U.S. Department of Energy

Project Report for Certified Reference Material 115: 1-Gram Unit Production and Certification of U Amount Content and U Isotope-Amount Ratios

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NBL Program Office
U. S. Department of Energy

Project Report for Certified Reference Material 115: 1-Gram Unit Production and Certification of U Amount Content and U Isotope-Amount Ratios

Department of Energy
NBL Program Office
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Summary:

Certified Reference Material 115 (CRM 115) was originally issued as a 235U depleted metal reference material for amount content analysis (assay). Since 1978, CRM 115 has been made available in units with a mass of approximately of 75 grams. This report describes the production of a set of 1-gram CRM 115 units, the re-analysis of uranium amount content, and the determination of certified U isotope-amount ratios (isotopic composition). Values and uncertainties from this work are incorporated into a revised certificate. The primary changes from previous revisions of the CRM 115 certificate are newly determined values and GUM compliant uncertainties for amount content and the inclusion of certified isotope-amount ratios along with quantities derived from these ratios (Table I).

Table I
Certified Attribute Values for CRM 115

<table>
<tr><td>Amount Content :</td><td colspan="12">0.99978 g U•g^{-1} metal</td></tr>
<tr><td>Uncertainty:</td><td colspan="12">0.00010 g U•g^{-1} metal</td></tr>
<tr><td></td><td colspan="12"></td></tr>
<tr><td></td><td colspan="4">$n(^{234}\text{U})/n(^{238}\text{U})$</td><td colspan="4">$n(^{235}\text{U})/n(^{238}\text{U})$</td><td colspan="4">$n(^{236}\text{U})/n(^{238}\text{U})$</td></tr>
<tr><td>Isotope-Amount Ratio:</td><td colspan="4">0.000007545</td><td colspan="4">0.0020337</td><td colspan="4">0.000032213</td></tr>
<tr><td>Uncertainty:</td><td colspan="4">0.000000018</td><td colspan="4">0.0000012</td><td colspan="4">0.000000084</td></tr>
<tr><td></td><td colspan="12"></td></tr>
<tr><td></td><td colspan="3">$n(^{234}\text{U})/n(\text{U})$</td><td colspan="3">$n(^{235}\text{U})/n(\text{U})$</td><td colspan="3">$n(^{236}\text{U})/n(\text{U})$</td><td colspan="3">$n(^{238}\text{U})/n(\text{U})$</td></tr>
<tr><td>Isotope-Amount Fraction (•100):</td><td colspan="3">0.0007530</td><td colspan="3">0.20295</td><td colspan="3">0.0032146</td><td colspan="3">99.79308</td></tr>
<tr><td>Uncertainty:</td><td colspan="3">0.0000018</td><td colspan="3">0.00012</td><td colspan="3">0.0000084</td><td colspan="3">0.00012</td></tr>
<tr><td></td><td colspan="12"></td></tr>
<tr><td></td><td colspan="3">$m(^{234}\text{U})/m(\text{U})$</td><td colspan="3">$m(^{235}\text{U})/m(\text{U})$</td><td colspan="3">$m(^{236}\text{U})/m(\text{U})$</td><td colspan="3">$m(^{238}\text{U})/m(\text{U})$</td></tr>
<tr><td>Isotope Mass Fraction (•100):</td><td colspan="3">0.0007403</td><td colspan="3">0.20039</td><td colspan="3">0.0031876</td><td colspan="3">99.79568</td></tr>
<tr><td>Uncertainty:</td><td colspan="3">0.0000018</td><td colspan="3">0.00012</td><td colspan="3">0.0000083</td><td colspan="3">0.00012</td></tr>
<tr><td></td><td colspan="12"></td></tr>
<tr><td>Molar Mass:</td><td colspan="12">238.0445912 g•mol^{-1}</td></tr>
<tr><td>Uncertainty:</td><td colspan="12">0.0000055 g•mol^{-1}</td></tr>
</table>

All uncertainties are expanded uncertainties ($U=k\bullet u_c$) with the coverage factor (k) of ~2. Note: ^{233}U was not detected in the CRM 115 material. The limit of detection determined for the $n(^{233}\text{U})/n(^{238}\text{U})$ ratio for the technique used to assess ^{233}U isotope-amount in the CRM 115 samples is 3.6 x10^{-9}.

Background Information:
Certified Reference Material 115 is a depleted uranium amount content reference material that is sold in units consisting of 75-gram metal bars. CRM 115 was first made available by New Brunswick Laboratory as a uranium amount content standard in 1978. The depleted uranium metal was produced by National Lead Company of Ohio and was then rolled into sheets and sheared into 8 metal strips at Rocky Flats, CO in 1974. Each of the strips was labeled with a letter “A” through “H”. In turn, each of the strips was sheared into ~75 gram pieces. Some of these pieces were packaged for distribution and others were stored in bulk. The most recent packing effort, prior to this project, was initiated in 2001 and completed in 2002. A total of 103 75-gram bars cut from the “B” strip were packaged for distribution and evaluated to confirm the certificate values.

The project, described here, is for the production of nominally 1-gram units of the CRM 115 depleted metal; determination of a GUM compliant certified uranium amount content; and the determination of certified values for uranium isotope-amount ratios. All of the samples processed for this project were chosen from materials packaged in 2001 and, therefore, are all from the “B” metal strip. The initial Scope of Work and Analysis Plan were written in January of 2009 and August of 2010 respectively. CRM unit production and analytical work was initiated in January 2011 and completed in November of 2011.

1-gram CRM 115 Sample Preparation:
Ten previously packaged 75-gram units of CRM 115 were chosen at random from the units in storage. These units were transferred to where the Buehler Samplmet abrasive cutting saw is located. Samples were removed from its packaging, pieces were cut appropriate for High Precision Titration, and then the majority of the metal was cut into approximately 1-gram pieces. The metal pieces had to be cut to size by “eye” due to the small size of 1-gram uranium metal pieces; the relatively large size of the saw; and the lack of an adjustable cutting stage or arm. This resulted in a fairly broad distribution of uranium sample masses. Also, relatively large end pieces (4 to 7 g) could not be cut smaller because of the size and orientation of the sample holder. Sample cutting resulted in a total of 245 metal pieces. The characterized values in this report are applicable to all of the cut metal pieces but the distribution of sample sizes planned for CRM units is between 1.0 g and 1.5 g for a total of 157 units. Eighty-one of these pieces, with weights between 1.1 g and 1.3 grams, have been packaged for distribution.

Two pieces from each of the CRM 115 metal bars were selected for High Precision Titrimetric uranium amount content determination. Only a single piece from each bar was processed for analysis. The analyzed pieces had masses between 2.5 g and 3.5 g. Another, approximately 1 gram, piece from each bar was chosen for dissolution to produce sample solutions for isotopic analysis and for Davies & Gray titrimetric analysis.

Uranium Amount Content Determination:
The initial characterization analyses, performed in 1975 and used to assign certificate values for CRM 115, consisted of a total of six NBL High-Precision Titrimetric Method (HPT) measurements on sample pieces from strips “A”, “D”, and “H”. The samples packaged and analyzed during the 2001-2002 campaign were all cut from strip “B”. The verification analyses for the packaged “B” material were entirely consistent with the original certified value indicating that there was no apparent strip-to-strip inhomogeneity. The measurement uncertainties cited in the original certificate (and subsequent revisions) consisted of twice the standard uncertainty for

the six HPT measurements but did not incorporate any potential “Type B” uncertainty components such as the uncertainty associated with the oxidimetric potential of the titrant used in the determination.

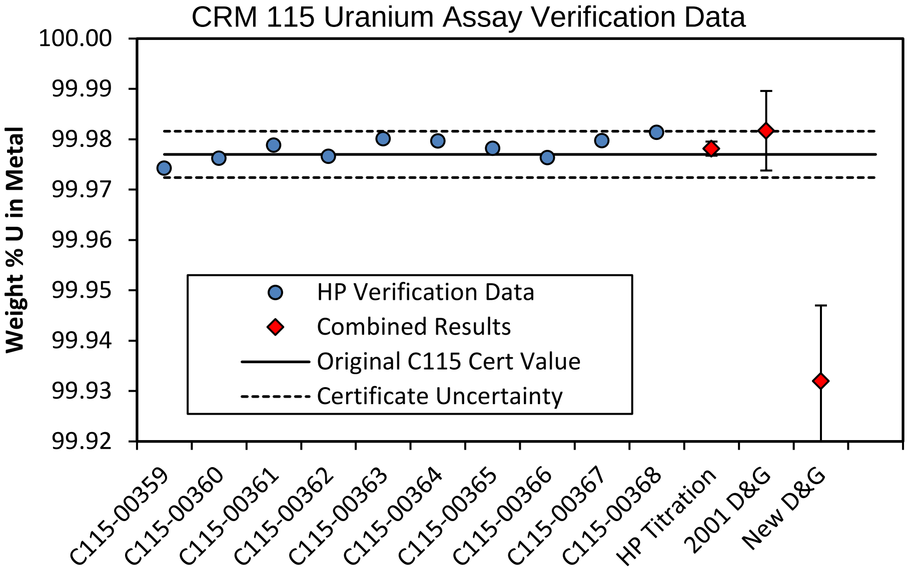
For the project described in this report, a set of samples was analyzed for the purpose of verifying the amount content of the newly cut and packaged material. The results from the completed verification analyses were compared to the original certification data and found to be statistically indistinguishable. The data comparison also revealed that the uncertainties for the original certificate were not GUM compliant and were based on a smaller data set than the verification analyses. Accordingly, it was decided that the verification data set would be used to establish a new certificate value for uranium amount content with a GUM compliant uncertainty. Analyses were performed using both the HPT method and the NBL Titrimetric method (Davies & Gray: D&G). National Institute of Standards and Technology (NIST) SRM 136e Potassium Dichromate Oxidimetric Standard was used for both the HPT and the D&G titrimetric methods. Note that the HPT amount content analysis method requires multi-gram samples but the CRM units created as part of this project are less than 1.5 g. Therefore, a 2-step approach was used to demonstrate homogeneity for the ~1-gram samples. The HPT method was used to compare the new samples with the original certificate values and to determine new, GUM-compliant certificate values. Then, the D&G analyses demonstrated that there is no apparent sample-to-sample variability at the 1-gram sample size.

The samples were transferred to the laboratory module for processing and analysis. Ten HPT amount content samples were prepared and analyzed. All measurements of material and reagents were performed by mass on checked and calibrated laboratory balances. Prior to sample dissolution, a simulated weighing experiment was performed to estimate an appropriate weighing uncertainty for the mass determinations of the metal and the potassium dichromate titrant. Metal and dichromate sample weights were corrected for buoyancy using values for material density and room temperature, atmospheric pressure, and relative humidity measured at the time of the weighings.

The D&G sample preparation and analyses were performed on ten samples. The samples were dissolved but uranium amount content analyses were only performed on four replicates of each of four samples over the course of two days. Metal and dichromate sample weights were corrected for buoyancy using values for material density and room temperature, atmospheric pressure, and relative humidity measured at the time of the weighings. Aliquots of the dissolved uranium metal for all ten samples were also stored in Savillex Teflon vials and transferred the mass spectrometric laboratory for analysis (see below).

Figure I shows the distribution of the verification data relative to the original certificate value. Note that the HPT data appear to be randomly distributed around the value determined for CRM 115 in 1975. For information purposes, the combined data are shown for the HPT data, the 2001 D&G verification data, and the new D&G data. The error bars for the combined data represent twice the standard uncertainty (i.e. 2 standard error of the mean) for the associated measurements. The most recent D&G measured values are notably biased (~0.05%) relative to the other data sets.

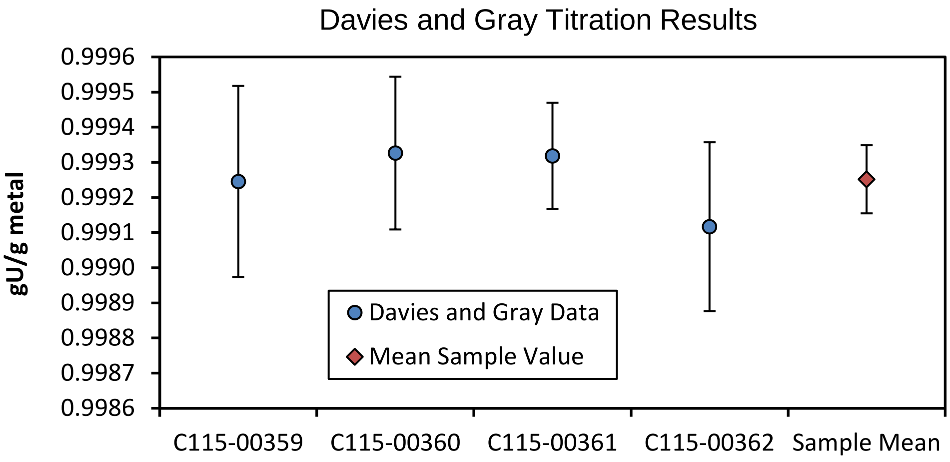
Figure I



The HPT verification analyses for amount content were performed on multi-gram samples while the D&G analyses were performed on samples that are the same size or smaller than those prepared for distribution. Figure II shows the sample data for the D&G analyses with the error bars representing twice the standard uncertainty for replicate analyses of the sample solutions. The Sample Mean represents the average of the mean values and the error bars are twice the standard uncertainty of mean sample values. This figure shows that, within the resolution of the measurement technique, the CRM 115 samples appear to be homogenous at the 1 gram size. An ANOVA analysis of the sample data sets yields an F statistic of 0.74 which is substantially lower than the F-critical value of 3.49, indicating that there is no statistically significant sample-to-sample variability. Although the observed measurement variability of the one gram samples (0.0049% standard uncertainty) is slightly larger than the cited uncertainty of the original CRM 115 certificate (0.0046%), this variability is likely due to the limited precision of the D&G technique as indicated by the dispersion of replicate analyses of the D&G sample solutions. As noted above, the replicate D&G analyses and the sample-to-sample analyses are consistently lower than the other measurements by approximately 0.05%. This is a strong indication of a uniformly distributed systematic bias component. Therefore, the bias in the D&G results should not negatively impact the utility of the D&G data to assess sample-to-sample homogeneity.

Statistical analysis of the original HPT data set and the data set reported here indicate that the new data are not significantly different from the original certificate values. The analysis yielded a t-test statistic of 0.70 where a statistic value would need to be larger than 1.0 to indicate a statistically significant difference between compared data sets.

Figure II



Uranium Isotopic Amount Determination:
The uranium isotopic compositions of 10 samples of CRM 115 were measured on the Triton Mass Spectrometer for certification of isotope-amount ratios. This work was performed in accordance with a previously approved analysis plan. Verification analyses for the n(^{235}U)/n(^{238}U) ratio were performed on six of the ten CRM 115 samples using the Modified Finnigan MAT261. These analyses were performed in accordance with a separately approved analysis plan.

Three different methods were used for the Triton mass spectrometry analyses. These included 1) “classical” Total Evaporation (TE: Callis and Cappis, 1994); 2) Modified Total Evaporation (MTE: Richter and Goldberg, 2004) with the ^{236}U isotope measured with a Secondary Electron Multiplier (SEM); and 3) MTE with the ^{236}U measured in a Faraday cup with 1x10^{12} Ω amplifier resistor. For both MTE techniques the ^{234}U isotope was measured in a Faraday cup with 1x10^{12} Ω amplifier resistor. The classic TE technique frequently yields systematically biased data for low abundance isotopes in uranium analyses but also produces high-accuracy high-precision results for n(^{235}U)/n(^{238}U) isotope-amount ratio measurements. Accordingly, only the n(^{235}U)/n(^{238}U) data were evaluated for the TE analyses performed during this study. All of the measured isotope-amount ratios for the MTE analyses were evaluated for isotopic composition. Certified Reference Material U030-A was used to perform an external mass bias correction and CRM 112-A was analyzed as a QC sample to verify measurement accuracy on all TE and MTE turrets.

The measurements performed on the MAT261 instrument were performed using the classical TE technique. Due to the much narrower dynamic range of the MAT261, with a maximum signal intensity of ~10 V and a minimum signal intensity in the 1-5 mV range, the precision of the measured ^{235}U/^{238}U ratio data is not sufficient for this project. The data from these analyses, however, were used to confirm the results obtained on the Triton mass spectrometer.

The isotope-amount ratios and associated uncertainties shown in Table 1 were determined from 72 separate n(^{235}U)/n(^{238}U) analyses and 40 separate analyses of n(^{234}U)/n(^{238}U) and n(^{236}U)/n(^{238}U). Samples were also tested to determine if the material contained measurable quantities of ^{233}U, but this isotope was not detected within the sensitivity of the analytical technique [n(^{233}U)/n(^{238}U) ratio $<3.6 \times 10^{-9}$]. The Triton mass spectrometer uranium isotope-amount ratios for each sample analyzed in this study showed that no statistically significant sample-to-sample viability is observed for any of the isotope-amount ratios.

Data comparison charts for this study are provided in Figures III A-C. The figures show isotope-amount ratio data from several analysis efforts. These data include: measurements from this certification study (Certification Data); MAT261 verification analyses from this study (MAT 261 Data); information values determined for the C115 repackaging project completed in 2002 (2002 Cert Data); and data from the original certification campaign completed in the 1970's (Original Data). The uncertainties for the "2002 Cert Data", the "Verification Data", and the "Certification Data" are expanded uncertainties (U=k•uc, k≈2). Uncertainties for the "Original Data" represent 2 times the Standard Uncertainty for the analyses. Insufficient information is available to determine GUM-compliant expanded uncertainty for the original data. It is clear from the charts in Figure III that the Certification Data is entirely consistent with the "2002 Cert Data" and the "Verification Data" but is significantly different from the "Original Data".

Figure III A

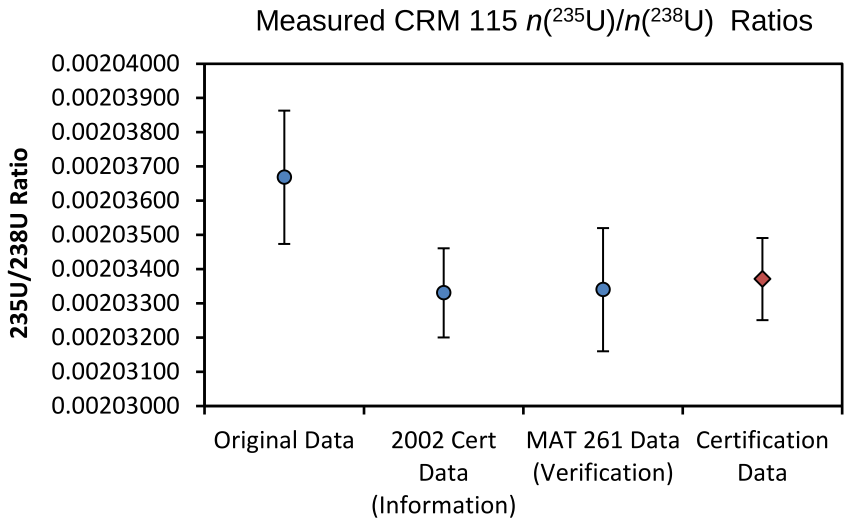
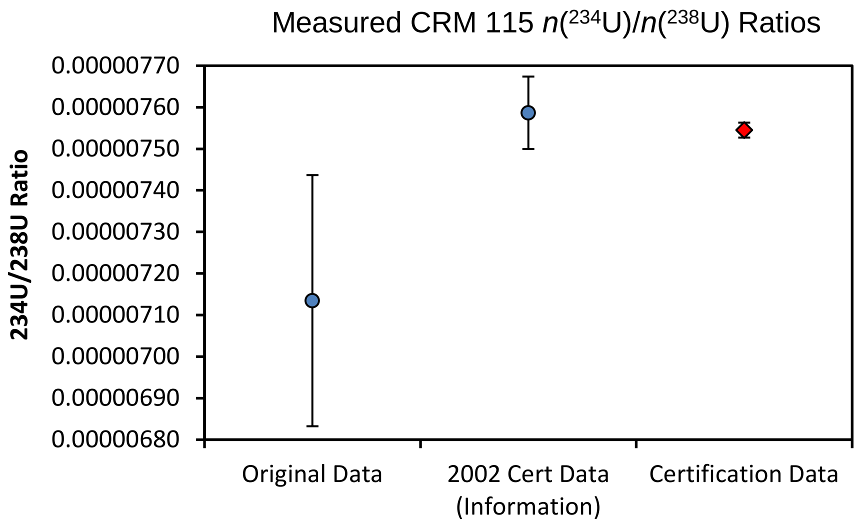
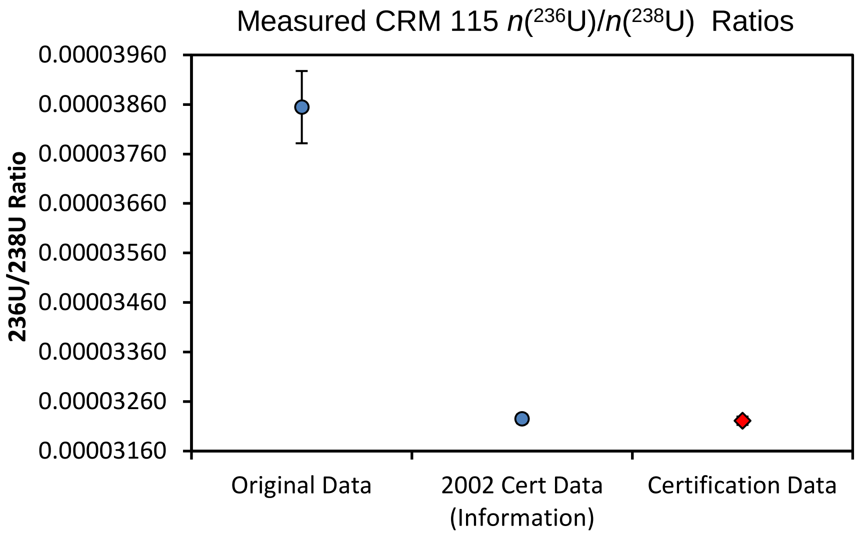

Measured CRM 115 *n*(^{235}U)/*n*(^{238}U) Ratios

Figure III B



For this study, only the MTE analysis method $n(^{234}U)/n(^{238}U)$ ratios are reported. TE values are not considered in data analysis. The error bars for the “Certification Data” are smaller than the data symbol.

Figure III C



For this study, only the MTE analysis method $n(^{236}U)/n(^{238}U)$ ratios are reported. TE values are not considered in data analysis. The error bars for the “2002 Cert Data” and the “Certification Data” are smaller than the data symbols.

Discussion:

The project described in this report incorporates 3 major efforts: 1) creation and packaging of small (~1 gram) samples of the CRM 115 metal for sale as a depleted uranium metal amount content and isotope-amount ratio CRM; 2) determination of a GUM-compliant value and uncertainty for uranium amount content; and 3) determination of GUM-compliant certified values and uncertainties for uranium isotope-amount ratios. Packaging, amount content, and isotopic analysis activities have been completed and the data has been evaluated for the project. Provided below is a more detailed discussion of issues related to amount content and isotope-amount ratio values for the CRM 115 material.

The amount content values for the ten samples analyzed by High Precision Titration are statistically indistinguishable from the CRM 115 certificate value originally determined in 1975 (and provided on the 1978 certificate) and are fully consistent with D&G determinations performed on "B" strip samples in 2001. The D&G titrations performed for this study are, internally, very consistent but show a significant (-0.05%) bias relative to other determinations for this material. A detailed discussion of the issues associated with these D&G measurements is beyond the scope of this report. It should be noted, however, that concerns about the quality of laboratory water used for reagent preparation had been raised and that notable biases in D&G results had been observed by NBL chemists during the period immediately following these measurements. Each of the 4 samples analyzed by D&G was analyzed in duplicate on each of 2 days. The data for all samples show limited variability for replicate analyses of the same sample solution. Nor is there a greater variability observed from day-to-day or from sample-to-sample. Accordingly, the precision of the D&G measurements appears to be excellent but the accuracy of the data is questionable. Based on this observation it was concluded that the data for the samples analyzed by D&G in this study show no evidence of sample-to-sample inhomogeneity between the ~1 gram CRM 115 samples analyzed.

The newly determined HPT uranium amount content value and expanded uncertainty for CRM 115 is considered to be applicable to both the newly packaged 1-gram sample units and to the CRM 115 material in general. The new High Precision Titration determination of uranium amount content cited in this report is traceable to NIST SRM 136e and is fully GUM compliant.

The isotope-amount ratio data, for the ten samples analyzed, also show no evidence of sample-to-sample inhomogeneity. These data indicate calculated values for isotope-amount fractions, mass fractions, and molar mass that are entirely consistent with information values provided in the July 2002 CRM 115 certificate (Table II). The June 1978 certificate only provided the ^{235}U isotope-amount fraction and this value is significantly different from the more recent isotope amount fraction determinations. The n(^{235}U)/n(^{238}U) isotope-amount ratios for all of the measurements from this study were corrected for mass bias using interspersed measurements of traceable CRM U030-A. In turn, the n(^{234}U)/n(^{238}U) and n(^{236}U)/n(^{238}U) ratios were "internally" corrected for mass bias using the measured n(^{235}U)/n(^{238}U) isotope-amount ratio. Thus, traceability for all of the isotope-amount ratio data derives from instrument calibration using CRM U030-A.

Table II
Comparison of Certificate Isotope Amount and Molar Mass Data

Certificate Date	**Molar Mass (g•mol-1)**	n(^{235}U)/n(U) • 100	m(^{235}U)/m(U) • 100
June 1978	238.045	0.20343 ± 0.00023	0.20087 ± 0.00023
July 2002	238.045	0.20291 ± 0.00013	0.20036 ± 0.00013
Revised 2012[1]	238.0445912 ± 0.0000055	0.20295 ± 0.00012	0.20039 ± 0.00012

[1] Proposed new relative Atomic Weight for CRM 115 to be provided in the 2012 re-issued certificate.

Interlaboratory Comparison:
JRC-Geel performed isotopic comparison measurements by Thermal Ionization Mass Spectrometry (TIMS) of NBL Certified Reference Materials C115 DU metal in 2014 and C116-A HEU metal in 2015. These measurements were performed under the auspices of the cooperative safeguards agreement between DOE and EURATOM, under Action Sheet 43 (AS43).

The objective of Action Sheet 43 is to strengthen the traceability of accountability measurements and ensure adequate quality of reference materials and safeguards laboratory measurements through coordination between JRC-Geel and NBL, being two primary providers of nuclear reference materials. JRC-Geel and NBL are not only providing certified nuclear reference materials (CRMs) but also have a long history as interlaboratory comparison providers to most of the world’s nuclear facilities, governments, safeguards organizations and laboratories in the field. AS43 links NBL and JRC-Geel’s measurement systems to ensure standard and traceable measurement quality at the highest metrological level, supporting international inspectorates with the capability to conduct independent measurements to verify operator declarations that are of high quality and traceable to the SI. Specific tasks in AS43 are the mutual participation in JRC-Geel REIMEP/NUSIMEP and SME (Standard Measurement Evaluation) interlaboratory comparisons, the availability of high-priority reference material and providing verification measurements for CRMs.

These uranium metal CRM’s are used widely for isotopic and uranium content, measurement calibration, quality control, measurement validation, and in the case of CRM 116-A serve as a base material for production of spikes used by analytical labs at reprocessing facilities for accountancy. The JRC-Geel results agreed well with the NBL certified property values. The results are in the report: Interlaboratory Comparison of New Brunswick Laboratory (NBL) Depleted Uranium Metal CRM 115 and Highly Enriched Uranium Metal CRM 116-A; M. Soriano, P. Croatto, P. Mason (US Department of Energy NBL Program Office); S. Richter (European Commission – Joint Research Center-Geel (EC-JRC-Geel)).

Conclusion:
New attribute values and uncertainties for CRM 115 are presented in Table I. For all future CRM sales and in response to inquiries concerning CRM 115 attributes, the values cited in Table I should be referenced. The change in molar mass resulting from the refined ^{235}U isotope-amount fraction relative to the value cited in the original certificate is fairly small. Therefore, it is not anticipated to have a significant effect on previous uranium amount content determinations performed on CRM 115. Due to this fact, the fact that only the ^{235}U isotope-amount fraction data was provided in the original certificate, and the negligible difference between the original and re-

analyzed amount content values, the new certified values represent a refinement of the previous certificate values rather than a major correction that would warrant a retraction of previous certificates.

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