

# **Uncertainties in Masses, Dimensions, Impurities, and Isotopics of HEU Metal Used in Critical Experiments at ORCEF**

**August 2012**

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Global Nuclear Security Technology Division

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HEU METAL USED IN CRITICAL EXPERIMENTS AT ORCEF**

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## ABSTRACT

This report documents uncertainties in the mass, dimensions, impurities, and isotopics of the highly enriched uranium (HEU) metal (oralloy) used in a wide variety of delayed critical experiments at the Oak Ridge Critical Experiments Facility (ORCEF) in the late 1950s, 1960s, and 1970s. Most of these experiments were performed in the east cell of ORCEF. The accuracies of the masses were much less than 1 gram, the dimensions to 0.0004 in., and 0.0177 wt % uncertainty for the  $^{235}\text{U}$  isotopic content of HEU. The total  $^{235}\text{U}$  uncertainty for a 25,000 gram mass of oralloy (nominal 93.15 wt%  $^{235}\text{U}$ ) is 0.054%, which corresponds to ~13 grams. This calculated uncertainty includes the uncertainties associated with impurity content, grams of uranium per grams of oralloy, and isotopic content. These data are of interest to the Working Party of Nuclear Criticality Safety (WPNCs) International Criticality Safety Benchmark Experiment Project (ICSBEP) because these HEU metal critical experiments at ORCEF have been or are being documented as benchmarks for nuclear criticality safety calculations for ICSBEP. This report is a collection of information from various sources, some of which are contained in previous reports and emails. These experiments may be the most accurately described critical experiments ever performed, mainly because of the combination of the Y-12 capabilities for accurately fabricating and defining the materials (mainly HEU metal, referred to as oralloy, an acronym for Oak Ridge alloy) and the care of the researchers in documenting the experiments.

## 1. INTRODUCTION

Documentation of delayed critical experiments with oralloy (HEU metal with >93 wt%  $^{235}\text{U}$ ) metal performed in the Oak Ridge Critical Experiment Facility (ORCEF)<sup>1</sup> as benchmarks to verify calculational capabilities for nuclear criticality safety have led to questions about the definition of the materials. These measurements are perhaps the most accurate critical experiments that have been performed because of the extremely low uncertainty in the neutron multiplication factor,  $k_{\text{eff}}$ . These low uncertainties result from the precisely defined materials and precisely defined delayed critical configurations. Some of these uncertainties are from personal communications with the researchers (many of those with knowledge of the accuracies in the metrology and analytical methods are deceased). Some are from supplemental tables of data, which were contained in summaries of the inspection reports and actual inspection reports and do not appear in the logbooks for the measurements. Other than the experimental logbooks that are available electronically, much of the documentation has been destroyed or stored, and the last time one of the authors (JTM) tried to trace some of the experimental details, he was confronted with a large number of unlabeled file boxes without any indication of what was in the boxes. Examination of these files would have taken months just to determine the contents. These uncertainties in the description of the HEU metal used in these measurements are of interest to the Working Party of Nuclear Criticality Safety (WPNCs) International Criticality Safety Benchmark Experiment Project (ICSBEP) because these HEU metal critical experiments at ORCEF have been or are being documented as benchmarks for nuclear criticality safety calculations for ICSBEP.<sup>2-7</sup>

This report documents uncertainties in the mass, dimensions, impurities, isotopics, and  $^{235}\text{U}$  content of the HEU metal (oralloy) used in a wide variety of delayed critical experiments at the ORCEF in the late 1950s, 1960s, and 1970s. Most of these experiments were performed in the east cell of ORCEF. In 2010, personnel from the National Nuclear Security Administration's (NNSA's) Y-12 National Security Complex (Y-12 NSC) reexamined the uncertainties in the descriptions of the HEU materials used in these critical experiments,<sup>8</sup> and a meeting was held at ORNL with personnel from Idaho National Laboratory, ORNL, and the Y-12 NSC to discuss these uncertainties.

## 2. MASS

Most of the masses are obtained from summary tables in the log books or are in the possession of the researchers who listed masses in grams. These masses were obtained from the certified inspection reports and rounded to the nearest gram. Thus, their uncertainty is plus or minus one-half of a gram since they were rounded up or down to the reported values.

A recent correspondence (email dated April 10, 2010) from Zeina Jabour of the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS), to Calvin Hopper of Oak Ridge National Laboratory (ORNL) documented the accuracy of the mass measurements at Y-12 at various times. These accuracies are typical of those in the metrology laboratory at Y-12. However, for measurements with the plant production scales, the uncertainties should be increased by a factor of 3. This email is as follows.

**From:** Jabbour, Zeina J. [mailto:zeina.jabbour@nist.gov]  
**Sent:** Thursday, April 22, 2010 2:54 PM  
**To:** Hopper, Calvin Mitchell  
**Subject:** RE: Request for historical mass measurement capabilities

Dear Dr. Hopper,

As we discussed during our telephone conversation, the NIST calibration of Oak Ridge 20 kg mass standard shows an uncertainty of 0.02 g in 1977, 0.007 g in 2000, and 0.003 g in 2009. Hope this helps. Please don't hesitate to contact me if you need more information.

Regards,  
Zeina

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***It states that the capability in 1977 was 0.02 grams. Thus, for all the measurements reported out in grams, the masses are uncertain by one-half of a gram.***

In the early 1970s when experiments were performed for an oralloy sphere at ORCEF, certified inspection reports from Y-12 were provided to ORCEF with the mass documented out to 0.01 gram for 20 kilogram parts. A portion of an inspection report stating the mass for one part of the oralloy sphere is given in Fig. 1.

		104 INSPT. DEPT. AUDIT <i>Bm</i> 6-16-71	
<b>LEGEND: METHOD OF RECORDING</b>			
*Record Actual Dimensions. (Maximum and Minimum, if applicable).		‡ Record deviation from single stated dimension in mils (1.0 = 0.001").	
†Record Actual Dimension using an X to the left of decimal for all inch measurements.		⊖ Record Average Deviation in mils. No Symbol - Indicates o.k. to be used.	
<input type="checkbox"/> CERTIFIED WEIGHT REQUIRED	WEIGHED BY <i>[Signature]</i>	WEIGHT <i>19,624.59g.</i>	
<b>DIMENSIONAL INSPECTION RESULTS</b>		<b>DIMENSIONAL INSPECTION DISPOSITION</b>	
PART MEETS DIMENSIONAL CRITERIA <input checked="" type="checkbox"/> YES <input type="checkbox"/> NO			
DATE <i>6/15/71</i>	INSPECTOR <i>D. A. Mingio</i>	DATE	PROJECT ENGINEER
QL AUDIT PERFORMED BY			
	REVISION	APPROVED	DATE
	<i>(TWO)</i>	<i>GB DK</i>	<i>6-9-71</i>
	<i>(ONE)</i>	<i>DW DR</i>	<i>12-29-70</i>
	<i>ORIG</i>	<i>DW DR</i>	<i>12-22-70</i>
			<i>E. MAEVENS</i>
			<i>MAEVENS</i>
			<i>MAEVENS</i>

**Fig. 1. Portion of the inspection report stating the weight of a part for the oralloy sphere assembled at ORCEF.**

While working on a paper to describe the oralloy sphere experiment, the author questioned the accuracy of the masses quoted in the inspection reports. He talked with several people around at that time and John Goggin was the only one who could provide any information. He said that in the early 1990s in or near the production area there was a large glass balance with temperature and humidity control that measured the mass of 20 kilogram parts to a precision of 0.001 gram and that they normally reported out the results to 0.01 gram. He said that this accuracy was produced by applying a correction for the difference in buoyancy of the oralloy and reference standard weights in air. He also said that this balance was not now operational, and he did not recall when it ceased operation.

While the uncertainty in mass measurements conducted in the Metrology Facility is well documented, those performed in the plant environment are not as well documented. As a conservative estimate for the uncertainty in mass measurements performed on the “shop floor,” the Metrology accuracy was multiplied by a factor of 3. In recent email from James Green, presently of the metrology laboratory at Y-12, the mass accuracy in 1960 was 0.089 gram for 20 kilogram samples traceable to the NBS (Table 1).

**Table 1. Mass measurement accuracies at the metrology laboratory of Y-12 Plant**

Year	Mass accuracy (gram)	
	Metrology lab	Plant scales
1960s	0.089	0.30
1977	0.020	0.06
2000	0.007	0.02
2009	0.003	0.009

In most cases, the masses from the inspection reports were rounded to the nearest gram in the log books. In the case of the HEU metal sphere parts, the masses are from the inspection reports.

*Certainly, the part masses quoted in the benchmark experiments with oralloy metal parts at the ORCEF are accurate to one-half a gram.*

### 3. DIMENSIONS

The oralloy dimensions quoted in the inspection reports for these experiments are given to 0.0001 in. These dimensions were transcribed into tables to this accuracy at the time of the experiments. Recently, in a meeting between staff from Y-12, ORNL, and members of the WPNCS ICSBEP, Y-12 staff stated that dimensions at that time were measured on a Moore machine and were accurate to 0.0001 in. However, in Ref. 8 (included as Appendix B in this report) it is stated that the accuracy of the Moore machine at the time was 0.0003 to 0.0005 in. It is assumed that the uncertainty in the dimensions of the oralloy parts measured at Y-12 at 70°F was 0.0004 in. (All inspection reports giving the dimensions stated that the dimensional measurements were performed at 70°F.)

*Dimensions of oralloy cylinders and annuli used in the ORCEF critical experiment with metal cylinders and annuli are accurate to 0.0004 in.*

### 4. ISOTOPICS

The isotopic content of the oralloy used in these experiments was taken from tables compiled by the researchers when the materials were delivered to ORCEF by Y-12. The values given in the table of isotopic composition of the oralloy are transcribed in weight percent to two decimal places from the isotopic analysis reports.

At the recent meeting mentioned above, Y-12 staff stated that the isotopic content reported for a given sample of the metal was obtained from the mean of two measurements of using thermal ionization mass spectrometry. Calculation of the combined uncertainties in isotopic content considers the precision and accuracy of the measurement and the uncertainties associated with the standard used to calibrate the instrument. During the time frame for the ORCEF experiments, the dominating contribution to overall measurement uncertainty for <sup>235</sup>U content is the uncertainty of the NBS standard (SRM U850 values are shown in Table 2). For many measurements, the uncertainty could be lower by the square root of the number of measurements if the uncertainties are statistically distributed. The precision in monthly averages of the oralloy enrichment measurements during this time period would be more accurate than the weight percents given in Table 2. However, the main contributor to the uncertainty is that for the standard samples from NBS.

**Table 2. Weight percent uncertainty in isotopic content of HEU uranium metal at ORCEF**

Isotope	Sample (MS-5)	NBS standard	Combined
234	0.0010	0.0014	0.0017
235	0.0050	0.0170	0.0177
236	0.0130	0.0011	0.0130
238 <sup>a</sup>	0.0140	0.0140	0.0198

<sup>a</sup>238 was calculated: (100 - %234 - %235 - %236)

Uncertainty in 238 is combined uncertainties from all other isotopes.

An example of average enrichments at Y-12 is given in Table 3 for the oralloy parts made over a period of ~1 month. These parts were made for the oralloy metal critical; the experiments were performed in the east cell of ORCEF. The measured isotopics for these 68 oralloy metal parts are listed in HEU-MET-FAST-051<sup>2</sup> and Appendix A. The standard deviation of the mean for the <sup>235</sup>U isotopic content is 0.00348%, which is a factor of 5 lower than the combined uncertainty of Table 2. The monthly averaged isotopics for all oralloy produced at Y-12 varied much less than uncertainty associated with a single reported value for a single oralloy part.

**Table 3. Average enrichments for oralloy parts for metal experiments in the east cell of ORCEF**

	Measured <sup>235</sup> U (wt %)	Measured <sup>234</sup> U (wt %)	Measured <sup>236</sup> U (wt %)	<sup>238</sup> U (wt %)
<b>Average</b>	93.14397	0.97265	0.24559	5.63779
<b>Std Dev</b>	0.02852	0.01672	0.01799	0.02418
<b>Std Dev of mean</b>	0.00346	0.00203	0.00218	0.002

*The uncertainty in a single measurement of the <sup>235</sup>U content of oralloy fabricated at the Y-12 plant was 0.0177 wt %. However, the standard deviation of the mean of all isotopic measurements made in each month was considerable less, and for the parts used in these measurements, as much as a factor of 5 lower. While this indicates that the precision of the measurement is well below that of the uncertainties in the NBS standard, the accuracy, and thus uncertainty, cannot be better than the value of 0.0177 wt% for the <sup>235</sup>U isotope.*

## 5. IMPURITIES

The concentration of metallic impurities in oralloy products was determined by DC-Arc emission spectroscopy, and the concentration of “gas” species was determined by combustion analyses – similar to modern Leco-type measurements (Table 4). The uncertainty in impurity measurements during this time frame is the least well characterized. In general, it was established that the uncertainty of these methods is estimated to be 70% for values measured below 10 micrograms/g-uranium and 20% for values measured above 10 micrograms/g-U.<sup>8</sup> Table 4 lists the mean, estimated uncertainty, and the measured range of impurities in the materials analyzed for the ORCEF experiments. The comparison between the experimental range of impurities and estimated uncertainty (based on the mean value) was performed to ensure that the estimated uncertainty was not larger than the experimental range of measurements, which would indicate that the criteria being used was not adequately large enough to describe the uncertainty of the measurement.

The sum of all uncertainties associated with this set of elemental impurities was determined to be ~100 micrograms/gram-U. However, it should also be added that for characterization of these oralloy parts, 10 impurity analyses were performed on samples collected from each part. Thus, the combined uncertainty for the impurity content in single oralloy part would be reduced by a factor of 10<sup>1/2</sup>. Applying this factor to each of the uncertainties associated with an impurity concentration provides an estimated total uncertainty in impurity concentration of ~35 micrograms/gram-U.

**Table 4. Experimental and calculated impurity levels and uncertainties<sup>a</sup>**

Element	Mean	Uncertainty	Range (Experimental)
		microgram/gram	microgram/gram-U
Ag	8	5.6	3–25
Bi	164	32.8	81–311
C	5	3.5	0–9
Co	5	3.5	2–15
Cr	7	4.9	4–12
Cu	25	5	10–40
Mg	3	2.1	2–3
Mn	56	11.2	25–89
N	30	6	30–
Na	27	5.4	15–50
Ni	100	20	100–
O	20	4	20–
Sb	38	7.6	10–80
Ti	1	0.7	1–
<b>Sum</b>	<b>489</b>	<b>112.3</b>	<b>303–634</b>

<sup>a</sup>Range calculated using 70% uncertainty for elements detected below 10 µg/g-U and 20% uncertainty for elements above 10 µg/g-U.

*A conservative estimate of the uncertainty (with respect to the purity of uranium) would be 100 micrograms per gram or a contribution of 0.01% to the uncertainty of the <sup>235</sup>U concentration of the metal.*

## 6. GRAMS OF URANIUM PER GRAM OF ORALLOY

The grams of uranium per gram of oralloy was determined by dichromate titration in the 1960s and 1970s. This method is similar to the modern Davies-Gray method. While the uncertainty in the total uranium from dichromate titration is dependent on several experimental factors, the major contributor to the uncertainty is the skill of the laboratory analyst. Skilled analysts can produce uncertainties as low as 0.03%. A realistic estimate of the uncertainty for these measurements for a highly purified uranium metal (oralloy) with the skilled Y-12 workforce at the time would be 0.05% or lower. For pure metals, uncertainties as low as 0.02% are achievable. The mean measured grams of uranium per gram for the oralloy parts used at ORCEF is 99.95 grams of uranium per gram of oralloy, which is in excellent agreement with the impurity analyses: sum of all impurities = 489 micrograms/gram-U.

## 7. SUMMARY OF UNCERTAINTY IN <sup>235</sup>U CONTENT

Because of the time frame in which the measurements associated with the certification of the ORCEF oralloy were performed, it is difficult to provide an accurate uncertainty. However a conservative estimate of the uncertainty can be obtained by taking the square root of the sum of the squares of the uncertainty

due to titration (0.05%), isotopic (0.0177%), and impurities (0.01%). A summary of the uncertainties in the  $^{235}\text{U}$  in a 25,000 gram mass of uranium (oralloy–nominal 99.95% metal) metal typical of that used in the ORCEF measurements from the grams of uranium per gram of metal from titration, the isotopic content of  $^{235}\text{U}$ , and the impurities is given in the Table 5.

**Table 5. Summary of uncertainty<sup>a</sup> in  $^{235}\text{U}$  mass for 25,000 grams of HEU used at ORCEF**

	Uncertainty (%)	U mass (grams)	$^{235}\text{U}$ (grams)	$^{235}\text{U}$ uncertainty (grams)
<b>Best</b>	0.027	25000	23286	6.2
<b>Estimated</b>	0.054	25000	23286	13
<b>Worst</b>	0.106	25000	23286	25

<sup>a</sup>Gram uncertainties should scale with the mass of the part.

*The total recommended uncertainty in the  $^{235}\text{U}$  mass is 0.054% and results in the assumption that the uncertainties in the grams uranium per gram of metal, the uncertainty in the isotopic content, and the uncertainty in the impurities are independent. However, these numbers are reduced if many samples are analyzed and the average values are used.*

## 8. CONCLUSIONS

**The uncertainties given in this report are considered conservative.**

### Mass:

Masses of 20 kilograms, oralloy parts (~93 wt %  $^{235}\text{U}$  enriched uranium metal) used in critical experiments at ORCEF at Y-12 are accurate to ½ gram.

### Dimensions:

Dimensions of oralloy parts used in the ORCEF critical experiment with metal cylinders and annuli are accurate to 0.0004 in.

### Isotopics

The uncertainty in a single measurement of the  $^{235}\text{U}$  content of oralloy fabricated at the Y-12 plant was 0.0177 wt %. However, the standard deviation of the mean of all isotopic measurements made in each month was considerably less, and for the parts used in these measurements, as much as a factor of 8 lower. One such analysis for oralloy parts fabricated at essentially the same time used at ORCEF gives a standard deviation of the mean wt %  $^{235}\text{U}$  of 0.0035 wt %. However, because most of the uncertainty comes from the standards at the NBS, the uncertainty in the isotopic content of  $^{235}\text{U}$  is assumed to be 0.0177%.

### Impurities:

For a particular spectrochemical impurity analysis, the uncertainty for elements <10 micrograms/gram-U is 70%, and for elements >10 micrograms/gram-U, the uncertainty is 20%. However, for these oralloy materials, 10 impurity analyses were performed, and the uncertainty was ~20% (about a factor of 3 less) for elements <10 micrograms per gram and ~6% for elements >10 micrograms per gram.

### Grams of uranium per gram of oralloy:

A realistic estimate of the uncertainty for these measurements for a highly purified uranium metal (oralloy) with the skilled Y-12 workforce at the time would be 0.05% or lower. For pure uranium metal,

uncertainties as low as 0.02% are achievable. The measured (mean) grams of uranium per gram of oralloy is 0.9995 grams of uranium per gram of oralloy, which is in excellent agreement with the impurity analyses.

#### ***Total Uncertainty in $^{235}\text{U}$ Mass***

The recommended total uncertainty in the  $^{235}\text{U}$  mass is 0.061% and results in the assumption that the uncertainties in the grams uranium per gram of metal, the uncertainty in the isotopic content, and the uncertainty in the impurities are independent. For a 25,000 gram sample of oralloy, this uncertainty is 13 grams.

## **9. REFERENCES**

1. *Safety Review of the Oak Ridge Critical Experiments Facility*, Oak Ridge National Laboratory, ORNL/TM-349 (1962).
2. Robert Elwood and John Mihalcz, *Uranium (93.2) Metal Cylinders (7-inch, 9-inch, 11-inch, 13-inch, and 15-inch Diameter) and Two 11-Inch-Diameter Interacting Uranium (93.2) Metal Cylinders*, NEA/NSC/DOC/(95)03/II Volume II HEU-MET-FAST-051.
3. John Bess, *Oralloy (93.2  $^{235}\text{U}$ ) Metal Annuli with Beryllium Core*, NEA/NSC/DOC/(95)03/I Volume II HEU\_MET\_FAST-059.
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7. Mackenzie L. Gorman and John D. Bess, *Grotesque: Complex Arrangement of Unreflected HEU (93.15) Metal Pieces*, NSC/DOC/(95)03/I Volume II HEU-MET-FAST-081.
8. T. Gregory Schaaff and Thomas T. Adams, *Regarding Measurement Uncertainty of Uranium Chemical Characterization between 1960 and 1970*, Y/DK-2374 (included in this report as Appendix B).

## APPENDIX A. ISOTOPIC ANALYSES FOR URANIUM METAL PARTS

The isotopic analyses for the uranium metal parts are given in Table A-1. All parts were made at the same time, and the variations for the parts are the uncertainty in the isotopic determination methods rather than differences in the uranium metal.

**Table A-1. Summary of uranium isotopics of metal cylinders, annuli, and plates for delayed-critical experiments reflected and/or internally moderated with polyethylene**

Part number	Measured $^{235}\text{U}$ (wt %)	Measured $^{234}\text{U}$ (wt %)	Measured $^{236}\text{U}$ (wt %)	$^{238}\text{U}$ (wt %)
2728	93.17	0.97	0.24	5.62
2729	93.15	0.99	0.26	5.60
2730	93.14	0.97	0.25	5.64
2731	93.13	0.97	0.22	5.68
2732	93.17	0.95	0.21	5.67
2733	93.15	0.96	0.26	5.63
2734	93.18	0.95	0.24	5.63
2735	93.12	0.98	0.25	5.65
2736	93.17	1.01	0.21	5.61
2737	93.08	0.99	0.29	5.64
2738	93.15	0.98	0.24	5.63
2739	93.16	0.96	0.25	5.63
2740	93.17	0.97	0.24	5.62
2741	93.18	0.96	0.25	5.61
2742	93.14	0.98	0.23	5.65
2743	93.14	0.98	0.23	5.65
2744	93.14	0.98	0.23	5.65
2745	93.20	0.96	0.22	5.62
2746	93.09	1.00	0.22	5.69
2747	93.16	0.98	0.19	5.67
2748	93.09	1.00	0.22	5.69
2749	93.19	0.98	0.25	5.58
2750	93.12	0.95	0.25	5.68
2751	93.13	0.98	0.24	5.65
2752	93.13	0.98	0.24	5.65

Table A-1 (continued)

Part number	Measured $^{235}\text{U}$ (wt %)	Measured $^{234}\text{U}$ (wt %)	Measured $^{236}\text{U}$ (wt %)	$^{238}\text{U}$ (wt %)
2753	93.12	0.95	0.25	5.68
2754	93.10	0.96	0.28	5.66
2755	93.10	0.96	0.28	5.66
2756	93.18	0.93	0.25	5.64
2757	93.20	0.96	0.23	5.61
2758	93.16	0.98	0.27	5.59
2760	93.13	0.99	0.24	5.64
2761	93.12	0.96	0.27	5.65
2762	93.13	0.97	0.27	5.63
2763	93.18	0.96	0.25	5.61
2766	93.16	0.98	0.27	5.59
2767	93.14	0.96	0.26	5.64
2768	93.14	0.92	0.26	5.68
2769	93.15	0.97	0.25	5.63
2770	93.13	0.99	0.26	5.62
2771	93.14	0.97	0.25	5.64
2773	93.17	0.97	0.24	5.62
2774	93.08	0.99	0.29	5.64
2775	93.15	0.98	0.24	5.63
2776	93.16	0.96	0.23	5.65
2778	93.16	0.96	0.23	5.65
2779	93.16	0.96	0.23	5.65
2780	93.13	0.98	0.25	5.64
2781	93.19	0.98	0.25	5.58
2782	93.20	0.96	0.23	5.61
2783	93.18	0.93	0.25	5.64
2784	93.13	0.99	0.24	5.64
2785	93.11	0.99	0.26	5.64
2786	93.14	0.98	0.24	5.64
2787	93.14	0.98	0.24	5.64
2803	93.14	1.00	0.23	5.63
2820	93.14	0.98	0.24	5.64
2821	93.14	0.98	0.24	5.64
2829	93.10	0.99	0.24	5.67
2848	93.18	0.99	0.24	5.59

Table A-1 (continued)

Part number	Measured $^{235}\text{U}$ (wt %)	Measured $^{234}\text{U}$ (wt %)	Measured $^{236}\text{U}$ (wt %)	$^{238}\text{U}$ (wt %)
2885	93.11	0.99	0.26	5.64
2886	93.11	0.99	0.26	5.64
3078	93.14	0.97	0.25	5.64
3101	93.14	0.97	0.25	5.64
3102	93.14	0.97	0.25	5.64
3103	93.14	0.97	0.25	5.64
3104	93.14	0.97	0.25	5.64
3105	93.14	0.97	0.25	5.64



**APPENDIX B**

**REGARDING MEASSUREMENT UNCERTAINTY OF URANIUM CHEMICAL  
CHARACTERIZATION BETWEEN 1960 AND 1970**





# **Regarding Measurement Uncertainty of Uranium Chemical Characterization between 1960 and 1970**

**Y-12  
NATIONAL  
SECURITY  
COMPLEX**

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J. Quinn    02/07/2012    (Signature on File)

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# **Regarding Measurement Uncertainty of Uranium Chemical Characterization between 1960 and 1970**

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## EXECUTIVE SUMMARY

This report describes historical methods developed and used at the Y-12 Plant during the time frame of experiments performed at the Oak Ridge Critical Experiment Facility (ORCEF). Using the dates provided in Mr. Hopper's letter (10 March, 2010), the analytical dates in question fall between the late 1950's to the mid-1970's. While most instrumentation and methods used during this era are obsolete, Analytical Chemistry personnel have attempted to estimate uncertainties associated with measurements used to characterize highly-pure uranium metal samples during this time frame. To estimate these uncertainties, the investigation has included inspection of archived records and conducted phone interviews with retirees who were intimate with the instrumentation methods used during this era. From these archived records and conversations, the major contribution to uncertainty in the weight-percent of  $^{235}\text{U}$  is measurement of total uranium by dichromate titration during this time-frame. However, quality control calculations limits imposed during this time frame and consideration of possible contributions of various measurements indicate that the uncertainty in the  $^{235}\text{U}$  content is likely between 0.04% and 0.1% (weight-percent).

## Historical Characterization of High-Purity Uranium Metal

Between ca. 1950-1970, most of the methods and instrumentation were developed and built (respectively) within the Oak Ridge complex specifically for the characterization of high-purity uranium metal ( $>0.999$  g-U/g). However, the retrieval of records pertaining to the analytical measurements presents a significant challenge – location, classification, incomplete records, etc. Personnel in the Analytical Chemistry Organization at Y-12 have visited the Y-12 Site's repository to inspect archived control charts, procedures and other records pertaining to the characterization of uranium metal during this time frame. In addition, multiple phone interviews were conducted to discuss what techniques were used and general operational aspects of the instrumentation.

From these records and conversations, four primary methods were utilized between ca. 1950-1970 to determine the purity of uranium metal: (i) dichromate titration for total uranium (or g-U/g), (ii) mass spectrometry for isotopic characterization, (iii) various forms of arc-based spectroscopy for elemental impurities and (iv) combustion analysis for carbon, nitrogen and oxygen. The following sections provide a brief description of the method and likely uncertainties associated with each method during this time frame.

### *Dichromate titration*

A dichromate titration (similar to the modern Davies-Gray method) was used to determine the concentration of uranium by ACO in the 60s & 70s. The uranium was completely dissolved in a combination of hydrochloric, sulfuric, and perchloric acids, which ensured the uranium was fully oxidized to the hexavalent state. The entire sample was then passed through a reducing-agent bed to reduce all of the uranium to a lower oxidation state (4+). A precisely weighed amount of NIST potassium dichromate was added in a slight excess to the solution. The resulting solution was then titrated with a reducing solution to a potentiometric endpoint. Results from this technique have the potential for very low uncertainty in determination of uranium concentration – especially for high-purity metals.

While the uncertainty of total uranium from dichromate titration is dependent on several instrumental factors (i.e. uncertainty in isotope ratios, multiple weighing steps), the major contributor to uncertainty is the skill of the laboratory analyst performing the measurements. Skilled analysts are capable of producing uncertainties as low as 0.03% in the g-U/g for high-purity metals using either dichromate or Davies-Gray methods. However, it would require substantial effort to locate and determine the exact uncertainty for measurements pertaining to the ORCEF experiments. However, since the international target values (ITV's) are developed based on historical measurements, it is assumed that the uncertainty for total uranium determination by dichromate titration would be of similar magnitude. The ITV for uncertainty in Davies-Gray titration is currently **0.14%** g-U/g. This would represent a conservative estimate in the g-U/g measurement by dichromate titration, primarily because ITV values are set substantially higher than typical uncertainties produced by skilled laboratories on all uranium-bearing materials. A more realistic estimate of uncertainty for this measurement on highly-purified uranium metal with a skilled workforce would be **0.05%** or lower (confirmed by

conversations with retirees). Typically, for pure metals and oxides, Davies-Gray and similar titration can achieve uncertainty of measurement values approaching **0.02%**.

### *Isotopic Mass Spectrometry*

The type of mass spectrometry used in the early 1960's to mid-1970's was the predecessor for modern thermal ionization mass spectrometry. The instrument used for these measurements was the MS-5 – a 1950-vintage uranium hexafluoride gas-source mass spectrometer, which was modified to allow for solids analysis. Solid uranium metal was dissolved in nitric acid and the solution was applied to a filament (approximately 300 to 400 micrograms of total uranium loaded). This filament was then inserted into the instrument at high-vacuum and heated to sufficient temperature to volatilize the uranium. The gas was then leaked into an electron impact ionization source to produce ions. The ions were accelerated and measured by mass spectrometry. In the MS-5 instruments, the ions were separated by their  $m/z$  by a magnetic field, which was scanned to focus the separated ion beam onto a single Faraday cup. [This is in contrast to modern multi-collector-style instruments where all ions of interest (i.e. 233, 234, 235, 236, 238) are measured simultaneously.]

The 1978 procedure Y/P65-233057 “Isotopic Abundance Measurements on the MS-300 Thermal Emission Mass Spectrometer” briefly describes the results of a comparison between the MS-5 instrument and the MS-300 instrument, which went into operation in the mid-1970's. From this study, the precision of the MS-5 was comparable to that of the MS-300. For 49 routine metal samples the mean weight percents and standard deviation (1-sigma) of the mean were:

Table 1: Precision of MS-5 Isotopic Ratios for NBS Standard Reference Material (U-930)

Isotope	Average (%)	Standard Deviation of Mean
234	0.999	0.001
235	93.170	0.005
236	0.445	0.013
238	Calculated from unity	

However, isotope ratio determination is dependent on the standard used to calibrate the instrument for operation. The accepted uncertainty of many isotopic standards used during this time frame was much higher than the standard deviation determined experimentally. For example, the commonly used SRM U-850 Certificate of Analysis provides the following:

Table 2: Typical Uncertainties for Isotopic Ratio Standard Reference Materials ca. 1970

Isotope	Average (%)	Uncertainty
234	0.6399	0.0014
235	84.988	0.017
236	0.3713	0.0011
238	14.001	0.014

The uncertainty values quoted on the Certificate of Analysis were determined from values obtained at National Bureau of Standards, Union Carbide Nuclear Company (Y-12) and Goodyear Corporation (Portsmouth). Because the standard reference material is used to calibrate the instrument, the uncertainty in the measurement for samples cannot

be smaller than the uncertainty known for the standard reference material. To estimate the measurement uncertainty, consider the variability of the measurement and the known standard:

$$\Gamma = \sqrt{(0.005)^2 + (0.017)^2} = 0.0177 \quad \text{Eq. 1}$$

This would likely be a minimum for the uncertainty during this time frame (1960-1970) for the MS-5 instrumentation.

The isotopic data included in the Hopper Letter was analyzed. The standard deviation of the mean for the  $^{235}\text{U}$  data provided was determined to be 0.03%. This standard deviation of the sample population is consistent with a measurement uncertainty of **0.02%**. This sample population standard deviation includes both the instrument uncertainty and the variability of the material analyzed over the time frame for the experiments.

#### *Elemental Impurity Analyses*

Between the 1950's and 1970's, elemental impurities in high-purity uranium metal were determined by a combination of techniques, depending on the elements of interest and customer needs. In the late 1950's to mid-1960's, a DC-arc emission spectrometer ("Old" Quantometer) was used to determine the concentration of 18 elements. In the mid-1960's, this instrumentation was replaced by another DC-arc emission spectrometer ("New" Quantometer), which was capable of measuring 24 elements. Both Quantometer systems allowed simultaneous measurement of elements using direct-reader technology, coupled to strip-chart recorders, which made a paper computer tape. The computer tapes were then processed with computer systems at the K-25 Gaseous Diffusion Plant. During this entire time frame, additional methods were used to quantify elements of interest not amenable to the Quantometer systems. The methods included DC-arc emission spectroscopy and spark-source mass spectrometry – both with photographic plate detection. Judging from the element list provided in the letter, it is likely that the major elemental impurity constituents were determined by either the "Old" or "New" Quantometer systems – depending on the date of analysis.

While we were unable to locate control charts associated with these two instruments in the archives, conversations with retired and current ACO personnel indicate that the two instruments were very similar with regard to uncertainty of measurement. While DC-arc spectrometry (direct-reader, non-photographic) is capable of <10% uncertainty of measurement, typically uncertainties in measurement are dependent on the concentration of the element of interest and the "brightness" of the emission lines used. Because the optical emission from uranium is complex, bright and nearly continuous across the visible-to-UV region, emission spectroscopic determination of elemental impurities suffers greatly at levels below ~10 ug/g-U for most elements. Generally, a conservative estimate of the uncertainty of the elemental concentration in highly-pure uranium metal is 20% of measured value when elements are above 10 ug/g-U and ranging up to 70% for elements below 10 ug/g-U.

The concentration of carbon, nitrogen and oxygen were determined by Leco-type analyses. One gram aliquots of the pure metal were subjected to combustion under various atmospheres (e.g. oxygen- or hydrogen-saturated environments) followed by

separation of gaseous species and detection of products (e.g. CO<sub>2</sub>, NO<sub>2</sub>, H<sub>2</sub>O, respectively). This technology was well-developed in this era of measurement and typically produced 3-20% uncertainty in the measurement of these elements, depending on the respective concentration. Again, a conservative estimate for uncertainty will be considered as 20% for the measurement of these elements.

Considering the elements listed in the Hopper Letter, the uncertainty in total impurities is quite similar to the uncertainty associated with the g-U/g determination by titration and the uncertainty associated with the isotopic characterization. Table 3 lists the average of all impurities for the samples, the calculated uncertainty (using criteria above) and the measured range of impurities in the materials analyzed for the ORCEF experiments.

Table 3: Experimental and Calculated Impurity Levels and Uncertainties

Element	Average	Range (Experimental)		Range (Calculated Uncertainty)*	
		Lower (ug/g-U)	Upper (ug/g-U)	Lower (ug/g-U)	Upper (ug/g-U)
Ag	8	3	25	2.4	13.6
Bi	164	81	311	131.2	196.8
C	5	0	9	1.5	8.5
Co	5	2	15	1.5	8.5
Cr	7	4	12	2.1	11.9
Cu	25	10	40	20	30
Mg	3	2	3	2.4	5.1
Mn	56	25	89	44.8	67.2
N	30	30	-	24	36
Na	27	15	50	21.6	32.4
Ni	100	100	-	80	120
O	20	20	-	16	24
Sb	38	10	80	30.4	45.6
Ti	1	1	-	0.3	1.7
Sum	489	303	634	378.2	601.3

\* Range calculated using 70% uncertainty for elements detected below 10 ug/g-U and 20% uncertainty for elements above 10 ug/g-U.

Using the criteria that elements detected below 10 ug/g-U have 70% uncertainty in measured value and those above 10 ug/g-U have 20% uncertainty produces a calculated range of values that is consistent with the measured range for nearly all elements. In addition, when considering the sum of the impurities the experimental and calculated ranges are consistent. Thus, a conservative estimate of the uncertainty (with respect to the purity of the uranium) would be 300 ug/g-U or a contribution of 0.03% to the uncertainty of <sup>235</sup>U concentration in the metal.

## Discussion and Summary

Because of the time frame of measurements associated with certification of ORCEF materials and limited personnel and archival information, it is difficult to provide an accurate value for uncertainty in the  $^{235}\text{U}$  content in all parts used at ORCEF. However, a conservative estimate for  $^{235}\text{U}$  content can be made by considering the likely measurement uncertainties associated the measurement techniques during this era. The simplest estimate considers the variability (uncertainty) with each measurement – similar to Equation 1:

$$\Gamma = \sqrt{(\text{Titration})^2 + (\text{Isotopic})^2 + (\text{Impurities})^2} \quad \text{Eq. 2}$$

$$\Gamma = \sqrt{(0.05)^2 + (0.0177)^2 + (0.03)^2} = 0.061\%$$

While this is an elementary approach to estimating the uncertainty association with the measurement of  $^{235}\text{U}$  content for the uranium disks used in the ORCEF experiments, it is consistent with quality control limits that were maintained for highly purified metal products during this era.

In addition the simple consideration of uncertainties associated with different measurement techniques, one should also consider the quality control calculations that were performed to ensure only accurate results were reported for high-purity uranium metal. After all measurements were performed, the summation of the experimentally determined uranium concentration and the impurities were required to be within a specific limit (99.95 to 100.05). While the origin of this limit is unknown, it was likely derived from repeated analyses of statistical controls within the Y-12 plant during this time frame. If this summation did not fall within the limit, the titration was performed again. If the summation still fell outside the limit, all analytical tests were performed again. This summation ensured that the results were accurate to within 0.1% for all the tests performed during this era of measurement.

Considering both the elementary consideration of uncertainty and the quality control limits imposed during this era, the uncertainty of  $^{235}\text{U}$  content is estimated to 0.1%. Because the major contribution to the calculated uncertainty is an estimate based on process knowledge and an educated guess for the uncertainty of the dichromate titration, it is possible that the uncertainty could be slightly lower. Because the titration involves a pure metal, it likely has minimal uncertainty (0.02%). With this uncertainty in Eq. 2, the total uncertainty of  $^{235}\text{U}$  content would be 0.04%. Thus, a conservative estimate of the  $^{235}\text{U}$  content uncertainty would be 0.1%, with a minimum estimate of  $^{235}\text{U}$  content uncertainty of 0.04%.