E-14	0.000000	0.000140	0.009010	0.003127
Date de	7	4.5E-14	0.000000	0.000142	0.009119	0.003165
Mesure	8	4.2E-14	0.000000	0.000150	0.009069	0.003164
28- 1-85	9	5.6E-14	0.000000	0.000143	0.009004	0.003067
	10	5.3E-14	0.000000	0.000132	0.009048	0.003133
Valeurs moyennes		0.000000	0.000144	0.009051	0.003133	
SD		0.000000	0.000006	0.000036	0.000036	
1	5.2E-14	0.000001	0.000147	0.009174	0.003160	
2	4.8E-14	0.000001	0.000158	0.009199	0.003107	
3	3.8E-14	0.000001	0.000151	0.009109	0.003212*	
Filament	4	5.3E-14	0.000000	0.000152	0.009102	0.003134
3	5	5.3E-14	0.000000	0.000154	0.009191	0.003145
	6	5.2E-14	0.000003	0.000153	0.009177	0.003161
Date de	7	5.2E-14	0.000000	0.000149	0.009155	0.003142
Mesure	8	5.2E-14	0.000000	0.000156	0.009117	0.003143
4- 2-85	9	4.8E-14	0.000000	0.000160	0.009056	0.003184
	10	5.3E-14	0.000000	0.000145	0.009072	0.003167
Valeurs moyennes		0.000001	0.000152	0.009135	0.003149	
SD		0.000001	0.000005	0.000031	0.000022	

Laboratoire	ORNL	Date	Echantillon	P415	Methode	GR
Signature	-----	11- 9-85	Correction	WITHOUT	Element	U
			Intensite			Element us/g
Bloc	Principal	233/238	234/238	235/238	236/238	
1	5.5E-14	0.963223	0.004703	0.049901	0.400314	
2	4.8E-14	0.964094	0.004718	0.049907	0.400603	
3	4.3E-14	0.962753	0.004706	0.049749	0.399571*	
Filament	4	5.7E-14	0.960875	0.004770	0.049978	0.400158
1	5	5.4E-14	0.961265	0.004739	0.049618	0.400987
6	5.0E-14	0.961906	0.004741	0.049841	0.400432	
Date de	7	5.0E-14	0.962868	0.004701	0.049740	0.400627
Mesure	8	6.0E-14	0.962981	0.004757	0.049866	0.401199
4- 2-85	9	5.5E-14	0.962870	0.004719	0.049682	0.400782
	10	4.8E-14	0.962791	0.004684	0.049952	0.401006
Valeurs moyennes		0.962563	0.004724	0.049823	0.400679	1455.4614
SD		0.000954	0.000027	0.000120	0.000346	
1	5.2E-14	0.965109	0.004750	0.049830	0.400797	
2	5.1E-14	0.963393	0.004811	0.049659	0.400632	
3	4.9E-14	0.963891	0.004794	0.049695	0.400600	
Filament	4	4.7E-14	0.964031	0.004747	0.049888	0.401567*
2	5	4.6E-14	0.961773	0.004711	0.049736	0.400323
6	5.5E-14	0.960619	0.004749	0.049798	0.400371	
Date de	7	5.2E-14	0.962065	0.004724	0.049625	0.401030
Mesure	8	5.1E-14	0.961747	0.004701	0.049609	0.400195
4- 2-85	9	5.0E-14	0.962426	0.004774	0.049683	0.400934
	10	4.9E-14	0.959574	0.004755	0.049848	0.400248
Valeurs moyennes		0.962463	0.004752	0.049737	0.400570	1455.3094
SD		0.001675	0.000035	0.000098	0.000305	

Appendix 2: Results using Average Bias Correction

Laboratoire	DRNL	Date	Echantillon	T015	Methode	GR		
Signature	11- 9-85	Correction	DISCRI		Element	PU		
			Intensite		Element	us/s		
	Bloc	Principal	238/239	240/239	241/239	242/239	244/239	
	1	1.1E-14	0.709714	3.456280*	1.511519	134.023087*	59.919079*	
	2	7.8E-15	0.708818	3.547873	1.538284	136.077209	60.883797	
	3	1.8E-14	0.719988	3.575430	1.562778	137.885803	61.833790	
	Filament	4	1.3E-14	0.743929	3.551374	1.543683	137.267975	61.572422
	1	5	1.4E-14	0.709887	3.576166	1.527012	136.670731	61.535141
	6	9.9E-15	0.740368	3.588090	1.578759	139.060165	62.405155	
	Date de	7	1.3E-14	0.729418	3.601479	1.531837	138.799454	62.543003
	Mesure	8	6.8E-15	0.761837	3.659660	1.617459*	141.570251	64.004562
22-10-84	9	8.3E-15	0.678505	3.603519	1.561113	138.541443*	63.103764*	
	10	1.9E-15	0.719650	3.606803	1.539154*	140.529312	63.352608	
Valeurs moyennes			0.722211	3.590044	1.544373	138.482620	62.266312	
SD			0.023173	0.033770	0.021964	1.891970	1.029001	
	1	1.6E-14	0.700773	3.608091	1.554893	137.853897	62.106987	
	2	1.4E-14	0.706078	3.545925	1.516456	136.649597	61.542244	
	3	1.2E-14	0.733861	3.593687	1.516018	137.789948	62.129230	
	Filament	4	1.7E-14	0.703927	3.547030	1.534634	135.716995	61.115799
	2	5	1.5E-14	0.716303	3.578154	1.547019	137.612656	62.107815
	6	1.4E-14	0.713048	3.590382	1.549752	138.367218	62.423153	
	Date de	7	1.3E-14	0.704784	3.553754	1.511353	135.879227	61.344578
	Mesure	8	1.7E-14	0.717402	3.582799	1.503594	137.072296	61.969078
22-10-84	9	1.6E-14	0.725998	3.572003	1.530999	137.775665	62.172146	
	10	1.5E-14	0.716475	3.550385	1.546185	136.939560	61.781986	
Valeurs moyennes			0.713873	3.572221	1.531090	137.165710	61.869301	
SD			0.010470	0.022031	0.018245	0.879315	0.414603	

Laboratoire	ORNL	Date	Echantillon	R015	Methode	GR
Signature		11- 9-85	Correction	DISCRI	Element	PU
			Intensite			Element ug/g
Bloc	Principal	238/239	240/239	241/239	242/239	244/239
1	1.6E-14	0.001610	0.047257	0.001355	0.000070	0.000002
2	1.4E-14	-0.001233	0.047412	0.001311	0.000065	0.000000
3	1.1E-14	-0.002334	0.046985	0.001309	0.000095	0.000004
Filament	4	1.8E-14	-0.001158	0.047044	0.001459*	0.000071
1	5	1.8E-14	-0.001022	0.047097	0.001373	0.000079
6	1.6E-14	0.000122	0.047072	0.001369	0.000076	0.000000
Date de	7	1.4E-14	-0.001593	0.047222	0.001355	0.000089
Mesure	8	1.6E-14	0.000795	0.047330	0.001402	0.000077
22-10-84	9	1.3E-14	-0.001144	0.047316	0.001366	0.000080
	10	1.5E-14	-0.000424	0.047517	0.001361	0.000082
Valeurs moyennes		-0.000638	0.047215	0.001356	0.000078	0.000002
SD		0.001181	0.000191	0.000030	0.000009	0.000002
1	2.4E-16	-0.015219	0.047144	0.001605*	0.000161*	0.000069*
2	2.9E-16	-0.009553	0.047336	0.001539	0.000131	0.000052*
3	6.5E-16	-0.001452	0.047373	0.001329	0.000108	0.000027
Filament	4	6.7E-16	-0.005547	0.046934	0.001402	0.000083
2	5	1.7E-15	0.003303	0.047051	0.001374	0.000067
6	1.5E-15	0.007986	0.047445	0.001335	0.000080	0.000004
Date de	7	5.4E-15	-0.003373	0.046807	0.001342	0.000080
Mesure	8	4.7E-15	0.015510	0.047160	0.001333	0.000071
22-10-84	9	1.3E-14	0.001705	0.046489	0.001308	0.000074
	10	1.1E-14	0.009745	0.046518	0.001360	0.000080
	11	1.7E-14	0.048042	0.046718*	0.001324	0.000066
	12	1.2E-14	0.026232	0.047152	0.001385	0.000065
Valeurs moyennes		0.006448	0.047037	0.001367	0.000082	0.000005
SD		0.017261	0.000323	0.000064	0.000020	0.000008
1	1.6E-14	-0.000149	0.046776	0.001357	0.000067	0.000007
2	1.4E-14	0.000013	0.047084	0.001335	0.000084	0.000006
3	1.3E-14	0.000018	0.046926	0.001367	0.000086	0.000003
Filament	4	1.3E-14	0.000816	0.047171	0.001348	0.000086
3	5	1.7E-14	0.000027	0.047161	0.001331	0.000080
6	1.6E-14	-0.000230	0.046559	0.001397	0.000075	0.000002
Date de	7	1.7E-14	0.000148	0.046665	0.001414	0.000081
Mesure	8	1.7E-14	-0.000424	0.046990	0.001407	0.000099*
22-10-84	9	1.6E-14	-0.000292	0.046721	0.001356	0.000078
	10	1.6E-14	0.000065	0.046714	0.001326	0.000076
Valeurs moyennes		-0.000001	0.046877	0.001364	0.000079	0.000003
SD		0.000339	0.000219	0.000032	0.000006	0.000003

Laboratoire	ORNL	Date	Echantillon	E015	Methode	GR		
Signature		11- 9-85	Correction	DIBCRI	Element	FU		
			Intensite			Element us/d		
	Bloc	Principal	238/239	240/239	241/239	242/239	244/239	
	1	1.6E-14	0.021901	0.392012	0.163546	0.076467	0.000008	
	2	1.2E-14	0.021643	0.392390	0.163152	0.077132*	0.000005	
	3	1.6E-14	0.021989	0.391732	0.162923	0.076136	0.000003	
	Filament	4	1.2E-14	0.021005	0.390917	0.162590	0.075833	0.000001
	1	5	1.5E-14	0.021822	0.390673	0.163145	0.075519	0.000009
	6	1.1E-14	0.022005	0.392228	0.162420	0.075861	0.000009	
	Date de	7	1.6E-14	0.022514	0.391356	0.163295	0.075933	0.000005
	Mesure	8	1.1E-14	0.022402	0.391085	0.163311	0.076065	0.000005
22-10-84	9	1.4E-14	0.022151	0.392698	0.163137	0.076270	0.000008	
	10	1.1E-14	0.021964	0.392601	0.164320*	0.076854	0.000014	
Valeurs moyennes			0.021940	0.391849	0.163058	0.076104	0.000007	
SD			0.000418	0.000688	0.000358	0.000392	0.000004	
	1	1.6E-14	0.021302	0.391506	0.163457	0.075950	0.000007	
	2	1.4E-14	0.021353	0.393094	0.163913	0.076221	0.000001	
	3	1.2E-14	0.021251	0.391246	0.162957	0.076141	0.000005	
	Filament	4	1.1E-14	0.021406	0.393462	0.164362	0.076336	0.000004
	2	5	1.6E-14	0.021616	0.393151	0.163342	0.076610	0.000003
	6	1.4E-14	0.021527	0.392959	0.163860	0.076648	0.000005	
	Date de	7	1.3E-14	0.021492	0.392928	0.163623	0.075671	0.000005
	Mesure	8	1.6E-14	0.021832	0.392995	0.163968	0.076198	0.000004
22-10-84	9	1.5E-14	0.021345	0.392738	0.163103	0.076713	0.000005	
	10	1.4E-14	0.021841	0.391988	0.163490	0.076695	0.000004	
	11	1.6E-14	0.020850	0.393908	0.163234	0.076857	0.000010	
Valeurs moyennes			0.021456	0.392725	0.163574	0.076367	0.000005	
SD			0.000289	0.000815	0.000421	0.000369	0.000002	
	1	1.6E-14	0.020791	0.390940	0.162323	0.075976	0.000009	
	2	1.4E-14	0.021480	0.391793	0.162461	0.076368	0.000007	
	3	1.3E-14	0.021810	0.391611	0.162766	0.075572	0.000002	
	Filament	4	1.8E-14	0.022350	0.391125	0.162849	0.076291	0.000005
	3	5	1.8E-14	0.021343	0.391359	0.163225	0.076463	0.000006
	6	1.9E-14	0.021359	0.391394	0.162089	0.075603	0.000009	
	Date de	7	1.8E-14	0.021626	0.392751	0.164215*	0.076162	0.000008
	Mesure	8	2.0E-14	0.021474	0.392629	0.163212	0.076566	0.000005
22-10-84	9	2.1E-14	0.022186	0.392900	0.163340	0.076076	0.000005	
	10	1.7E-14	0.022198	0.392202	0.162257	0.077266*	0.000009	
Valeurs moyennes			0.021662	0.391870	0.162727	0.076120	0.000007	
SD			0.000481	0.000707	0.000467	0.000353	0.000002	

Laboratoire ORNL		Echantillon F315		Methode GR				
Signature	Date 11- 9-85	Correction	DISCRI	Element	FU			
		Intensite			Element us/s			
	Bloc	Principal	238/239	240/239	241/239	242/239	244/239	
	1	1.7E-14	0.004623	0.070318*	0.011318	0.883775	0.395876	
	2	1.7E-14	0.004717	0.069549	0.011081	0.883828	0.396636	
	3	1.6E-14	0.004702	0.069810	0.011251	0.884506	0.397090	
	Filament	4	1.6E-14	0.004528	0.069916	0.011199	0.885388	0.397449
	1	5	1.6E-14	0.004640	0.069995	0.011283	0.885848	0.398932
	6	1.6E-14	0.004723	0.069477	0.011031	0.884168	0.398015	
	Date de	7	1.5E-14	0.004712	0.069853	0.011159	0.884823	0.397767
	Mesure	8	1.5E-14	0.004683	0.070074	0.011325	0.887589	0.399682
22-10-84	9	1.5E-14	0.004854	0.069486	0.011259	0.887477	0.399303	
	10	1.4E-14	0.004789	0.070221	0.011251	0.888952	0.401346	
Valeurs moyennes			0.004697	0.069820	0.011216	0.885835	0.398210	
SD			0.000089	0.000267	0.000098	0.001810	0.001623	
							10.1596	
	1	1.6E-14	0.004598	0.070209	0.011113	0.887899	0.399623	
	2	1.4E-14	0.005123	0.069953	0.011286	0.890984	0.400633	
	3	1.2E-14	0.004319	0.070169	0.011445*	0.890598	0.400338	
	Filament	4	1.6E-14	0.004633	0.069911	0.011190	0.889202	0.399432
	2	5	1.4E-14	0.004940	0.070074	0.011232	0.887601	0.399202
	6	1.6E-14	0.004859	0.070022	0.011293	0.889880	0.402322	
	Date de	7	1.4E-14	0.004069	0.070307	0.011313	0.887861	0.400663
	Mesure	8	1.2E-14	0.004199	0.069996	0.011199	0.888934	0.402785
22-10-84	9	1.7E-14	0.005431	0.070130	0.011097	0.887374	0.400733	
	10	1.4E-14	0.004983	0.069661*	0.011144	0.888526	0.402784	
Valeurs moyennes			0.004715	0.070086	0.011207	0.888886	0.400851	
SD			0.000432	0.000129	0.000080	0.001270	0.001343	
							10.1948	

Laboratoire	ORNL	Date	Echantillon	M215	Methode	GR		
Signature	11- 9-85		Correction	DISCRI	Element	PU		
Element us/s								
Filament	Intensite							
	Bloc	Principal	238/239	240/239	241/239	242/239	244/239	
	1	1.8E-14	0.029050	0.425882	0.177397	1.563408	0.667099*	
	2	1.8E-14	0.029385	0.427303	0.178081	1.570256	0.672584	
	3	1.8E-14	0.028843	0.427194	0.178374	1.568455	0.673062	
	4	1.7E-14	0.028895	0.427136	0.178820	1.568387	0.673527	
	5	1.6E-14	0.028742	0.427366	0.178593	1.574358	0.673316	
	6	1.7E-14	0.028917	0.427404	0.178235	1.567862	0.673024	
	Data de	7	1.5E-14	0.028912	0.427243	0.178363	1.572702	0.673254
	Mesure	8	1.4E-14	0.028765	0.425696*	0.179425	1.570532	0.674635
31- 1-85	9	1.7E-14	0.029473	0.428854	0.180600*	1.577649	0.676226	
	10	1.5E-14	0.029190	0.428836	0.178885	1.573839	0.675765	
Valeurs moyennes		0.029017	0.427469	0.178464	1.570745	0.673933	6.3731	
SD		0.000254	0.000907	0.000570	0.004046	0.001300		
Element us/s								
Filament	1	1.4E-14	0.028981	0.426456	0.182194*	1.571917	0.672311	
	2	1.4E-14	0.028965	0.427366	0.179167	1.573614	0.672400	
	3	1.1E-14	0.028673	0.428137	0.178978	1.573493	0.673459	
	4	1.2E-14	0.029187	0.426463	0.179636	1.574849	0.677900	
	2	8.7E-15	0.029024	0.428493	0.178426	1.573248	0.674996	
	6	1.8E-14	0.028776	0.426715	0.178795	1.575564	0.675442	
	Data de	7	1.9E-14	0.028672	0.428414	0.178467	1.576696	0.676932
	Mesure	8	1.7E-14	0.029155	0.427894	0.178397	1.574435	0.677414
	5- 2-85	9	1.7E-14	0.029046	0.428363	0.178106	1.573989	0.675903
		10	1.7E-14	0.028888	0.426448	0.178842	1.576032	0.676970
		11	1.7E-14	0.029227	0.426878	0.178244	1.576147	0.678613
		12	1.6E-14	0.029008	0.427109	0.179098	1.576353	0.675524
Valeurs moyennes		0.028967	0.427395	0.178760	1.574695	0.675655	6.3568	
SD		0.000186	0.000822	0.000452	0.001490	0.002076		

Laboratoire	ORNL	Echantillon	M315	Methode	GR		
Signature	Date	Correction	DISCRI	Element	PU		
		Intensite			Element us/s		
Bloc	Principal	238/239	240/239	241/239	242/239	244/239	
1	1.7E-14	0.028912	0.425593	0.177606	1.508453	0.642977	
2	1.6E-14	0.028768	0.424572	0.178794	1.506941	0.641002	
3	1.6E-14	0.028435	0.426193	0.178570	1.510800	0.644772	
Filament	4	1.6E-14	0.028967	0.424397	0.178118	1.513346	0.642542
1	5	1.6E-14	0.029161	0.425764	0.177652	1.512223	0.644823
6	1.6E-14	0.028536	0.425986	0.177567	1.515913	0.646551	
Date de	7	1.6E-14	0.029100	0.426106	0.177920	1.516145	0.645057
Mesure	8	1.5E-14	0.028850	0.425238	0.178562	1.514405	0.644129
1- 2-85	9	1.6E-14	0.028521	0.424171	0.177302	1.512647	0.643344
	10	1.6E-14	0.028827	0.424672	0.177224	1.511544	0.646440
Valeurs moyennes		0.028808	0.425269	0.177931	1.512242	0.644164	6.3908
SD		0.000246	0.000762	0.000558	0.002978	0.001738	
1	1.7E-14	0.028912	0.425593	0.177606	1.508453	0.642977	
2	1.6E-14	0.028768	0.424572	0.178794	1.506941	0.641002	
3	1.6E-14	0.028435	0.426193	0.178570	1.510800	0.644772	
Filament	4	1.6E-14	0.028967	0.424397	0.178118	1.513346	0.642542
2	5	1.6E-14	0.029161	0.425764	0.177652	1.512223	0.644823
6	1.6E-14	0.028536	0.425986	0.177567	1.515913	0.646551	
Date de	7	1.6E-14	0.029100	0.426106	0.177920	1.516145	0.645057
Mesure	8	1.5E-14	0.028850	0.425238	0.178562	1.514405	0.644129
22-10-84	9	1.6E-14	0.028521	0.424171	0.177302	1.512647	0.643344
	10	1.6E-14	0.028827	0.424672	0.177224	1.511544	0.646440
Valeurs moyennes		0.028808	0.425269	0.177931	1.512242	0.644164	6.3697
SD		0.000246	0.000762	0.000558	0.002978	0.001738	

Laboratoire DRNL		Echantillon		R015	Methode GR
Signature	Date 11- 9-85	Correction	DIBSCRI	Element U	Element ug/s
		Intensite	233/238	234/238	235/238
	Bloc	Principal	0.000020	0.000055	0.007244
	1	4.9E-14	0.000019	0.000051	0.007160
	2	4.7E-14	0.000019	0.000050	0.007198
	3	4.4E-14	0.000019	0.000050	0.007308
	Filament	4	5.3E-14	0.000020	0.000057
	1	4.8E-14	0.000018	0.000057	0.007193
	6	4.1E-14	0.000015	0.000054	0.007248
	Date de	7	3.4E-14	0.000020	0.000057
	Mesure	8	4.7E-14	0.000015	0.000049
24- 1-85	9	3.1E-14	0.000024	0.000059	0.007117
	10	4.1E-14	0.000027*	0.000057	0.007219
	Valeurs moyennes		0.000019	0.000054	0.007198
	SD		0.000003	0.000004	0.000058
		1	5.8E-14	0.000025	0.000047*
		2	6.1E-14	0.000018	0.000055
		3	6.6E-14	0.000023	0.000050
	Filament	4	5.4E-14	0.000021	0.000052
	2	5.4E-14	0.000016	0.000053	0.007234
	6	5.4E-14	0.000016	0.000054	0.007353
	Date de	7	5.4E-14	0.000023	0.000056
	Mesure	8	5.3E-14	0.000019	0.000054
24- 1-85	9	5.2E-14	0.000021	0.000055	0.007240
	10	5.3E-14	0.000023	0.000055	0.007301
	Valeurs moyennes		0.000021	0.000054	0.007255
	SD		0.000003	0.000002	0.000060
		1	5.0E-14	0.000021	0.000051
		2	4.7E-14	0.000018	0.000051
		3	4.5E-14	0.000021	0.000057
	Filament	4	5.2E-14	0.000022	0.000054
	3	5.0E-14	0.000022	0.000062*	0.007264
	6	4.7E-14	0.000020	0.000055	0.007268
	Date de	7	4.5E-14	0.000015*	0.000051
	Mesure	8	5.6E-14	0.000023	0.000047
4- 2-85	9	5.6E-14	0.000022	0.000050	0.007234
	10	5.3E-14	0.000025	0.000052	0.007232
	Valeurs moyennes		0.000022	0.000052	0.007265
	SD		0.000002	0.000003	0.000040

Laboratoire	ORNL	Date	Echantillon	E015	Methode	GR	
Signature	11- 9-85		Correction	DISCRI	Element	U	
			Intensite			Element	
	Bloc	Principal	233/238	234/238	235/238	us/u	
	1	5.2E-14	0.000000	0.000136	0.008961	0.003053	
	2	4.8E-14	0.000000	0.000142	0.008853	0.003046	
	3	4.4E-14	0.000000	0.000154	0.008895	0.003092	
Filament	4	5.0E-14	0.000000	0.000140	0.008836	0.003081	
	1	5	4.3E-14	0.000000	0.000137	0.008898	0.003106
	6	3.8E-14	0.000000	0.000150	0.008949	0.003106	
Date de	7	5.0E-14	0.000000	0.000157	0.008874	0.003093	
Mesure	8	4.2E-14	0.000001	0.000143	0.008909	0.003062	
25- 1-85	9	4.5E-14	0.000000	0.000147	0.008877	0.003066	
	10	3.7E-14	0.000000	0.000138	0.008884	0.003153*	
Valeurs moyennes			0.000000	0.000144	0.008894	0.003078	
SD			0.000000	0.000007	0.000039	0.000023	
	1	5.2E-14	0.000000	0.000160*	0.008971	0.003146	
	2	4.9E-14	0.000000	0.000143	0.008971*	0.003149	
	3	4.6E-14	0.000000	0.000148	0.008968	0.003088	
Filament	4	5.2E-14	0.000001	0.000141	0.008946	0.003064	
	2	5	4.9E-14	0.000000	0.000146	0.008925	0.003115
	6	4.7E-14	0.000000	0.000137	0.008911	0.003104	
Date de	7	4.5E-14	0.000000	0.000140	0.008919	0.003141	
Mesure	8	4.2E-14	0.000000	0.000148	0.008969	0.003141	
28- 1-85	9	5.6E-14	0.000000	0.000141	0.008904	0.003044	
	10	5.3E-14	0.000000	0.000130	0.008948	0.003110	
Valeurs moyennes			0.000000	0.000142	0.008931	0.003110	
SD			0.000000	0.000006	0.000036	0.000036	
	1	5.2E-14	0.000001	0.000145	0.009073	0.003136	
	2	4.8E-14	0.000001	0.000155	0.009098	0.003084	
	3	3.8E-14	0.000001	0.000149	0.009098	0.003189*	
Filament	4	5.3E-14	0.000000	0.000150	0.009002	0.003111	
	3	5.3E-14	0.000000	0.000152	0.009089	0.003122	
	6	5.2E-14	0.000003	0.000150	0.009075	0.003138	
Date de	7	5.2E-14	0.000000	0.000147	0.009054	0.003119	
Mesure	8	5.2E-14	0.000000	0.000153	0.009017	0.003119	
4- 2-85	9	4.8E-14	0.000000	0.000157	0.008956	0.003161	
	10	5.3E-14	0.000000	0.000143	0.008972	0.003143	
Valeurs moyennes			0.000001	0.000150	0.009034	0.003126	
SD			0.000001	0.000005	0.000050	0.000022	

Laboratoire ORNL		Echantillon P215			Methode GR
Signature -----	Date 11- 9-85	Correction	DISCRI	Element U	Element us/s
		Intensite			
	Bloc Principal	233/238	234/238	235/238	236/238
	1 5.4E-14	0.788458	0.003915	0.042485	0.332504
	2 5.5E-14	0.787668	0.003922	0.042591	0.332614
	3 5.2E-14	0.789249	0.003969	0.042316	0.333593
	Filament 4 5.6E-14	0.787986	0.003919	0.042517	0.333079
	1 6.1E-14	0.788025	0.003911	0.042426	0.333477
	6 6.1E-14	0.787422	0.003938	0.042228	0.332379
	Date de 7 5.3E-14	0.787331	0.003970	0.042397	0.332251
	Measure 8 6.1E-14	0.785913	0.003888	0.042284	0.333096
28- 1-85	9 7.1E-14	0.786560	0.003856	0.042381	0.332285
	10 7.3E-14	0.785013	0.003901	0.042300	0.332483
Valeurs moyennes		0.787352	0.003919	0.042393	0.332776
SD		0.001240	0.000035	0.000115	0.000496
					1420.2003
	1 5.3E-14	0.789310	0.003897	0.042220	0.333297
	2 5.4E-14	0.789694	0.003931	0.042170	0.333387
	3 5.9E-14	0.788120	0.003912	0.042068	0.332387
	Filament 4 5.8E-14	0.789307	0.003971*	0.042661*	0.332494
	2 5 5.5E-14	0.788749	0.003911	0.042482	0.333359
	6 5.7E-14	0.788181	0.003893	0.042344	0.332061
	Date de 7 5.5E-14	0.788569	0.003886	0.042381	0.333131
	Measure 8 5.6E-14	0.787954	0.003938	0.042234	0.333123
5- 2-85	9 5.4E-14	0.788137	0.003868	0.042247	0.332802
	10 5.6E-14	0.787233	0.003861	0.042320	0.332613
	11 5.5E-14	0.787573	0.003917	0.042454	0.332708
	12 4.9E-14	0.787091	0.003902	0.042310	0.332703
Valeurs moyennes		0.788327	0.003902	0.042294	0.332839
SD		0.000829	0.000024	0.000122	0.000422
					1421.9669

Appendix 3: Results using Internal Standards

Laboratoire	ORNL	Date	Echantillon	T015	Methode	BR	
Signature		11- 9-85	Correction	INTERNAL	Element	PU	
			Intensite			Element us/s	
Bloc	Principal	238/239	240/239	241/239	242/239	244/239	
1	2.3E-14	0.718763	3.581169	1.560158	137.385590	61.781883	
2	1.4E-14	0.731182	3.600544	1.527949	138.187469	62.142326	
3	1.7E-14	0.712481	3.575350	1.511673	136.096634	61.202286	
Filament	4	1.6E-14	0.695608	3.582434	1.510847	138.642090*	62.346935*
1	5	1.6E-14	0.722812	3.575400	1.509024	136.524826	61.394726
6	1.5E-14	0.709383	3.492383	1.497852	135.149216	60.776093	
Date de	7	1.7E-14	0.718936	3.604654	1.550712	137.974319	62.046814
Mesure	8	1.5E-14	0.708296	3.582249	1.556146	138.551392	62.306492
22-10-84	9	1.7E-14	0.725163	3.520029	1.516963	136.376541	61.328144
	10	1.6E-14	0.730029	3.652730	1.592273*	139.752441	62.846424
Valeurs moyennes		0.717265	3.576694	1.526814	137.333160	61.758354	
SD		0.011001	0.044145	0.023133	1.429503	0.642933	
1	2.0E-14	0.725595	3.517885	1.525577	136.593140	61.425812	
2	2.1E-14	0.726923	3.572320	1.490986	136.626038	61.440483	
3	2.3E-14	0.721396	3.565702	1.532130	138.017776	62.066433	
Filament	4	1.6E-14	0.738764	3.557059	1.506658	136.504074	61.385651
2	5	1.6E-14	0.719367	3.569364	1.538518	135.923950	61.124844
6	1.5E-14	0.711565	3.632668	1.534683	138.447327*	62.259678*	
Date de	7	1.6E-14	0.714591	3.554692	1.512104	136.315353	61.300861
Mesure	8	1.7E-14	0.725115	3.623860	1.532714	136.642365	61.448002
22-10-84	9	1.7E-14	0.720102	3.502915	1.512345	136.428070	61.351715
	10	1.7E-14	0.707891	3.498169	1.506577	135.702637	61.025326
Valeurs moyennes		0.721131	3.559464	1.519229	136.528152	61.396564	
SD		0.008782	0.045363	0.015682	0.646940	0.290924	

Laboratoire ORNL	Date	Echantillon	P215	Methode	GR		
Signature -----	11- 9-85	Correction	INTERNAL	Element	PU		
		Intensite			Element us/a		
	Bloc	Principale	238/239	240/239	241/239	242/239	244/239
	1	1.7E-14	0.004497	0.069976	0.011211	0.888791	0.399685
	2	1.7E-14	0.004560	0.069805	0.011239	0.887841	0.399258
	3	1.6E-14	0.003858	0.069900	0.011381	0.886749	0.398767
Filament	4	1.6E-14	0.004075	0.069680	0.011126	0.883221	0.397180
	1	1.5E-14	0.004506	0.069924	0.011223	0.881632	0.396466
	6	1.4E-14	0.005282	0.070020	0.011244	0.892824	0.401499
Date de	7	1.4E-14	0.003019	0.070141	0.011493*	0.889527	0.400016
Mesure	8	1.7E-14	0.004152	0.070443*	0.011309	0.888407	0.399512
22-10-84	9	1.5E-14	0.005368	0.069757	0.011214	0.888033	0.399344
	10	1.4E-14	0.003601	0.070011	0.011204	0.881263	0.396300
Valeurs moyennes		0.004292	0.069913	0.011239	0.886829	0.398803	
SD		0.000719	0.000145	0.000071	0.003698	0.001663	10.1596
	1	1.5E-14	0.004739	0.070108	0.011126	0.881051	0.396205
	2	1.4E-14	0.004040	0.069760	0.011275	0.882357	0.396792
	3	1.3E-14	0.004528	0.069643	0.011197	0.886182	0.398512
Filament	4	1.7E-14	0.004433	0.069856	0.011205	0.883371	0.397248
	2	1.5E-14	0.005159	0.069747	0.011300	0.883760	0.397423
	6	1.4E-14	0.004869	0.070187	0.011352	0.891766	0.401023
Date de	7	1.5E-14	0.004609	0.069811	0.011291	0.883992	0.397527
Mesure	8	1.0E-14	0.004266	0.070170	0.011372	0.888894	0.399732
22-10-84	9	1.6E-14	0.004168	0.070040	0.011231	0.879835	0.395658
	10	1.4E-14	0.004327	0.070348	0.011191	0.887569	0.399136
	11	1.6E-14	0.004215	0.069864	0.011208	0.884767	0.397876
	12	1.3E-14	0.005453	0.070326	0.011290	0.888717	0.399652
Valeurs moyennes		0.004567	0.069988	0.011253	0.885189	0.398065	
SD		0.000425	0.000239	0.000072	0.003527	0.001386	10.1338

Laboratoire ORNL		Echantillon		M115		Methodes GR		
Signature -----	Date 11- 9-85	Correction	INTERNAL			Element	FU	
		Intensite					Element us/s	
Bloc	Principal	238/239	240/239	241/239	242/239	244/239		
1	1.7E-14	0.028449	0.424866	0.178910*	1.502430	0.641731		
2	1.3E-14	0.028697	0.426818	0.178843	1.512362	0.646200		
3	1.6E-14	0.027965	0.424636	0.177065	1.497969	0.639724		
4	1.3E-14	0.027662	0.426031	0.178527	1.511645	0.645878		
5	1.1E-14	0.027882	0.428993*	0.178150	1.504958	0.642869		
6	1.8E-14	0.029014	0.426196	0.177559	1.502887	0.641937		
7	1.5E-14	0.028690	0.425440	0.177917	1.505440	0.643086		
8	1.3E-14	0.029178	0.423723	0.178361	1.506199	0.643427		
22-10-84	9	1.7E-14	0.029092	0.427645	0.178430	1.509961	0.645120	
10	1.4E-14	0.027531	0.423850	0.177522	1.498947	0.640164		
Valeurs moyennes		0.028416	0.425467	0.178042	1.505280	0.643014		
SD		0.000614	0.001329	0.000572	0.004955	0.002229	6.3518	
1	1.6E-14	0.028839	0.425735	0.177669	1.500302	0.640774		
2	1.5E-14	0.028373	0.426092	0.178224	1.502564	0.641792		
3	1.3E-14	0.028682	0.426156	0.178719	1.510189	0.645223		
4	1.7E-14	0.028936	0.424413	0.177095	1.492218	0.637137		
5	1.6E-14	0.028725	0.425605	0.178147	1.506228	0.643441		
6	1.5E-14	0.028669	0.426100	0.178036	1.505745	0.643223		
7	1.4E-14	0.029063	0.428050*	0.178379	1.511067	0.645618		
8	1.7E-14	0.029021	0.425568	0.177208	1.496407	0.639022		
22-10-84	9	1.5E-14	0.028478	0.425029	0.177605	1.504468	0.642649	
10	1.4E-14	0.029101	0.424458	0.177373	1.493660	0.637786		
Valeurs moyennes		0.028789	0.425462	0.177846	1.502285	0.641666		
SD		0.000247	0.000679	0.000537	0.006351	0.002947	6.3653	

Laboratoire	ORNL	Date	Echantillon	M315	Methode	GR		
Signature	11-9-85		Correction	INTERNAL	Element	PU		
Bloc	Intensite	Principal	238/239	240/239	241/239	242/239	244/239	Element us/a
1	1.8E-14	0.028919	0.426251	0.178991	1.518285	0.528196*	0.648866	
2	1.6E-14	0.028977	0.425620	0.178049	1.515514	0.523473	0.647618	
3	1.4E-14	0.028801	0.426247	0.177976	1.518150	0.523473	0.648805	
Filament	4	1.7E-14	0.028278	0.427987*	0.178366	1.510420	0.533325*	
1	5	1.7E-14	0.028718	0.426048	0.178641	1.520827	0.51200	
6	1.6E-14	0.028989	0.427181	0.178982	1.513583	0.523473	0.647527	
Date de	7	1.6E-14	0.028735	0.424730	0.177815	1.517360	0.509561	
Measure	8	1.5E-14	0.028435	0.426518	0.177930	1.513922	0.644940	
22-10-84	9	1.7E-14	0.028981	0.426026	0.177885	1.517778	0.648638	
	10	1.6E-14	0.029063	0.425844*	0.177326	1.509561	0.644940	
	11	1.6E-14	0.028690	0.424669	0.177351	1.513922	0.646902	
	12	1.5E-14	0.029171	0.426520	0.176764*	1.517870	0.648679	
Valeurs moyennes			0.028813	0.425981	0.178119	1.516651	0.648130	6.3474
SD			0.000261	0.000788	0.000571	0.004123	0.001855	
1	1.7E-14	0.028879	0.426133	0.178055	1.514164	0.529641	0.647011	
2	1.6E-14	0.028702	0.425603	0.179658	1.517828	0.523473	0.648660	
3	1.6E-14	0.028422	0.426455	0.178789	1.513583	0.523473	0.646750	
Filament	4	1.6E-14	0.028867	0.425933	0.179402	1.520761	0.533325*	
2	5	1.6E-14	0.029128	0.426247	0.178053	1.517337	0.523473	
6	1.6E-14	0.028509	0.426443	0.177946	1.527367	0.526211	0.649980	
Date de	7	1.6E-14	0.029036	0.427166	0.178801	1.526211	0.52952	
Measure	8	1.5E-14	0.028781	0.426352	0.179494	1.524432	0.51631	
22-10-84	9	1.6E-14	0.028451	0.425281	0.178227	1.524432	0.644729	
	10	1.6E-14	0.028845	0.424437*	0.177030	1.509091	0.644729	
Valeurs moyennes			0.028762	0.426179	0.178546	1.520041	0.649656	6.3366
SD			0.000240	0.000543	0.000832	0.006766	0.003044	

Laboratoire ORNL	Date	Echantillon	T015	Methode GR		
Signature -----	11- 9-85	Correction	INTERNAL	Element U		
		Intensite		Element us/d		
Bloc	Principal	233/238	234/238	235/238	236/238	
1	5.7E-14	152.651596	0.738145	6.821004	64.413673	
2	6.1E-14	150.047302	0.726216	6.699794	63.314896	
3	5.2E-14	153.681946	0.757211	6.853540	64.848442	
Filament	4	4.5E-14	153.532623	0.741751	6.877919	64.785645
1	5	3.8E-14	149.696182	0.727818	6.680737	63.166687
	6	5.0E-14	151.240784	0.741739	6.769894	63.818424
Date de	7	4.0E-14	151.485443	0.744268	6.768496	63.921574
Measure	8	4.7E-14	152.630768*	0.744189	6.761883*	64.404808*
24- 1-85	9	3.5E-14	150.475998	0.741988	6.691845	63.495728
	10	5.2E-14	152.015930	0.750940	6.774693	64.145576
Valeurs moyennes		151.647537	0.741427	6.770880	63.990070	
SD		1.447799	0.009328	0.070931	0.610912	
						↓
	1	5.5E-14	152.197311	0.746019	6.776237	64.222008
	2	5.4E-14	151.752747	0.737038	6.746340	64.034447
	3	4.9E-14	150.865051	0.734938	6.704988	63.659782
Filament	4	4.5E-14	153.379791	0.755665	6.815146	64.720993
2	5	4.4E-14	151.132050	0.743475	6.769897	63.772617
	6	4.0E-14	150.544434	0.733862	6.690825	63.524624
Date de	7	5.3E-14	152.096008	0.750701	6.794683	64.179359
Mesure	8	4.7E-14	149.596115	0.738231	6.680040	63.124516
28- 1-85	9	4.6E-14	149.815994	0.729078	6.690672	63.217354
	10	5.3E-14	152.600113	0.738860	6.782688	64.391991
	11	4.8E-14	152.072403	0.744312	6.825433	64.169365
Valeurs moyennes		151.459290	0.741107	6.752469	63.910641	
SD		1.177749	0.007805	0.052917	0.496933	

Laboratoire ORNL		Echantillon	P415	Methode GR		
Signature -----	Date 11- 9-85	Correction	INTERNAL	Element U		
Bloc	Intensite Principal	233/238	234/238	235/238	236/238	Element us/s
1	5.6E-14	0.939233	0.004609	0.049155	0.396327	
2	4.8E-14	0.939797	0.004623	0.049152	0.396545	
3	4.4E-14	0.93655*	0.004604	0.048940	0.395239*	
Filament	4	5.8E-14	0.940122	0.004687	0.049330	0.396702
1	5	5.4E-14	0.943093	0.004667	0.049055	0.397955
6	5.0E-14	0.940525	0.004657	0.049176	0.396872	
Date de	7	5.0E-14	0.940670	0.004614	0.049052	0.396933
Measure	8	6.0E-14	0.942819	0.004677	0.049239	0.397840
4- 2-85	9	5.5E-14	0.941271	0.004634	0.049014	0.397187
	10	4.8E-14	0.942190	0.004603	0.049310	0.397574
Valeurs moyennes		0.941080	0.004638	0.049143	0.397106	1422.8274
SD		0.001360	0.000032	0.000128	0.000574	
Bloc	Intensite Principal	233/238	234/238	235/238	236/238	Element us/s
1	5.3E-14	0.939909	0.004650	0.049049	0.396612	
2	5.1E-14	0.940359	0.004719	0.048946	0.396892	
3	4.9E-14	0.939916	0.004699	0.048953	0.396615	
Filament	4	4.8E-14	0.943576	0.004666	0.049253	0.398159
2	5	4.6E-14	0.940188	0.004627	0.049067	0.396730
6	5.5E-14	0.941111	0.004672	0.049191	0.397119	
Date de	7	5.3E-14	0.942748	0.004648	0.049027	0.397810
Measure	8	5.1E-14	0.939713	0.004615	0.048927	0.396529
4- 2-85	9	5.0E-14	0.942144	0.004693	0.049057	0.397555
	10	4.9E-14	0.941305	0.004682	0.049279	0.397201
Valeurs moyennes		0.941097	0.004667	0.049075	0.397113	1422.8533
SD		0.001338	0.000033	0.000126	0.000564	

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