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HIGH ACCURACY DETERMINATION OF ^{235}U IN NONDESTRUCTIVE ASSAY STANDARDS BY GAMMA SPECTROMETRY

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High precision gamma spectrometry measurements have been made on five sets of uranium isotope abundance reference materials for nondestructive assay (NDA). These sets are intended for international safeguards use as primary reference materials for the determination of the ^{235}U abundance in homogeneous uranium bulk material by gamma spectrometry. The measurements were made to determine the count rate uniformity of the ^{235}U 185.7 keV gamma-ray as well as the ^{235}U isotope abundance for each sample. Since the samples were packaged such that the U_3O_8 is infinitely thick for the 185.7 keV gamma-ray, the measured count rate was not dependent on the material density. In addition, the activity observed by the detector was collimated to simulate calibration conditions used to measure bulk material in the field. The sample-to-sample variations observed within the 5 sets of samples ranged between 0.005–0.11% (1s) with standard deviations of the mean ranging from 0.01–0.02%. This observed variation appears to be due predominantly to counting statistics and not to material inhomogeneity and/or packaging. The results of this study indicate that accuracy of ^{235}U determinations via gamma spectrometry, in the range of few hundredths of a percent (2σ), is achievable. The main requirement for achieving this level of accuracy is a set of standards whose ^{235}U isotope abundances are known to within 0.01% (2σ).

Introduction

Gamma spectrometry has been one of the nondestructive assay (NDA) techniques that has found increased application in recent years for determining uranium isotope abundances.[1–5] It is an NDA technique that can be used to perform on-line data acquisition as well as automated data evaluation and processing. With the use of high resolution germanium detectors, it is possible to achieve high accuracy in gamma counting. However, the measurement accuracy and precision obtainable by this technique are dependent upon the reference materials being used as standards. If these reference materials have been poorly or improperly evaluated, then the final measured results suffer. In order to ensure that this does not occur, the measure-

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ments leading to the development and production of reference materials should be of sufficient quality to improve the precision and accuracy of analyses made in the field.[6-8]

This philosophy was followed in the development and production of a set of ^{235}U isotope abundance reference materials for gamma spectrometry. These reference materials, proposed by the National Bureau of Standards (NBS) as SRM 969[9] and the Commission of the European Communities as EC NRM 171,[10] were the result of a joint research effort between the Central Bureau for Nuclear Measurements (CBNM) Geel, Belgium and NBS. This set is intended for international safeguards use as primary reference materials for the determination of ^{235}U abundance in homogenous uranium bulk material by gamma spectrometry. The bulk materials are in the form of uranium oxide (U_3O_8) with nominal isotope abundances (^{235}U weight percent) of 0.31, 0.71, 1.94, 2.95 and 4.46. These materials have been characterized chemically by CBNM, NBS and the U.S. Department of Energy New Brunswick Laboratory (NBL) for ^{235}U to total uranium (^{235}U/U) homogeneity and isotope abundance, uranium content and material impurities.[9,10] It is the intent of this paper to describe the high accuracy and high precision gamma spectrometry measurements were at NBS, and to evaluate the level of accuracy potentially achievable by gamma spectrometry.

Experimental

Description of the reference materials

Each set of five reference materials (SRM 969 or EC NRM 171) was packaged from the same batches of uranium oxide with nominal percent ^{235}U isotope abundances of 0.31, 0.71, 1.94, 2.95, and 4.46. A total of 140 samples containing 200 g of U_3O_8 each, were produced from each of the batches. Each 200 g sample was hand pressed into an aluminum can fabricated at NBS under controlled tolerances of ±0.01 mm for the dimensions of 80 mm O. D., 70 mm I. D. and 90 mm high with a 2.00 mm thick window. The hand pressing changed the U_3O_8 pour density from a range of 0.7–0.9 g/cm^3 to 2.5 g/cm^3 for the 0.31%, 0.71%, 1.94%, and 2.95% materials and from 1.77 g/cm^3 to 3.4 g/cm^3 for the 4.46% material. As a result of pressing the oxide, the material thickness perpendicular to the can window for each batch became 5.2 g/cm^2 ±5% corresponding to 99.9% "infinite thickness" for the ^{235}U 185.7 keV gamma-ray.

Each can was filled, fitted with an ultrasonic device for integrity checks, sealed by automatic tungsten inert gas (TIG) welding and uniquely labeled. The labeling identified the organization responsible for distributing the reference materials, i.e., NBS for the Office of Standard Reference Materials and CBNM for the Commission of the European Communities. In addition, each can was labeled with its isotope abundance in nominal weight percent (0.31% = 031) as well as a three digit sequential number in which numbers from 001–070 were assigned to CBNM and 071–140 were assigned to NBS. A complete reference material set then was formed by combining the cans that had the same sequential number and the same window thickness to ±0.001 mm.

These reference materials were chemically characterized by NBS, CBNM, and NBL. These measurements provided information about the homogeneity of the ^{235}U/U isotope abundances to <0.06%, the uranium content of the material and its reproducibility from sample to sample to <0.04% as well as the level of chemical impurities including H_2O present in the material. In addition, the concentration of the gamma emitting uranium isotopes (^{232}U, ^{233}U, ^{237}U and ^{239}U) and daughter products (^{237}Np) were determined relative to ^{235}U as well as the atom abundances of ^{234}U, ^{236}U, and ^{238}U (Ref. 9, 10).

Counting standards

The counting standards consisted of a set of three prototype 200 g U_3O_8 samples which had been developed earlier to determine the feasibility of the programs. These counting standards were prepared by CBNM[9,10] in the same manner as the reference materials with the exception of the aluminum cans. The prototype cans were fabricated with a flat bottom while the reference material cans were produced with a 1 mm recessed bottom which prevented any scratching of the can window. The isotope measurements of these samples were performed using thermal ionization mass spectrometry (ThIMS) by CBNM, and certified to have ^{235}U/U abundances (in atom%) of 2.9788±0.0090, 0.7201±0.0021 and 0.2978±0.0009, respectively. They were identified as SD-524, SD-528 and SD-521. In addition, gamma-spectrometry measurements (GS) were also performed on the samples by NBS and CBNM to verify the findings of CBNM-ThIMS. Although all three counting standards were used during the course of this work, the primary counting standard was considered to be the 2.9788 atom% sample.

Counting system

The system used for this study consisted of an Ortec Gamma X type high purity germanium detector, a Canberra 3105 high voltage supply, a Canberra 2021 S amplifier and a Nuclear Data ND 6620 computer-based analyzer system. The amplifier time constant was set at 6 μs, and an ADC conversion gain of 8192 channels was used. At low count rates, this system has a resolution of 1.69 keV full width at half maximum (FWHM) for the 1332 keV gamma-ray of ^{60}Co and efficiency of 7.99% relative to a 3" × 3" NaI(Tl) detector at 25 cm. The resolution observed in this study for the 186 keV gamma-ray from ^{235}U varied from 0.95 keV (FWHM) for the 031 samples (15% dead time) to 1.00 keV for the 446 samples (22% dead time). Separation of the 183 keV and 186 keV gamma-ray was such that the channel between these photo-peaks contained approximately 0.02% (above background) of the net 186 keV counts. The 071, 194, 295 and 446 samples were counted until approximately $5 \cdot 10^6$ net counts were accumulated in the 186 keV photo-peak (2–12 h live times). The counting statistics observed for the 186 keV photo-peak were typically 0.04–0.06%. The 031 samples were counted overnight which produced approximately $2.5 \cdot 10^6$ net counts in the 186 keV photo-peak. Typically, the observed counting statistics for the 031 samples were 0.10%.

Collimator

The collimator assembly (see Fig. 1) used in this work was fabricated from a lead brick. A U-shape configuration with a radius of 40.5 mm and a depth of 35 mm was machined into the top surface of the lead to allow a rigid resting place for the aluminum cans and to maintain identical counting geometry from one sample to another. The actual collimator was then machined to a 50 mm diameter with a 15 mm thickness. A copper plate (12 cm X 12 cm X 6 mm) with a 70 mm diameter opening, for the germanium detector endcap, was then affixed to the base of the collimator. This entire assembly was then fitted with four mounting screws, allowing the assembly to be supported by the floor of the detector shield and not the detector.

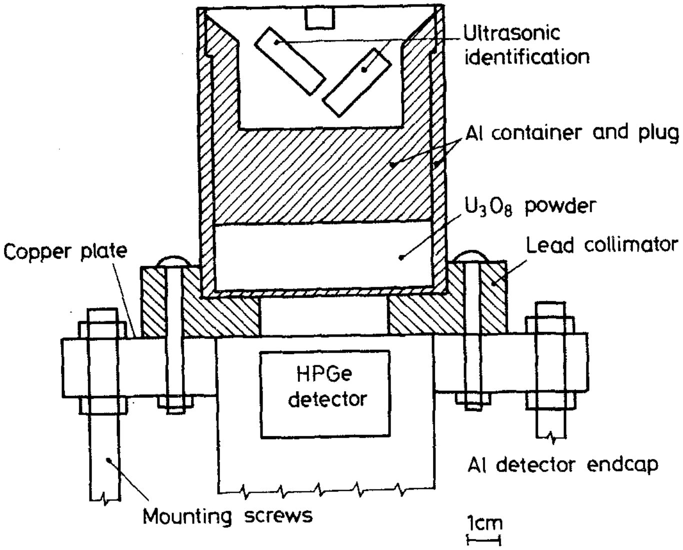

Fig. 1. Set-up for gamma-spectrometry for counting U_3O_8 reference samples used by NBS

Peak integration methods

Three different methods were used to integrate the 186 keV ^{235}U photo-peak: a Gaussian-fitting routine; a channel by channel doublet summation of the combined 183 (small) and 186 keV photo-peaks, and a channel by channel singlet summation of the 186 keV photo-peak alone. The channel between the 183 and 186 photo-peaks was included as part of the 186 photo-peak for the singlet summation method. Both peak and background regions for the two summation methods were selected symmetrically around the 186 keV photo-peak centroid.

Corrections

A number of corrections to the observed count rate for the 186 keV photo-peak were applied including those for pulse pileup, ^{234}Pa and ^{234m}Pa interference, differences in container geometry for the samples compared to the standards, and difference in the packing density of the 446 sample compared to the standards. The pulse pileup correction was made according to equation 1.

$$I_0 = I \exp\left[\frac{C(R-L)}{L}\right] \tag{1}$$

where I_0 – corrected intensity,
I – observed intensity,
C – pileup constant,
R – real (clock) time,
L – live time.

In view of the unusual spectral shape of the collimated uranium samples, the high detector efficiency for low energy gamma- and X-radiation, the relatively long amplifier time constant (6 μs), and the relatively high dead time (15–22%), particular attention was paid to determining the pileup constant. To determine this constant, the three prototype standards were counted on a second detector-analyzer system for which the pileup correction was much less important, and the activity ratios were compared to those observed with the main system. This second system contained a collimator with a much smaller diameter opening to reduce the counting rate, a Ge(Li) detector with normal (low) efficiency for low energy radiation, and an amplifier whose time constant was set at 2 μs. With this system, the pileup corrections ranged from 1.012 for the SD-521 (0.2978% ^{235}U) sample to 1.014 for the SD-524 (2.9788% ^{235}U) sample; dead times were between 4.2 and 5.1%. Since the pileup corrections were so similar, small errors in the pileup constant of this (second) system were negligible; a 1% error in the pileup constant would only produce a 0.002% error in the activity ratios. The pileup constant for the main system was then calculated by comparing the activity ratios observed for the two systems.

Both the ^{234}Pa and ^{234m}Pa daughters of ^{234}Th in the ^{238}U decay chain have gamma-rays very close to the 185.7 keV photo-peak of ^{235}U, and thus interfere with the ^{235}U determination. The magnitude of this interference was determined by using a specially prepared sample containing 200 g of NBS SRM U-0002 which is certified to have a ^{235}U isotope abundance of 0.01755±0.00005 atom%. This sample was counted using the same facilities as the SRM 969/EC NRM 171 samples. After correcting for the ^{235}U isotope abundance in this highly depleted sample, the 186/258 photo-peak region ratio was used to remove the Pa interference from the uranium reference materials. Since the correction was made totally from Pa gamma-rays, establishment of equilibrium between ^{238}U and ^{234}Th was not necessary.

The 186/258 photo-peak region ratios were determined (and applied) separately for each of the summation methods. Since both summation methods used the same photo-peak and background channels for the depleted U_3O_8 and the samples, the correction based on the 186/258 photo-peak region should also minimize possible spectrum shape effects due to the background from the ^{238}U content of the samples.

Although differences in window thickness among samples (and standards) were small (<0.1 mm), corrections for the attenuation of the 186 keV gamma-ray by the aluminum cans were necessary and were applied according to

$$R_c = R_o\ (1 + 0.034\ t) \tag{2}$$

where R_c – sample count rate corrected for thickness difference,
R_o – observed sample count rate,
t – thickness difference between sample and standard.

A correction was necessary for the geometry difference between the samples and the standards. The samples have a 1.0 mm lip (to protect the thin window) while the SD standards have a flat bottom. A 1.0 mm spacer was prepared approximating the difference between the two types of cans, and SD-524 standard was counted with and without the spacer, three times each, alternating between geometries. Approximately $5 \cdot 10^7$ counts were obtained in the 186 keV photopeak for each determination, and the ratio of the counts in the two positions was used to obtain the 0.214% correction for the geometry difference.

It was necessary to make a correction for the higher packing density of the 446 samples compared to the packing densities of the 031–295 samples as well as the prototype samples. As discussed above, when the sample container was raised by 1 mm the count rate decreased by 0.214%. However, the higher packing density of the 446 samples caused a higher count rate than the other samples, since on the average these samples were closer to the detector than the others. Since direct calculation of this correction factor was difficult, it was approximated by comparing the "average heights" (the level of 50% attenuation of the 185.7 keV gamma-ray) between samples and standards. The thickness of U_3O_8 necessary for 50% attenuation was calculated from

$$I/I_0 = 0.50 = \exp(-1.263\ t_{50}) \tag{3}$$

where I – observed intensity of the 185.7 keV gamma-ray,
I_0 – intensity of the 185.7 keV gamma-ray with no absorption,
t_{50} – thickness of U_3O_8 needed to absorb 50% of the emitted gamma-rays and with 1.263 being the attenuation coefficient of U_3O_8 cm^2/g.

This 50% thickness (in g/cm^2) was converted to the "average height" by dividing by the packing densities of the 446 samples and the standard. The difference in this average height was 0.5811 mm. This value was multiplied by 0.214% per 1 mm to arrive at the –0.1244% correction used for the higher packing density of the 446 samples. It should be noted that this correction is collimator specific.

Results and discussion

Peak integration methods

Of the three methods used for peak integration, it was expected that the two summation methods would be superior to the Gaussian fitting method for a number of reasons. The Gaussian fitting method introduces added uncertainties since gamma-ray peaks are not truly gaussian. In addition, the peak integration routine that was used freely chose its own boundaries for both the peak and the background regions of each spectrum. Different regions could thereby be chosen for the different samples within a set, increasing the intra-abundance variability, and different regions could be chosen for the samples as compared to the standards, thus affecting the accuracy.

If the detector resolution were identical for samples and standards, i.e., if the samples and standards were of the same isotopic composition, or if they were counted at very low dead times, then the singlet summation should be the best method to use since the doublet method includes a large number of background channels as part of the peak, thus automatically increasing the random error. However, the singlet method is susceptible to small changes in peak resolution, since relatively narrow peak regions must be used to exclude the 183 keV peak. If the resolution for the samples and standards are different, the singlet method can provide biased results as counts are shifted out of the peak region. Since the resolution observed in this study varied from 0.95 keV to 1.00 keV, for the 186 keV peak of ^{235}U, this effect was potentially a serious problem. The doublet method is not susceptible to minor changes in resolution. However, inclusion of the 183 keV peak, as well as a number of background channels on the high energy side of the 186 keV peak (to maintain peak symmetry) results in a very large peak region. The doublet method contains more than twice as many channels as the singlet method. The doublet method is therefore much more sensitive to any non-linearity of the background under the peak. The background under the 186 keV peak is due predominantly to non-linear perturbations by the 186 keV gamma-ray itself, and to compton scattering of higher energy gamma-rays from the decay of ^{238}U daughters. The non-linear effects on the background by the 186 keV peak itself can be eliminated by choosing peak and background regions which are symmetric about the peak centroid. However, any non-linearity in the background radiation originating from the decay of ^{238}U can provide a systematic bias, since lower abundance samples (or standards), having smaller peak-to-background ratios, are affected to a much greater extent than are those with higher isotope abundances. One method to reduce this potential bias is to subtract the underlying ^{238}U background spectrum from the mixed ^{235}U/^{238}U (and daughters) spectra of the real samples and standards. This can be done by subtracting the background spectrum (on a channel-by-channel basis) before peak integration (summation), or by using an appropriate peak interference ratio to subtract the net effect of background non-linearity after peak integration. As discussed above, the ratio of the 186/258 keV peaks from the ^{238}U daughters spectrum (determined by counting the 200 g sample of SRM U-0002, and correcting for ^{235}U content) was used to correct for the ^{238}U interference by multiplying this interference ratio by the observed 258 keV peak area from each sample and standard spectrum, and then subtracting the calculated interference. Since peak summation for the SRM U-0002 sample was accomplished using the same peak and background regions as was used for the other samples and standards, this procedure removed not only the ^{234}Pa and ^{234m}Pa direct interferences, but also eliminated any effect from background non-linearity Since this non-linearity correction was included, it was felt that the doublet summation method would provide the best, unbiased peak areas for determining the ^{235}U abundances of the samples. If the SRM U-0002 sample were not used to determine the ^{238}U interference, however, the doublet summation method might not be the method of choice in view of its greater sensitivity to non-linearity of the background. Although the singlet method is potentially biased for accurate abundance determinations when resolution varies between samples and standards, it provides the smallest sample-to-sample variability, within a set of samples, due to its better counting statistics, and therefore is a more sensitive method for determining potential sample-to-sample differences.

A comparison of the results obtained for the three methods bears out these predictions. The singlet method did indeed provide the best precision, approximately 25% better than the doublet method for the depleted and natural samples, and approximately 50% better than the gaussian fitting for all five isotope abundances. For the enriched samples, the precision observed using the singlet method was only about 5% better than for the doublet method, resulting from the better peak-to-background ratios of these samples. However, a clear trend (bias), as a function of isotope abundance, was observed for the results obtained by the singlet method as compared to those from the doublet method. The abundances determined by the singlet summation and gaussian fitting methods were normalized to those obtained by the doublet method and are listed in Table 1. The singlet results for the natural and depleted samples are 0.05–0.06% greater than those obtained by the doublet method. The singlet results, as compared to the doublet results, then decrease with increasing ^{235}U abundance. The best agreement for the two methods, within 0.01%, occurs for the 295 series of samples where the ^{235}U abundance is essentially the same for the samples and for the primary counting standard. The differences between the results of the two summation methods can best be explained by the increasing loss of counts from the 186 keV peak, as determined by the singlet method, as the detector resolution worsened. The observed full width at half maximum (FWHM) for the 186 keV peak was 0.95 keV for both the natural and depleted samples, 0.96–0.97 for the 194 series of samples, 0.97–0.98 for the 295 series, and 0.99–1.00 keV for the 446 series of samples. Since the peak resolution for the 295 series and for the SD-524 counting standard was identical, the fraction of peak counts lost by the singlet summation method of the standard spectra was identical to that of the spectra of the samples. The 0.01% difference between the ratios of results from the two summation methods, for the 031 and 071 series, is probably due to random fluctuations in the background and is not significant.

Table 1
Percent differences observed between the doublet summation method and other peak integration routines

Sample	Gaussian fitting	Singlet summation
031	+0.050	+0.047
071	+0.241	+0.058
194	+0.139	+0.027
295	+0.084	−0.007
446	−0.040	−0.034

The results obtained from the Gaussian fitting routine, when compared to the doublet summation method (Table 1), were surprisingly good. The difference between the two methods was typically 0.1%, and in all five cases the difference was less than 0.25%. This is considerably better than was expected considering the difficulties involved in peak fitting. The fitting routine used was a relatively simple one, and integration of the 186 keV peak, which was superimposed on top of a relatively complex background spectrum and partially overlapped the much smaller 183 keV peak, presented one of the more difficult challenges for accurate peak integration. Clearly, the nearly Gaussian peaks obtained from this detector played a rôle in achieving these results.

Nondestructive assay standards (SRM 969)

The results obtained, using the doublet summation method, for the ^{235}U/U isotope abundances of the five NDA standards which make up SRM 969, are listed in Table 2. Sample standard deviations (1s), standard deviations of the mean ($1s/\sqrt{n}$) and relative standard deviations of the mean are also listed in this table. The observed precision (1s) for the natural and depleted samples was approximately 0.1%, relative to the mean value, and the relative standard deviations of the mean were approximately 0.02%. This variability was largely due to the counting statistics, which were elevated by the large number of background channels included in the peak region used for the doublet summation method. As discussed above, considerably better precision was obtained with the singlet method. Observed relative standard deviations for the enriched samples were typically 0.06%, and the relative standard deviations of the mean were approximately 0.01%. Although counting statistics accounted for most of the observed variation, a small amount of additional variability was observed for each set of samples. Typically the sample standard deviation was about 0.01% greater than expected from the counting statistics. This appears to be due to differences in counting geometry and not to material variability, or to peak integration problems. The colli-

Table 2
^{235}U/U abundances (atom PPM) observed in SRM 969
by gamma-spectrometry using the doublet summation method

Sample	Mean	1s	1s (mean)	1s (mean) %
031	3205.3	4.2	0.8	0.025
071	7208.1	7.8	1.6	0.022
194	19660.	11	2.3	0.012
295	29830.	20	4.1	0.014
446	45158.	28	5.8	0.013

Table 3
Comparison of ^{235}U/U abundances (atom PPM) determined by gamma-spectrometry with certified values

Sample	Gamma-spectrometry*	Certified	Difference %
031	3205.3± 2.7	3206± 2	–0.022
071	7208.1± 5.8	7209± 5	–0.012
194	19660. ±16	19664±14	–0.020
295	29830. ±24	29857±21	–0.091
446	45158. ±36	45168±32	–0.022

*Uncertainties for gamma-spectrometry represent the estimated 95% confidence intervals.

mator used for this work contained four legs and was placed on the floor of the detector shield. It was not securely attached to the shield and thus could move. If the collimator were rotated, any deviation from a perfect plane by the floor of the detector shield could affect the height of the sample above the detector. In addition, small irregularities in the lead walls of the portion of the collimator used to hold the sample could slightly elevate one side of the sample, and thus increase the sample to detector distance. Shifting of the collimator was observed for some counts of the SD-524 standard.

The values determined (this work) by gamma spectrometry (GS) are compared with the certified values in Table 3. The uncertainties listed for GS are the estimated overall uncertainties at the 95% confidence level. The method used to calculate these uncertainties is described below. The ^{235}U abundances determined by GS for four of the five materials differ from the certified values by only 0.01–0.02% on a relative basis. The GS value for the 295 series, however, is 0.09% less than the certified value. It should be noted that the relative uncertainty for the certified value for the 295 series is 0.07%, and that the GS value is only 0.02% outside of this 95% confidence interval. However, the relative uncertainties for the other four materials are also 0.07%, and agreement between the GS and certified values is considerably better, indicating, perhaps, an overestimation of the uncertainties for both the GS and certified values, at least for four of the five materials. The various uncertainties in the GS measurement process were therefore examined to see if any of them could explain the disagreement for the 295 series, and yet allow the observed agreement for the other four materials. No such source of error could be identified. One potential source of error for the GS measurements lies in the accuracy of the ^{235}U/U abundances used for the standards, since relative, not absolute measurements were made. Such an error, however, would affect all five sets of samples to the same extent since the same standards were used for all five series. Another possibility is an incorrect subtraction of the ^{238}U spectral interference. This error, however, would affect the samples with lower isotope abundances to a much greater extent since a relatively greater correction was required; the correction for the 031 series was ten times greater, relative to its ^{235}U/U abundance, than for the 295 samples. Errors in the pulse-pileup correction also could not explain the observed results. Such an error would also affect the other samples. Compared to the 295 samples, an error in the pileup correction would affect the 446 samples in one direction (producing higher or lower ^{235}U abundance), while the 031, 071 and 194 samples would be affected in the opposite direction, and to differing degrees. In fact, since the main counting standard had essentially the same ^{235}U abundance as the 295 samples, errors in subtracting the ^{238}U interference and in the pulse-pileup correction would have almost no effect on the final result for the 295 samples. One rather remote possibility is that the collimator had shifted position during the time period in which the 295 samples were counted. However, the SD-524 standard was counted several times during this time period (interspersed among the 295 samples) and no difference was observed. Another remote possibility is that the sample containers for the 295 series are somehow different from those for the other material, thus causing some type of counting geometry problem. This possibility can be eliminated since the dimensions of each sample container were checked prior to filling. In fact, containers were selected to maximize the similarity among the six cans to be used for each individual SRM set containing one sample of each of the five different materials (abundances) and one empty container to be used to count unknown samples. Thus a significant difference among the containers used for all of the samples in the 295 series, compared to those used for the other four materials, is virtually impossible. In view of the similarities of the procedures used for the five different materials, additional sources of error which would affect only the 295 samples are extremely unlikely. Thus a likely explanation of the GS results is that the "true" value for the ^{235}U abundance of the 295 series is probably closer to the lower end of the certified confidence interval than to the midpoint, while the "true" values for the other four samples lie relatively close to the certified values (midpoints of the certified confidence intervals).

An examination of the individual results used to determine the certified values may be useful in supporting the above conclusion. The certified values listed in Table 3 were jointly determined by NBS and CBMN from results obtained by thermal ionization mass spectrometry (ThIMS) at both NBS and CBNM, and from uranium hexafluoride mass spectrometry (UF_6MS) at CBNM. Details of the analytical methodology used can be found in References 9 and 10. The certified values were computed by equally weighing the UF_6MS results and the combined ThIMS results.[9,10] The NBS ThIMS results and the CBNM ThIMS results were equally weighted, and since two separate ThIMS analyses were done at CBNM, they were averaged before com-

Table 4
Comparison of individual determinations of $^{235}U/U$ abundances (atom PPM) in SRM 969*

Method	Material				
	031	071	194	295	446
GS-this work	3205.3±2.6	7208.1± 5.8	19660±16	29830±24	45158±36
CBNM-UF_6MS	3204.9±1.6	7209.6± 1.7	19658± 4	29843± 5	45167± 8
NBS-ThIMS	3207.6±5.2	7206.9± 6.8	19664±17	29869±22	45138±33
CBNM-ThIMS No. 1	3208.5±4.6	7215.4± 7.7	19685±21	29890±38	45227±49
CBNM-ThIMS No. 2	3203.8±4.9	7208.5±12.1	19665±15	29859±43	45174±60
NBL-ThIMS	3203 ±7	7207 ± 7	19657±15	29843±39	45162±39
Certified	3206 ±2	7209 ± 5	19664±14	29857±21	45168±32

*Mass spectrometry values reported in this table are from reference 10, and are rounded to 5 significant digits if more were given. Uncertainties listed for the mass spectrometry values are 2s, and those for gamma-spectrometry are the estimated 95% confidence intervals. Individual $^{235}U/U$ abundances for the two CBNM-ThIMS are not reported separately in reference 10. The values listed above were calculated from the individually reported $^{235}U/^{238}U$ abundances, in this reference, using the manner specified.

bining them with the NBS ThIMS results. Thus, the final weighing of results were as follows: UF_6MS-50%; NBS ThIMS-25%; CBNM ThIMS 1–12.5% and CBNM ThIMS 2–12.5%. Additional ThIMS values were provided by NBL, however, these results were not used in the computation of the certified values. The uncertainty for each certified value was estimated by combining the uncertainties of the mass spectrometry measurements with any possible deviation of the $^{235}U/U$ ratio due to inhomogeneity. The resulting uncertainties were then enlarged to 0.07%.[9,10]

The individual results of the mass spectrometry determinations[9,10] are listed in Table 4. Those determined by UF_6MS were considered to be the most accurate of the individual mass spectrometry results used for certification. The uncertainties listed for UF_6MS[9,10] were three to eight times smaller than those listed for the individual ThIMS measurements, and the weighing factor used for the UF_6MS results, in determining the certified values, was two to four times greater than those used for the individual ThIMS results.[9,10] The results listed in Table 4 for the NBS-ThIMS, CBNM-UF_6MS and NBL-ThIMS are the values obtained from References 9 and 10, rounded to five significant figures. The individual values for the $^{235}U/U$ ratios for the two separate CBNM-ThIMS determinations are not given in this reference, only the average of the two sets of values. However, the individual values for the $^{235}U/^{238}U$ ratios determined by CBNM-ThIMS are given in References 9 and 10. The individual $^{235}U/U$ ratios listed in Table 4 were then calculated from these $^{235}U/^{238}U$ ratios, as well as the $^{234}U/^{238}U$ and the $^{236}U/^{238}U$ ratios, in the manner described in Reference 9 and 10. The individual MS results, as well as the GS results, were then normalized to the certified values and are plotted in Fig. 2. As can be seen from this figure, the CBNM ThIMS 1 results are consistently higher than the certified values, by approximately 0.1%, and they are also higher than all of the other results. If the other values are unbiased, then the certified values are biased by approximately 0.01–0.02%, by the CBNM 1 results which received a relative weight of 12.5% in

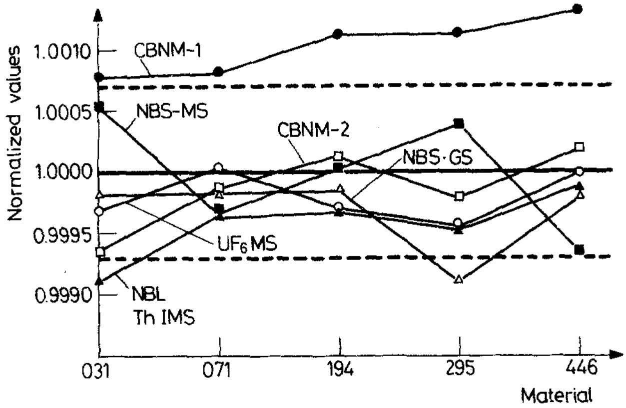

Fig. 2. ^{235}U measurement by various methods normalized to the certified value (dashed line indicates the ±0.07% uncertainty)

the certified value. For the 071 and 194 sets of samples, the three other values used for certification, as well as the GS and NBL ThIMS results, were all relatively close together. This close agreement indicates that, except for the small (0.01%) effect of the CBNM ThIMS 1 value, the "true" ^{235}U abundances of these materials should be very close to the certified value (near the midpoint of the certified range). Agreement for the other three series is not quite as good. However, for the 031 and 446 series, the CBNM ThIMS 2 results and the NBS ThIMS results surrounded the UF_6MS results, and since the UF_6MS results were considered to be the most accurate (discussed above), potential biasing effects on the certified values should tend to cancel. Thus, the "true" abundances of the 031, and 446 series should also lie very close to the certified values. Effects on the certified value for the 295 series may be more serious since both the NBS ThIMS and CBNM ThIMS 2 results are higher than the UF_6MS results. The "true" ^{235}U abundance for the 295 series may be considerably further from the certified value, although not outside of the certified range.

The NBS ThIMS value for the ^{235}U/U abundance of the 446 series is considerably lower than the other two results used for certification. Potential biasing effects on the certified value should be minimal as the –0.07% difference between the NBS ThIMS value and the certified value is almost exactly balanced by the +0.13% difference of the CBNM ThIMS 1 results, which received only half the weighing as did the NBS ThIMS values. The value determined by UF_6MS is almost identical to the certified value, and the GS and NBL results tend to confirm the certified value, as differences are less than 0.03%. For the 031 series, the CBNM ThIMS 2 result was 0.07% lower than the certified value, while the NBS ThIMS result was 0.05% higher. These results tend to balance each other and thus should have not overly biased the certified value. The close agreement between the GS result and the certified value (0.02%) tends to confirm this observation. Although the NBL result is lower than the certified value by 0.09%, the relative uncertainty for the NBL value (0.2%) is more than twice as great as for any of the other NBL determinations, perhaps indicating analytical difficulties.

The CBNM ThIMS 2 and the NBS ThIMS results for the 295 series were respectively 0.05% and 0.09% higher than the UF_6MS value. In addition, the CBNM 1 results appear to be biased in the high direction (discussed above). If the UF_6MS value is unbiased, and its stated uncertainty, 0.02%[9,10] is realistic, then the "true" value may be on the lower side of the certified confidence interval. The UF_6MS value is 0.05% less than the certified value, as is the NBL value. The GS value for the 295 series is 0.09% below the certified value, and 0.02% outside of the associated confidence interval. In view of the agreement between the GS results and the certified values of the other four sets of samples, typically 0.02%, and since no potential source of error could be identified which would affect the GS results for only the 295 series (discussed above), the most likely explanation of the difference between the certified and GS values for the 295 set of samples is that the "true" ^{235}U abundance is really between the UF_6MS value and the lower edge of the certified range.

It was difficult to make a reasonable estimate of the overall uncertainty for the gamma-spectrometry results in view of the large uncertainties given for the ^{235}U abundances of the standards available. Since the results were determined relative to a set of standards, uncertainties in the isotope abundances of the standards could contribute significantly to the final results. The $^{235}U/U$ abundances of the three counting standards were each certified by CBNM, using ThIMS. The relative uncertainty associated with each of the certified values was 0.3%. This uncertainty seems quite large for ThIMS determinations of ^{235}U abundances. Although given as the 95% confidence intervals, these uncertainties appear to be on the conservative side and perhaps they are more representative of absolute bounds, or the "at least 95% confidence intervals," than the true 95% confidence interval. The observed agreement between the GS results and the certified values is clearly much better than could be expected if the true uncertainties in each of the three standards were 0.3%. The average difference between the two sets of values was 0.045%, including that for the 295 series. It was therefore felt that for the purpose of estimating the GS uncertainties, a more realistic estimate of the relative uncertainties in the isotope abundances of each of the standards (at the 95% confidence level) would be 0.1%. This is not inconsistent with typical determinations of ^{235}U abundances by ThIMS. Although the ^{235}U/U abundances of the samples were determined relative to the SD-524 standard, the observed abundance for the SD-528 standard was higher than the certified value, and the abundance for the SD-521 standard was lower than the certified value, as determined using the SD-524 standard. Thus if the samples were compared to all three SD standards, instead of just the SD-524 standard, the calculated abundances would not be significantly different. Therefore, the combined relative uncertainty for the three standards was considered to be 0.1% divided by the square root of three, or 0.058%. This value (0.058%) was used just for the purpose of making a reasonable estimate of the GS uncertainties and should not be considered as having any other significance.

Other sources of error could be evaluated in a more direct manner. The observed precision includes many of the random sources of variation. The combined uncertainty due to counting statistics of the samples, sample container differences, the small collimator position shifting, and other types of sample-to-sample differences were evaluated as the observed standard deviation of the mean multiplied by the appropriate t-value for the 95% confidence interval. The uncertainty due to the counting statistics of the standards was also calculated in a straightforward manner as 1.96 times the combined 1σ uncertainty for the multiple counts of the standards, and was typically 0.028%.

Uncertainties in the pulse-pileup correction were also considered. Propagating the uncertainties from counting statistics in determining the pileup constant yielded a 2σ uncertainty of 0.3% in the value of this constant. In view of the relatively similar dead times of the samples and standards, this uncertainty produced a 0.01–0.02% relative uncertainty in the calculation of the isotope abundances for the samples.

Another important potential error lies in the subtraction of the ^{238}U interference. This is particularly important for the lower abundance samples in view of the relatively greater value of the interference subtracted. The uncertainty from counting statistics in determining the 186 to 258 keV peak ratio in the U-0002 SRM was 0.51% at the 2 σ level. Since 87.7% of the 186 keV counts were from the ^{235}U in the U-0002 sample, the uncertainty in the ratio of 186/258 keV counts from the ^{238}U daughters was 0.51/0.123, or 4.1%. The correction required for the 031 series was 0.67% greater (on a relative basis) than for the SD-524 standard, and the uncertainty due to this correction for the 031 series was 0.027% of its ^{235}U abundance. It should be remembered that this ^{238}U interference correction (0.67%) includes both the direct interference from ^{234}Pa and ^{234m}Pa, as well as a correction for any nonlinearity the background radiation of the ^{238}U spectrum, and is, therefore, counting system specific. Thus it cannot be directly compared to literature values for the Pa interference, as this is just the first term of the ^{238}U correction applied in this work. In a similar manner, the uncertainty in this correction for the natural samples is 0.012%, relative to its ^{235}U abundance, and <0.005% for the enriched samples.

Two related sources of error are the correction for the geometry difference between the samples and standards, and the packing density correction for the 446 series of samples. The magnitude of the first correction was 1.00214; i.e.; the observed count rate was 0.214% greater when the standard was brought 1.0 mm closer to the detector. The uncertainty associated with this value was the combined uncertainty due to counting statistics (2σ) for the ratio of the count rates at the two different geometries, and was equal to 0.023% relative to each of the count rates, or to the abundance of each standard. The magnitude of the effect of the different packing density for the 446 series was 1.00124. Since it was determined from the above geometry correction, and the effective height difference of the 446 series was 0.58 mm (compared to 1.0 mm for the standard geometry difference), it has an uncertainty due to counting statistics of 0.013% relative to the ^{235}U abundance of the 446 series. Although this correction was formulated by an approximation, any error due to the approximation itself is probably negligible compared to the 0.013% uncertainty, as this is more than 10% of the 0.124% calculated increase in count rate resulting from the higher packing density.

Except for the uncertainty of the standards, all other uncertainties were due to counting statistics and so can be considered as random errors. The uncertainty of the standards was an estimate at best, and since the "true" ^{235}U/U abundance in the SD-524 standard could be either higher or lower than the certified value used to compute the sample abundances, it was decided to combine this uncertainty with the random errors in quadrature. Thus the relative uncertainty (at the 95% confidence level) for each series of samples was calculated by combining, in quadrature, the 95% uncertainties due to observed precision, counting statistics of the standards, ^{235}U/U abundance of the counting standards (estimated uncertainty), ^{238}U interference, pulse-pileup correction and geometry differences. Relative uncertainties of 0.09% for the depleted samples, and 0.08% for the natural and enriched samples were found. As discussed above, approximately 70% of these overall uncertainties is associated with the uncertainties of the ^{235}U/U abundance of the standards.

Areas for improvement

By the conclusion of this experiment, a number of possible improvements for future studies were noted. The first, and most important improvement would be to use a set of standards whose ^{235}U/U abundances were well known, and whose geometries matched the samples. As described above, approximately 70% of the estimated analytical uncertainties in this work resulted from the uncertainties in the standards. A better set of standards would also allow a more accurate determination of the pileup constant and the ^{238}U interference correction ratio, thus reducing the overall uncertainty. In addition, by matching abundances of samples and standards, the magnitude of the corrections required for pulse-pileup and ^{238}U interference would be minimized, thus further reducing the analytical uncertainty. Matching the container geometries for samples and standards would also eliminate the geometry correction necessary in this work, and thus remove an important source of error. Significant improvements in the counting statistics for both the samples and standards could also be obtained by counting for longer times. Approximately $5 \cdot 10^6$ peak counts were obtained for each of the natural and enriched samples. Increasing the counting time to 48 hours would increase the number of observable counts by a factor of 4–24 (including the depleted samples), and would reduce the counting uncertainties by a factor of 2–5 for the samples as well as the standards, and would thus reduce the combined uncertainty due to counting statistics by of a factor of 3–7.

Improvements in the counting system used for this study are also possible. Despite the excellent resolution and stability of this counting system, the high efficiency of the Gamma X detector for low energy radiation, combined with the long amplifier shaping time, greatly increased pulse-pileup. Use of a conventional Ge(Li) or Ge(HP) detector, in conjunction with a smaller amplifier shaping time, would significantly reduce the number of pileup events. Such a reduction would improve the measurement in two ways: a greater number of 186 keV counts would be observed in the peak of each spectrum, as a direct result of smaller pileup losses, and, the number of background counts under each peak would be reduced by decreasing the random summing of lower energy gamma- and X-radiation. In addition, use of a detector with a lower efficiency for low energy radiation would result in a smaller system dead time, allowing more counts to be obtained for a given real time. A decrease in the number of counts processed by the detector would probably also minimize the observed decrease in detector resolution as a function of increasing ^{235}U abundance. If resolution differences between samples and standards can be totally eliminated, it might be possible to use the singlet summation method, with its inherently better counting statistics, for peak integration. Alternatively, a thin, planar detector with a large surface area might prove useful in reducing the background under the 186 keV ^{235}U peak resulting from compton scattering of the higher energy gamma-rays emitted by the ^{238}U daughters. However, this possibility has not been tested.

Some improvements in the design of the collimator are also possible. As mentioned above, some shifting of the collimator position was apparent during the course of this study. This could be minimized by using a collimator with three legs, instead of four, and by permanently, or at least semi-permanently, attaching the legs of the collimator to the floor of the detector shield. In addition, the portion of the collimator which holds the sample should be coated with Teflon, or a similar substance, to prevent irregularities in the walls from occasionally elevating a sample slightly above the normal counting position.

Potential accuracy of gamma-spectrometry measurements

From the results obtained in this study, it appears that the ultimate limit on the achievable accuracy for ^{235}U/U measurements is dependent on two factors: the counting statistics which can be reasonably obtained for the samples and the standards, and the accuracy to which the ^{235}U/U abundances of the standards are known. By proper experimental design, other sources of error should be negligible. In this study, approximately $5 \cdot 10^6$ peak counts were obtained for all but the 031 series of samples. With the improvements in the counting system described above, and with the use of longer counting times (up to a few days), $1 \cdot 10^8$ counts could be obtained for enriched samples. The corresponding 2σ uncertainty for this number of counts is 0.020%, assuming the background contribution to the uncertainty is negligible. The combined 2σ uncertainty for one count of a sample and one count of a standard would be 0.028%, however, by using multiple (n) samples (or standards), or by using (n) multiple counts uncertainties could be reduced by the square root of n. For example, 25 sample counts and 25 standard counts would have a combined 2σ uncertainty of 0.006%. For natural and depleted samples, $2 \cdot 10^7$ (gamma-ray) counts could reasonably be obtained. The corresponding 2σ combined uncertainty for 25 counts of the samples and 25 counts of the standards would be 0.013%.

In practice, the major limitation to accuracy has been the uncertainties associated with the standards. With a small number of standards, accuracy is limited to approximately that of each standard, as most of the improvement obtained by using multiple standards would probably be negated by the additional uncertainties associated with the pileup and ^{238}U corrections necessary when standards with different abundances are used. Except for SRM 969, whose abundances were determined in this work, few materials are available in the 200 gram quantities needed for the GS procedure, with ^{235}U/U abundances known to better than 0.1% (relative). Even with SRM 969, whose five abundances are certified to 0.07% each, the potential accuracy achievable by GS would probably not exceed 0.05%. However, if a set of standards were available with abundances known to 0.01%, overall uncertainties of 0.01–0.02% (including counting statistics) should be attainable. Samples whose abundance was close to that of one of the standards could be compared directly to that standard. Since the corrections necessary for pileup and ^{238}U interference would be essentially the same for sample and standard, the small uncertainties of these corrections would have essentially no effect on the uncertainty of the final result (^{235}U/U abundance). Samples with abundances between two standards would be compared to both standards, and so additional uncertainties from the required corrections would be balanced by the smaller combined uncertainty associated with the use of two standards instead of one.

Although such a well characterized set of standards is not currently available, it appears likely that one could be produced. NBS has certified SRM U-0002 as having a ^{235}U/U abundance of 0.01755±0.00005%,[11] and SRM U-970 as having a ^{235}U/U abundance of 97.663±0.003%.[11] If these materials could be made homogeneous for the 186 keV gamma-ray, then standards with ^{235}U/U abundances above 0.6% could be produced with two sigma uncertainties of 0.01% or less. Standards with ^{235}U/U abundances of 0.3% could be made with relative uncertainties of 0.02% (2σ). Note that sufficient homogeneity for subsampling is not required, and that the exact amount of material within the standard is not critical, as long as it is infinitely thick for the 186 keV gamma-ray. With a set of standards made in this manner, it should be possible to determine ^{235}U/U abundances with a 2σ overall uncertainty of 0.02–0.03%, on a relative basis, for depleted and natural level samples (^{235}U/U = 0.3–0.7%), and with an overall uncertainty of 0.01–0.02% for enriched samples.

Conclusions

This work has demonstrated that it is possible to achieve relative precisions of 0.05%, and standard deviations of the mean of 0.01%, with gamma-spectrometry measurements. The average difference observed between GS and certified values for five isotope abundance standards (SRM 969) was less than 0.05% on a relative basis. To obtain these results it was important to consider all potential sources of error in the measurement process. If all errors are carefully controlled, and if a set of well characterized standards are available, it appears that accuracies of a few hundredths of a percent, at the 95% confidence level, can be obtained by gamma spectrometry.

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