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UCRL-TR-203333

# *On the Use of $^{233}U$-$^{236}U$ Double-Spike for TIMS Measurements of Uranium Isotopes: A Simulation Study*

*Ross W. Williams*

**April 6, 2004**

## ISPO-504

A report prepared for the International Atomic Energy Agency under SP-1 Task Proposal 02/SAL-001: Double-Spike Simulation Study for TIMS Measurements

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This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

**Abstract**

Synthetic ion beams with instantaneous and temporal characteristics appropriate to thermal ionization mass spectrometry (TIMS) were mathematically generated and analyzed to determine the effects of using a mixed $^{233}U$-$^{236}U$ spike (double-spike) in the analysis of uranium isotopes. The instantaneous beam characteristics are the intensities (e.g., counts per second) modeled with a Poisson distribution plus a component of random noise that simulates the detection processes. Several beam intensity and mass fractionation vs. time functions were modeled to simulate a range of sample sizes and the commonly employed methods of data collection. These beam profiles were also generated with different noise levels, and signal-to-noise vs. analytical precision diagrams are presented. Modeling focused on natural uranium, where $^{238}U/^{235}U$ = 137.88, and on the ability of a given method to determine precisely and accurately small variations in this ratio. Practical limits on precision were determined to be 20-30 ppm, which is consistent with precision seen for other elements by state-of-the-art TIMS. The TIMS total evaporation method was compared directly with the double-spike method. While similar analytical precisions are obtained with either method, the double-spike method of correcting for analytical bias gives more accurate results. The results of a total evaporation analysis will deviate from true by more than the analytical precision if as little as 0.05% of the signal is not integrated, whereas the accuracy and precision of the double-spiked analyses are always linked.

## Introduction

The IAEA Safeguards program requires precise and accurate measurements of uranium isotopic composition so that small variations from expected compositions may be viewed with confidence. Simply, the task set for the mass spectrometrist is to make such measurements, and over the last ten years, improved instrumentation and analytical methods have increased U-isotopic precision to a few parts-per-thousand (per mil, ‰). Recently, there have been reports of precision on U-isotopic analyses in the sub-per mil level using the double-spike method. This report summarizes a simulation study of this method undertaken and designed to compare specifically thermal ionization mass spectrometry analytical methods and determine which should give the greatest precision and accuracy.

## Background

### The Double-Spike

The double-spike for uranium is a combination of $^{233}U$ and $^{236}U$, which, added to a sample, allows corrections to be made for analytical bias. Any deviation observed in the $^{233}U/^{236}U$ relative to the known spike ratio can be used to correct the $^{235}U/^{238}U$ for a similar deviation. Both $^{233}U$ and $^{236}U$ are products of nuclear reactions and either do not occur in pre-nuclear era natural uranium, or as has been shown for $^{236}U$, occur at infinitesimal abundances due to natural neutron capture processes. However, they are often present in nuclear fuel cycle materials, so that careful determination of the un-spiked isotopic composition is necessary for accurate isotopic analyses of these materials. Natural uranium, uncontaminated with anthropogenic uranium, in secular equilibrium, is comprised of $^{238}U$ (99.27454 atom %), $^{235}U$ (0.72001 atom %), and $^{234}U$ (0.00545 atom %). The relative isotopic compositions of $^{238}U$ and $^{235}U$ are generally held to be invariable in natural uranium, and come from mass spectrometric analyses of $^{238}U/^{235}U$ of 137.88 ($^{235}U/^{238}U$ = 0.00725268). All ratios in this report are atomic ratios.

Thermal ionization mass spectrometry (TIMS) has long been the pre-eminent analytical method for measuring uranium isotopic composition, and all international U-isotopic standards have been certified using TIMS. For U, the sample is loaded on a refractory metal filament (generally rhenium), which is resistively heated. The source of the ions is usually held at a high positive potential, and the positive ions produced are accelerated by this electric potential through ion focusing lenses into the flight-tube, through the magnetic sector mass analyzer, and on to the detectors. Most TIMS are designed to run at constant accelerating potential and the mass of interest is selected by varying the strength of the magnetic field. As the ions transit the magnetic field, their radius of curvature depends on their energy, which is a function of their mass/charge ratio and the accelerating potential, and on the strength of the magnetic field. Single collector instruments generally have a single focus point, and beams of different mass/charge ratios are brought to the detector by changing the magnetic field, or “peak-jumping”. Multi-collector instruments have detectors aligned along a focal plane defined by the magnet geometry, so that ion beams of several masses can be detected simultaneously.

Temporal variations in ion-beam intensity that may be seen during single collector peak-jumping are seen simultaneously in the different mass beams on a multi-collector instrument. As a result, the $^{235}U/^{238}U$ ratio measured by peak-jumping is intrinsically less precise than that measured by simultaneous multi-collection.

The detectors commonly used in TIMS are of two types: Faraday collectors or cups that integrate the beam current, or total charge per unit time, are ideal for larger beam intensities; and ion-counting or pulse-counting detectors, which can be of several types and are used for lower beam intensities. The natural unit of beam intensity is current (I) measured in amperes (units of coulomb/second), but the signals from Faraday cups are often converted to volts (V) because the voltage measured across a known resistor is used to determine these relatively small ion-currents. Most mass spectrometry systems use $10^{11}$ ohm (R) resistors, and all beam intensities in this report given in volts make this assumption. From $V = I \times R$, and the further assumption that all beam current is from ions with unit charge ($q = 1.602176 \times 10^{-19}$ coulomb), one obtains the following conversions: 1 volt = $1 \times 10^{-11}$ amps = $6.2415 \times 10^{7}$ ions/second. Strictly, counts per second (cps) is the direct reading from a pulse-counting system, and is converted to ions/second by applying the counting system calibration parameters, such as corrections for dead-time and detection efficiency. In this report cps will be used more loosely to indicate beam intensity, and will be used interchangeably with volts. The conversion factor of 62400 cps per millivolt (mV) may be useful to keep in mind.

Pulse-counting systems for TIMS are of three basic types: electron multipliers in which the ions impinge directly on the first dynode of the multiplier string; channeltron multipliers, in which the ions again impinge directly, but the discrete dynodes are replaced functionally by a continuous path for multiplication of the cascading electrons; and the Daly detector, which is a photo-multiplier based system. Ions impinging on the Daly-knob, a highly-polished Al knob held at about –30kV, produce a shower of electrons which in turn, activate a phosphor, and are counted as light pulses. Simultaneous pulse-counting of uranium ion beams requires the detectors to have small physical dimension on the order of the mass dispersion. Channeltron-based systems have been available for several years and miniaturized electron multiplier-based systems are now being installed on the latest generation of TIMS. The beam intensity that can be analyzed by pulse-counting is limited by the tolerance of the detector materials to impinging ions, but more importantly by its physical recovery time and the signal processing time, collectively known as the dead-time of the system. A dead-time of 12 nanoseconds results in loss of 1.5% of the signal at beam intensities of 20 mV or about $1.25 \times 10^{6}$ cps. At higher count rates, the uncertainty in the dead-time correction and the possibility of non-linear effects quickly obviates any advantage pulse-counting may have over Faraday collectors in terms of signal to noise.

## Mass Spectrometry

Factors Affecting Precision

Analytical precision is a qualitative term and is used here to indicate the repeatability of a measurement. Precision is often quoted based on the standard deviation of a series of measurements from a single analysis. This has been aptly named the "internal precision", for it represents the dispersion of a set of measurements around the internal mean value of that analysis. The so-called "external precision" is based on the dispersion of a set of separate unrelated measurements of the same sample, or the reproducibility, and is usually larger than the internal precision. In the modeling results presented here, it was not possible to assess the effects of the variations that are likely in multiple sample loadings and runs. These variations may be in sample preparation, filament preparation and sample loading, run temperature, source and analyzer pressure; even the chemistry of the residual gas in the mass spectrometer; and their effects can only be determined experimentally. Therefore, precision, as used here, is the internal precision or repeatability, which can be calculated directly from the model results and is quoted at the 2-sigma level of confidence.

The major parameters controlling the precision that can be obtained by TIMS analyses of uranium isotope ratios are the absolute ion beam intensities. Ion beams, whether measured on Faraday or pulse-counting detectors, obey discrete-particle physical laws and have Poisson distributions. The standard deviation of this distribution is the square root of the number of counts, and counting statistics can be used to predict the precision that can be obtained on ratio measurements. In general, more precise ratios will be obtained at greater beam intensities, and simultaneous Faraday multi-collection will be far more precise than pulse-counting. However, the signal measured is not only due to the ion beams, but includes a component of electronic noise associated with the detection system. Noise is an additive function that increases the dispersion and distorts the Poisson distribution, with the result that the signal to noise ratio is a better indicator of the precision than the beam intensity alone. Faraday detectors have intrinsically higher noise than pulse-counting detectors, and so are better suited to higher beam intensities, and vice versa.

Factors Affecting Accuracy

As defined in NIST Technical Note 1297, Appendix D: "accuracy of measurement" is "closeness of agreement between the result of a measurement and the value of the measurand." For this study the measurand of interest is the atomic ratio $^{235}U/^{238}U$ and the value of the measurand is 0.00725268, which is the widely accepted value for natural uranium. Natural uranium was chosen for the modeling to explore the ability of the double-spike technique to detect accurately small variations in $^{235}U/^{238}U$.

For TIMS analyses, a bias in the measured isotopic composition is caused by fractionation of $^{235}U$ and $^{238}U$ during volatilization from the hot filament. The magnitude

of this mass fractionation depends on the sample itself and the filament preparation technique, but more importantly, on the time-temperature path of the sample during analysis. It is always the case that the lighter isotope is volatilized preferentially to the heavier one, so that the earliest $^{235}U/^{238}U$ ratios measured on a sample in the process of warming up to run temperature will be biased high relative to the value of the measurand, which will be called here, the true value. Figure 1A shows a model fractionation profile for a sample during TIMS analysis, where the earliest instantaneous fractionations are the greatest (in this case more than 1%), but diminish as the run proceeds until a stable run temperature and a constant fractionation are attained. As can be seen in Figure 1B, from the beginning, the residue (the sample remaining on the filament) is isotopically heavier than the starting composition, and the instantaneous emission is always lighter than the residue by an amount proportional to the fractionation factor. At some point, the instantaneous emission is equal to the starting composition and the measured $^{235}U/^{238}U$ equals the true value, but after this point, it will always be biased to heavier than the true value.

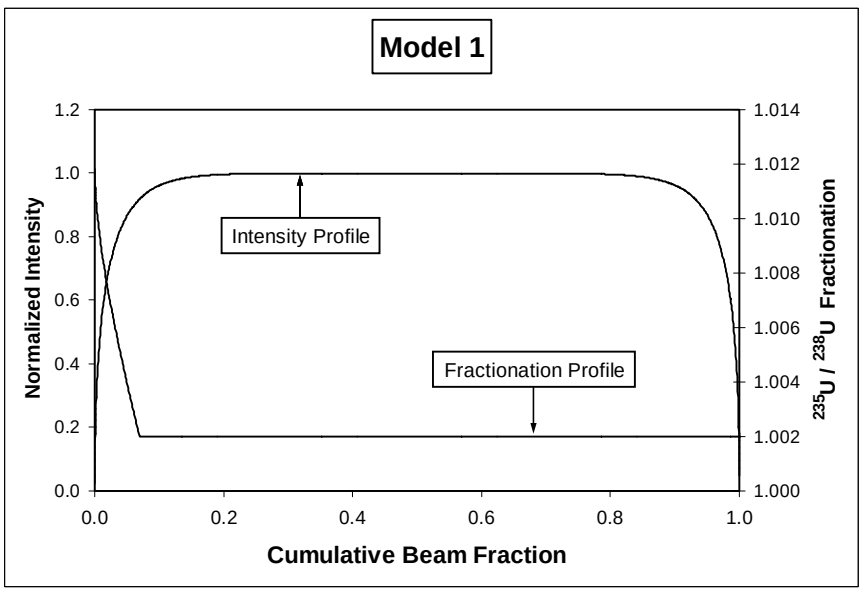


Figure 1A. The normalized Intensity Profile developed for Model 1 was based on an idealized TIMS run where the filament current is increased to a stable emission temperature and maintained at that point until sample depletion. The $^{235}U/^{238}U$ fractionation shown on the right axis for the Fractionation Profile can be thought of as the emission factor from the filament for $^{235}U$ relative to $^{238}U$ at any point in the sample analysis. The analysis proceeds from left to right, and time is related to the cumulative beam fraction through the intensity profile.

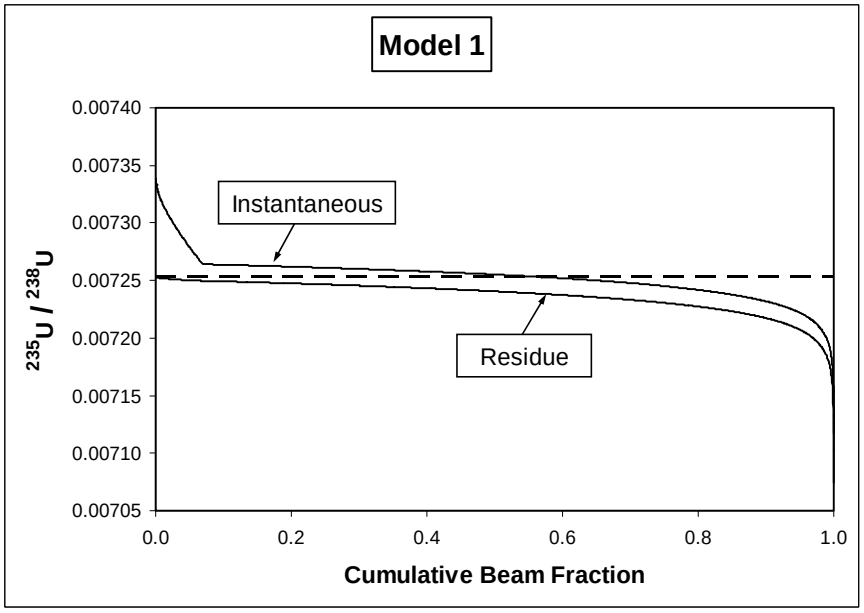


Figure 1B. The effects on the isotopic ratios are shown here for the Model 1 beam profile (the combined intensity and fractionation profiles) presented in Figure 1A. The Instantaneous beam is the isotopic composition that will be generated from the Residue at any point in time according to the Fractionation Profile in Fig. 1A.

The art of TIMS has always been to analyze samples in a manner that will give reproducible fractionation and intensity profiles and hence, a known bias. Results corrected with an externally derived bias factor can only be as accurate as the external reproducibility. However, variations in beam profile and mass fractionation trends because of sample-specific effects may produce inaccurate results, but the assessment of external reproducibility for each unknown sample is impossible. The TIMS total evaporation and the double-spike methods were developed to improve the accuracy of uranium isotopic analyses by minimizing these sample-specific effects.

## The Total Evaporation Method

The basic premise of the TIMS total evaporation method is independent cradle-to-grave integration of the $^{235}U$ and $^{238}U$ ion beams so that the entire sample is analyzed. The early, high $^{235}U/^{238}U$ beams are integrated with the late, low $^{235}U/^{238}U$ beams. These ion beams must necessarily sum to the original starting composition providing the following assumption is true: that the measured ion beams represent the total sample emission, and there is no occult fractionation or sample loss. In practice, during a TIMS total evaporation analysis, a certain amount of sample loss is inevitable due to low signal intensities at the beginning and end of the analysis. The practical effect of this signal loss is observed as bias on the analysis of standard reference materials, and has been quantified by the modeling presented below.

The Double-Spike Method

The double-spike method relies on addition of a mixed $^{233}U$-$^{236}U$ spike (the double-spike) to the sample prior to analysis of the uranium isotopic composition. It is assumed that the fractionation behavior of $^{235}U$ relative to $^{238}U$ will be mirrored by $^{233}U$ relative to $^{236}U$. Accurate $^{235}U/^{238}U$ measurements can then be calculated from data taken at any stage during the TIMS run providing that first, an un-spiked analysis of the sample has been made, and second, that the double-spike isotopic composition is well known. For the modeling presented below, the intrinsic $^{233}U$ and $^{236}U$ in the sample were assumed to be zero, and the double-spike corrections on the $^{235}U/^{238}U$ were applied as simple linear correction factors determined by comparing the fractionated $^{233}U/^{236}U$ with the known value. The $^{233}U/^{236}U$ of the double-spike was set as 1.0. In practice, it is possible to prepare U double-spikes with any isotopic composition, but a 1:1 $^{233}U$:$^{236}U$ atom ratio is preferred, because the internal precision can be affected by radical differences in spike isotope abundances.

## Scope

The scope of this study was limited to determining the relative merits of the TIMS total evaporation method and the double-spike method of determining the isotopic composition of natural uranium. The scope was focused further by attempting to determine the maximum accuracy that can be attained using modern multi-collector instruments running at $^{235}U$ beam currents of $1.162 \times 10^{-14}$ amps (ca. 1.16 mV, 72.5 kcps) or greater. That is, all modeling was done assuming Faraday multi-collection. In general, the conclusions of this study are applicable to smaller beams on pulse-counting detectors, to mixed pulse-counting and Faraday multi-collection, and to single-collector peak jumping analyses as well.

## Modeling

The Synthetic Beam

It was assumed that the variability in an ion beam at a given intensity is described by the Poisson distribution, and the Poisson random number generator in Microsoft Excel©, was used to generate the synthetic ion beams. The first step in this process was the description of the beam intensity versus time profile as in Figure 4B. One thousand steps were used to describe each profile. The maximum beam intensity was selected and the idealized model beam intensities in units of counts-per-second (cps) were calculated from the normalized profile for each of the 1000 steps. Ten data points were then generated according to the Poisson distribution for that idealized beam intensity. During data analysis these ten data points were treated as different runs of the same model. A single run of the model generated a data set of forty-thousand intensities, as follows: four isotopes × ten intensities per step × 1000 steps in the beam profile. An example of this

primary beam generation process is given in Figure 2. The data points in this figure are the mean of those ten randomly generated beam intensities, and they are plotted as deviations in percent from the idealized beam.

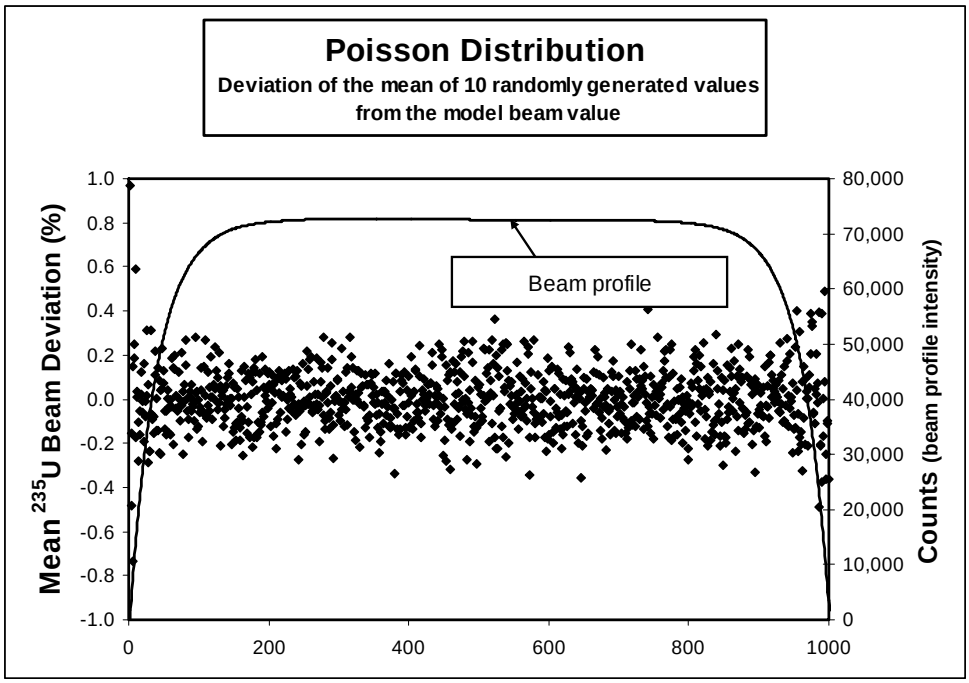


Figure 2. An example of primary beam modeling using intensities generated according to the Poisson distribution. The smooth curve is a $^{235}$U beam profile shown plotted on the scale given on the right-hand vertical axis. Ten separate beam intensities were randomly generated for the idealized model mean given by the profile intensity. The points are plotted on the scale given by the left-hand axis as the deviations of the mean of those ten values from the modeled intensity. From theory, the relative 1-standard error on the mean of 10 Poisson distributed values around 70000 is approximately 0.12 %, and the generated data are consistent with this.

Additional details of the calculation of the idealized beam intensities are given here. First, the $^{238}$U beam is generated according to the normalized profile and the maximum intensity chosen. From this, the total sample reservoir of $^{238}$U is calculated. The total sample reservoir of $^{235}$U, $^{233}$U and $^{236}$U are also fixed by the $^{238}$U, because the $^{235}$U/$^{238}$U is assumed natural and double-spike isotopes are both set at one-tenth of the $^{238}$U. Second, for each of the 1000 steps, the idealized $^{235}$U, $^{233}$U, and $^{236}$U beams are calculated from the fractionation profiles and the calculated composition of the uranium remaining in the residue (*i.e.*, on the filament). The $^{236}$U is calculated to deplete in step with the $^{238}$U, and the $^{233}$U and the $^{235}$U are calculated to fractionate from $^{236}$U and $^{238}$U respectively, according to the fractionation factor at that step. Mass balance is maintained exactly for $^{238}$U and $^{236}$U, and to within 50 parts-per-billion for the other isotopes.

Table 1 gives the three different sets of maximum beam intensities that were generated for each model. The different idealized intensities for each isotope were calculated from the $^{238}$U beam according to the assigned isotopic composition and the fractionation profile. The fractionation profiles shown in Figure 1A and Figures 4A and 4B were

chosen to match the isotopic effects as seen in uranium analyses made by the TIMS total evaporation method at New Brunswick Laboratory (Steven Goldberg, personal communication). The salient features of these profiles are an early enhancement of the $^{235}U/^{238}U$ by approximately 1.2%, which rapidly declines as the beam intensity (filament temperature) increases. After the near-maximum beam intensity is reached and the emission has stabilized, a constant fractionation factor for $^{235}U/^{238}U$ of 1.002 (+0.2%) closely reproduces the New Brunswick Laboratory fractionation trends.

Table 1. Modeled maximum beam intensities

| Isotope | Low | Medium | High |
|---|---|---|---|
| $^{238}U$ | $1 \times 10^7$ cps | $1 \times 10^8$ cps | $5 \times 10^8$ cps |
| $^{235}U$ | $7.25 \times 10^4$ cps | $7.25 \times 10^5$ cps | $3.63 \times 10^6$ cps |
| $^{236}U$ | $1 \times 10^6$ cps | $1 \times 10^7$ cps | $5 \times 10^7$ cps |
| $^{233}U$ | $1 \times 10^6$ cps | $1 \times 10^7$ cps | $5 \times 10^7$ cps |

The maximum beam intensities for $^{235}U$, $^{236}U$ and $^{233}U$ are idealized from the natural uranium isotopic composition and by fixing $^{238}U/^{236}U = 10$ and $^{233}U/^{236}U = 1$.

Simulation of the detection process for mass spectrometry requires modeling the noise intrinsic to the detection system. As mentioned above, the beam intensities chosen are all appropriate for the use of Faraday detectors. Three different levels of Faraday detector noise were modeled using a Gaussian random number generator to produce noise distributions with absolute standard deviations of 4, 20 and 100 microvolts (1 microvolt = 62.4 cps). The 4 and 20 microvolt noise levels are comparable to the ranges that might be seen on different commercial TIMS. Realistically, a Faraday detector system exhibiting a characteristic 100 microvolt noise level would probably be taken out of service and repaired or replaced. Nevertheless, the 100 microvolt noise level is useful in the context of modeling. Forty different random distributions of 1000 points each were generated for each of the three different noise levels. Further randomization of the noise applied to any particular beam intensity was assured by randomly selecting an element from the 40 × 1000 noise array to apply to an element of the 4 isotope × 10 intensity × 1000 step beam intensity array. The selection algorithm was such that each noise element was used once and only once per model calculation. Examples of the Faraday noise data sets are shown in Figure 3. For the model calculations, the mean of each noise spectrum was set to zero and the random noise value (positive or negative) was added to the beam intensity.

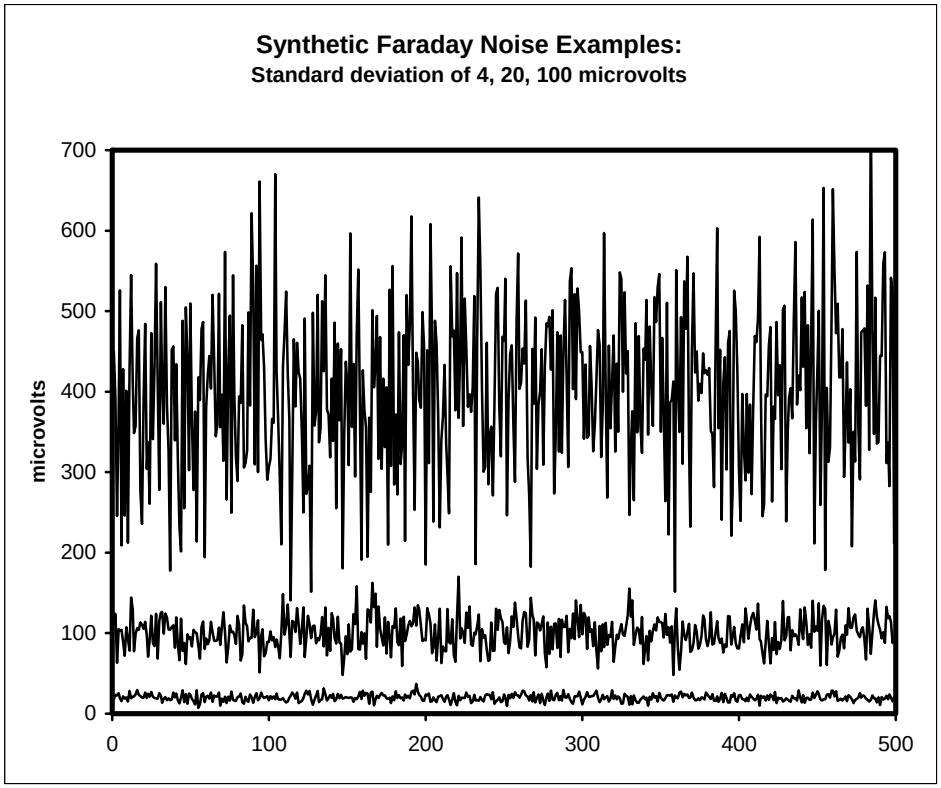


Figure 3. Examples of the random Faraday noise spectra with standard deviations, from bottom to top, of 4, 20 and 100 microvolts. The offsets from zero are arbitrary for the purpose of graphical display

For each (beam profile/fractionation) model, the three different noise distributions were applied to each of the three different beam intensities, giving a total of nine different synthetic beam records. These nine beam records have a characteristic maximum signal to noise ratio, abbreviated as S/N. The S/N for $^{235}$U, which is always the smallest of the four beams modeled, are given in Table 2, and are the values used in Figures 5 through 8. Note that essentially identical $^{235}$U S/N are seen for two different signal intensities at two different noise levels (*i.e.*, 2900 and 580). As will be discussed further below, it is possible from these models to discern the relative effects on the analytical precision of higher signal intensity versus lower noise level.

Table 2. The maximum $^{235}$U S/N for the nine beam records generated for each model

| $^{235}$U Intensity | Noise Distribution; 1-SD (microvolts) | | |
|---|---|---|---|
| | 4 | 20 | 100 |
| Low | 290 | 58 | 11.6 |
| Medium | 2900 | 580 | 116 |
| High | 14500 | 2900 | 580 |

## The Models

Model 1, which is the generic TIMS intensity and fractionation profile, collectively called the beam profile, shown in Figure 1, proved to be remarkably accurate when compared

to actual TIMS data sets for isotopic uranium analysis. The smooth intensity profile should allow effects of the Faraday noise rather than variation in beam intensity to dominate the analytical precision. The mechanism for the generation of the individual beam profiles has been explained above.

Model 2, shown in Figure 4, was created to replicate actual TIMS total evaporation analyses as closely as possible, and also to simulate a less-ideal, more real-world ion beam that is quite erratic. A random step function was used to generate the variations in beam intensity seen on the broad plateau. The details of calculation for this model are the same as for Model 1. Figures 4A and 4B illustrate the difference between the time axis (*i.e.,* the step number) and the cumulative beam fraction, which is calculated as fraction of the total sample that has been consumed. Very little of the total beam fraction comes from the early and late, lower intensity ion beams. Even so, as shown below, these small beam fractions are critically important to the accuracy of the total evaporation analysis.

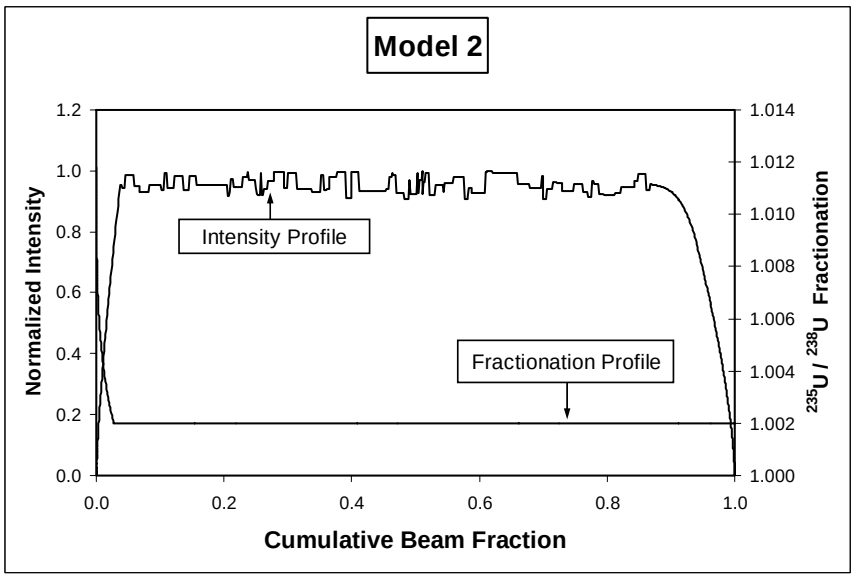


Figure 4A. A beam profile representation of Model 2 similar to Figure 1A.

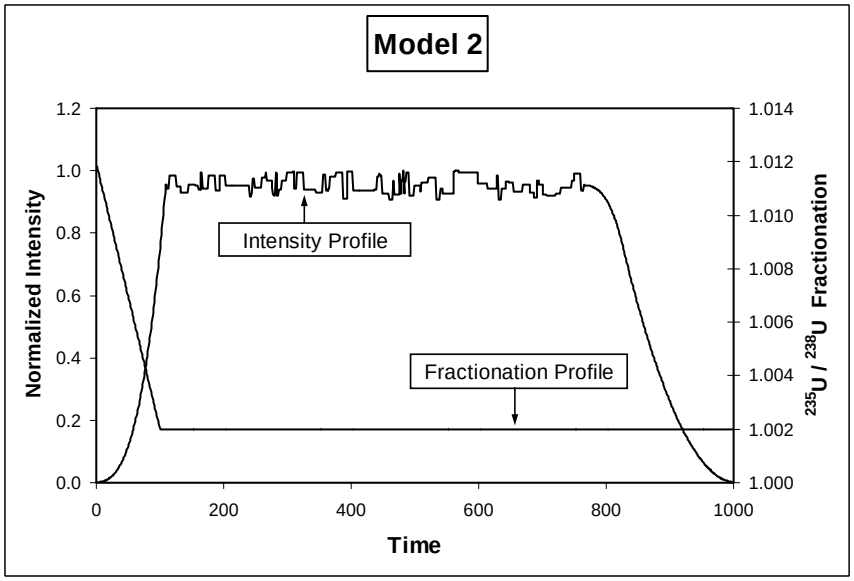


Figure 4B. The same beam profile for Model 2, except plotted relative to time instead of the cumulative beam fraction.

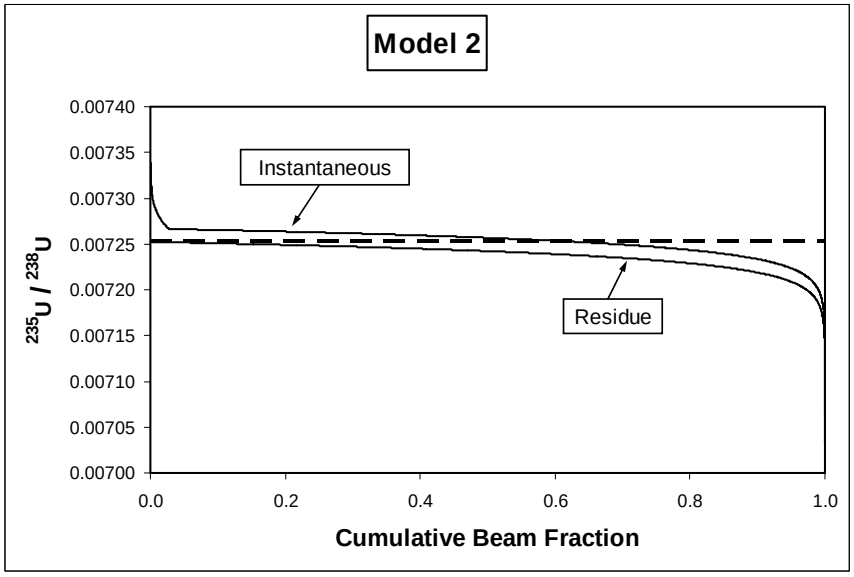


Figure 4C. This figure shows the isotopic composition of the instantaneous emission and the residue (filament reservoir) for the TIMS total evaporation method Model 2. This model closely predicts the results of actual uranium isotopic analyses.

## Synthetic Data Analysis

### Precision

The model beam intensities were chosen and the synthetic data were generated assuming simultaneous collection on Faraday detectors, for the purpose of determining the best precision that can be expected from a double-spiked analysis of isotopic uranium. Figure 5 shows the results of 25 independent beam generations and resulting double-spike

calculations for the Model 1 beam profile at the low beam intensity with the 4 microvolt noise. The points are plotted as deviations from the true $^{235}U/^{238}U$ in parts-per-thousand (per mil, ‰). The data were divided into 20 blocks of 500 ratios and the mean for each block is plotted with two different sets of error bars. The error bars on the solid triangles are 2-standard deviations on the population of 25 runs, and the error bars on the open circles are 2-standard errors on the mean for the 500 ratios. The standard error on the mean is always smaller than the population parameter as expected. However, the standard deviation of the population is a better indication of the repeatability, and it is this value that is used for precision in Figures 7 and 10. Figure 6 shows the results for 25 runs of Model 1 at low beam intensity with the 20 microvolt noise.

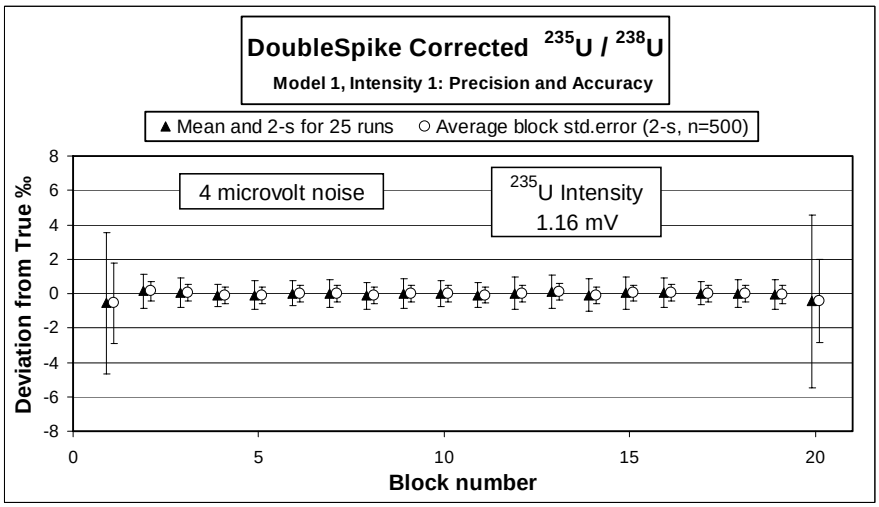


Figure 5. Double-spike corrected results for the model calculation of the low intensity $^{235}U$ beam with 4 microvolt noise. The S/N is 290 and the 2-sigma precision and accuracy are approximately 0.9 per mil. This result is plotted as the right-most solid triangle on Figure 7.

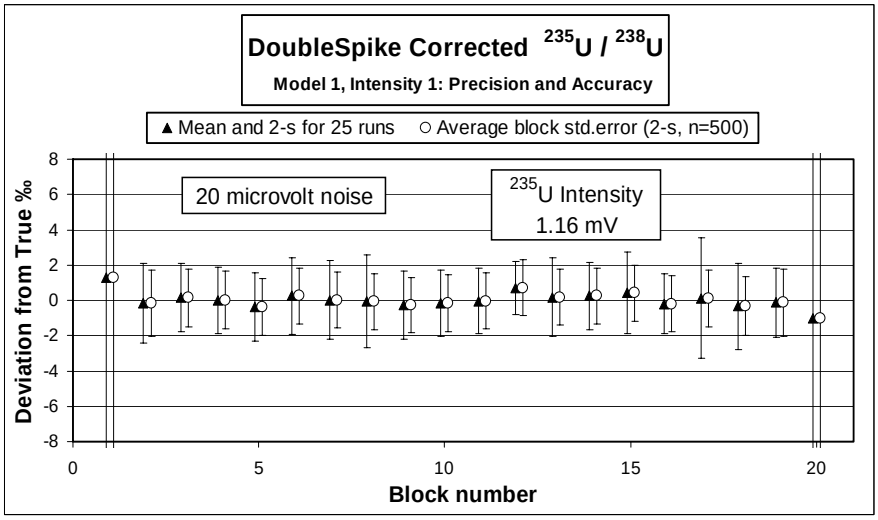


Figure 6. Results for the model calculation as in Figure 5, but with 20 microvolt noise. The S/N is 58 and the 2-sigma precision and accuracy are approximately 2 per mil. This result is plotted as the right-most solid circle on Figure 7.

From these figures it is evident that the precision and accuracy of double-spike corrected analyses are linked. When the beam intensity has grown to a level where signal dominates over noise, which in this case begins with the second block of data, the accuracy of the double-spike corrected ratios is given by the repeatability or precision. Of course, the underlying assumption is that the double-spike $^{233}U/^{236}U$ ratio is accurate. One further caveat is that the precision and accuracy shown here for the double-spiked analyses only indicate the potential of the method, and do not necessarily represent the true analytical reproducibility. That reproducibility cannot be modeled with computer simulations; it must be determined by experiment.

The nine different S/N given in Table 2 were analyzed using the double-spike to calculate the $^{235}U/^{238}U$ as described above. The precision/accuracy of these models is plotted in Figure 7, where precision on the bottom axis refers to $^{235}U/^{238}U$. Note that the precision is practically identical for the points at S/N = 580 for the 20 and 100 microvolt noise levels. Also note, that the high intensity beam / 20 microvolt noise at S/N = 2900 gives more precise results than the medium intensity beam / 4 microvolt noise at the same S/N. This indicates that, as the noise level decreases, higher beam intensity becomes more important to precision than lower noise. Or, as expected, the ultimate precision is determined by counting statistics. The practical limit on precision of 30 ppm was estimated by extrapolating the 4 microvolt noise curve to the highest level beams that can be detected using Faraday cups on some modern TIMS instruments.

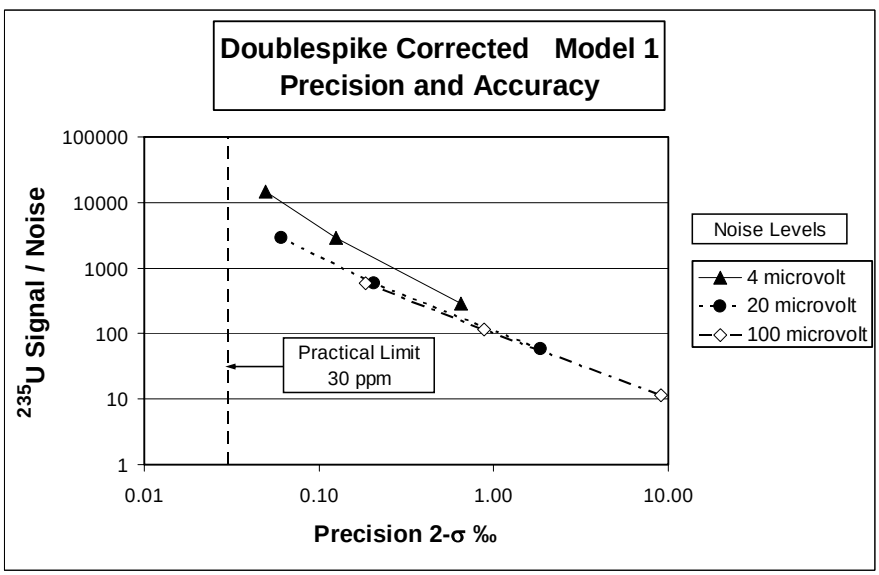


Figure 7. A log-log plot of S/N versus precision in per mil, showing analysis of the double-spike method applied to Model 1 for the nine different S/N ratios in Table 2. The precisions were calculated as described above and shown in Figures 5 and 6.

The values for precision given in Figure 8 for the total evaporation method applied to Model 1 are 2-standard deviations of a population of 250 calculations of the simulated ion beams at each S/N ratio (25 independent runs × 10 beams per run). For a given S/N the values are slightly more precise than those for the double-spike method (Figure 7). This slight difference in precision between the two methods is probably due to the use of

the $^{233}U$ and $^{236}U$ beams in the double-spike method. The practical limit on precision for the total evaporation method, estimated as above, is 20 ppm.

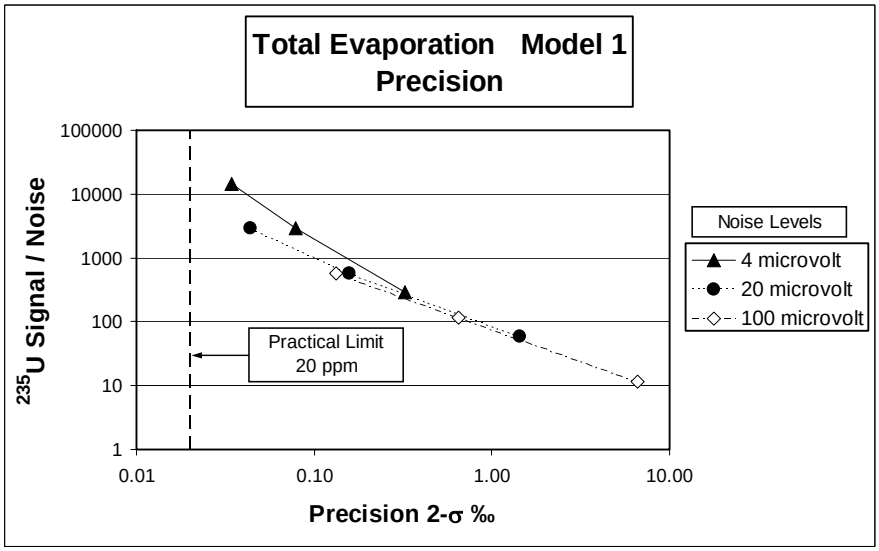


Figure 8. The values for precision for the total evaporation method applied to Model 1 are 2-standard deviations on populations of 250 calculations for each S/N.

The precisions obtained for the total evaporation method applied to Model 2 are practically identical to those obtained for Model 1. They are slightly worse for Model 2, which may be ascribed to the beam profile (see Figure 4B vs. 1A). The fact that these precisions are not more different is due to the mode of data sampling, *i.e.*, simultaneous multiple Faraday acquisition. For the same reason, the precision for double-spike corrected Model 2 shown in Figure 10 is indistinguishable from that for Model 1 (Figure 7).

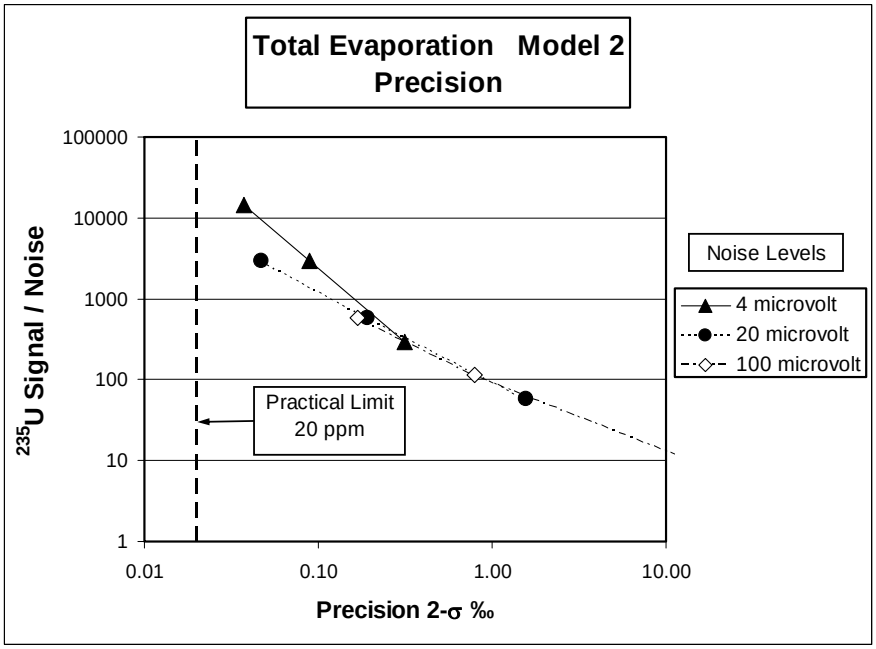


Figure 9. Precision for the total evaporation method applied to Model 2 (Figures 4A, B, C).

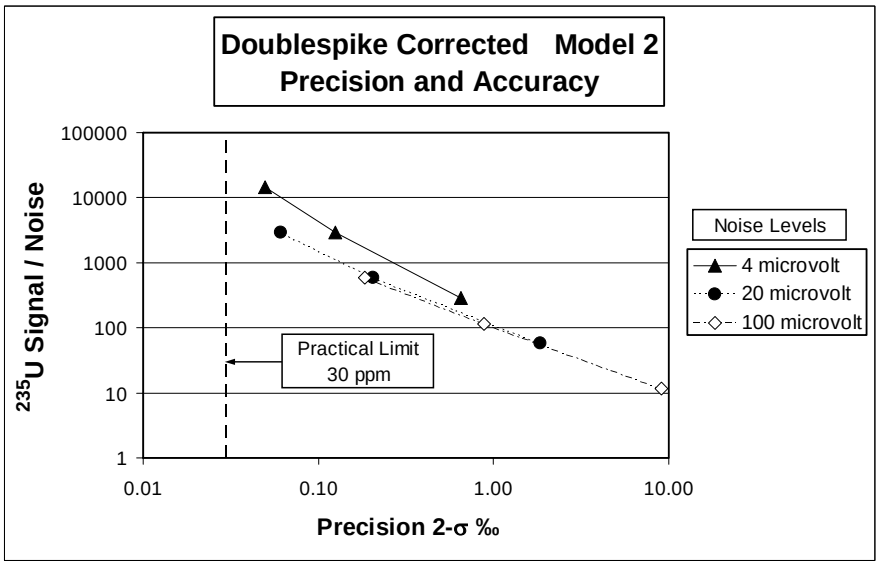


Figure 10. Precision for the double-spike method applied to Model 2, calculated as for Figure 7.

In summary, the precision of the total evaporation method is slightly better than the double-spike method for analysis of natural uranium isotopic compositions. The accuracy of the double-spike method is equivalent to its precision. Using simultaneous Faraday data acquisition techniques, both methods are relatively insensitive to fluctuations in ion-beam intensity. Increasing the beam intensity, *i.e.*, higher signal, will give more precise results than decreasing the noise level, even though both result in greater S/N.

## Accuracy

Limitations on the accuracy of the double-spike method for isotopic uranium analysis are imposed by the analytical precision on the sample analysis and by the double-spike calibration. Where appropriate, the sample analysis must include an analysis of the un-spiked isotopic composition to determine intrinsic $^{233}$U and $^{236}$U. The double-spike may also contain a small amount of $^{235}$U and $^{238}$U and the uncertainty in the isotopic composition of the spike should be propagated appropriately. It is likely that the magnitude of the uncertainties that would be propagated from the minor isotope composition of the sample and the double-spike will be small relative to the analytical uncertainty. Therefore, the accuracy on the double-spike analysis is directly linked to the analytical uncertainty and will be similar to the precision predicted in Figure 10.

In contrast, the accuracy for the total evaporation method is critically dependent on complete integration of the entire sample emission. Further, the effects of a small amount of signal loss are large relative to the predicted repeatability (the precision, *e.g.*, Figures 8 and 9). Regardless of whether the signal is lost at the start of the analysis where the $^{235}$U/$^{238}$U is greater than true, or at the end of the analysis where the $^{235}$U/$^{238}$U is less than

true (see Figure 1B), the analyses for Model 1 and Model 2 will be biased to low $^{235}U/^{238}U$. This effect is shown in Figure 11. Loss of as little as 0.05% of the true total signal (*i.e.*, the sample) at the beginning of the analysis, will bias the results to low $^{235}U/^{238}U$ by 0.4 ‰. This bias is greater than the predicted precision for most of the total evaporation models (Figures 8 & 9). In contrast, double-spike corrected analyses are not biased, as shown by the dashed line in Figure 11. The results of similar calculations for Model 2 are shown in Figure 12.

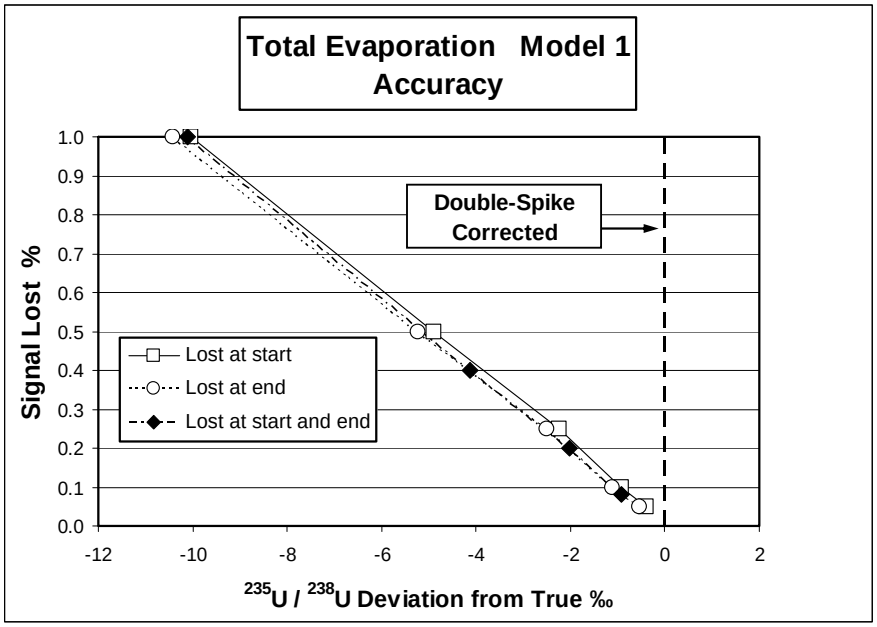


Figure 11. Percent signal lost versus bias induced in the $^{235}U/^{238}U$ ratio for the total evaporation method. Even small amounts of signal loss result in easily detectable bias, regardless of whether the loss occurs at the beginning or the end of the analysis.

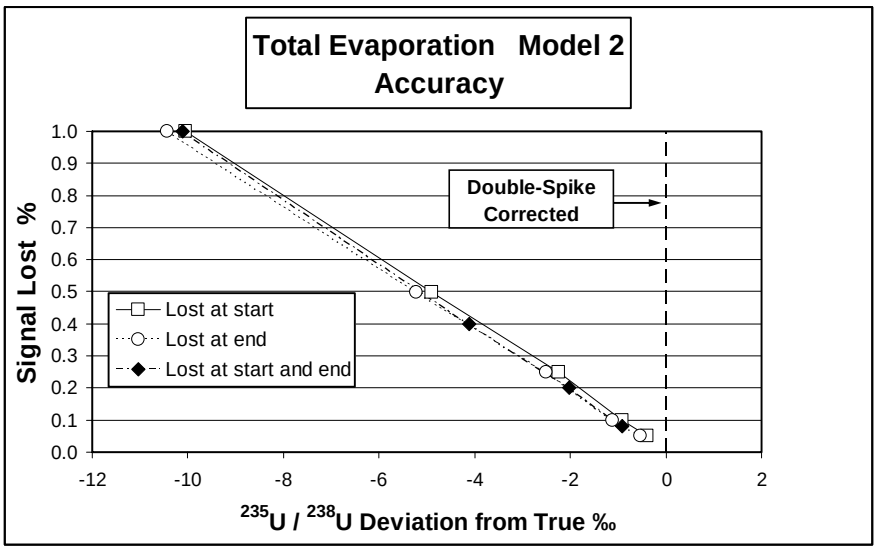


Figure 12. The effects of signal loss on accuracy for the total evaporation method calculated for Model 2.

## Conclusions

Calculations based on synthetic ion beams generated to simulate double-spike analyses of isotopic uranium by TIMS have shown the following:

1) The absolute signal intensity is relatively more important than the detector noise level in obtaining the most precise analyses. The ramification of this simple observation is that at a fixed signal to noise ratio, a larger signal on a higher noise Faraday detector is more precise than a smaller signal on a lower noise pulse-counting detector. Simultaneous collection of multiple ion beams on Faraday detectors is the most precise data collection technique. Following this, in order of decreasing precision, is mixed detector simultaneous Faraday / pulse-counting data collection, simultaneous pulse-counting, and then peak-jumping analyses. Earlier assessments did not reveal the true potential the double-spike method because they relied primarily on peak-jumping analyses.
2) The precision on a double-spike analysis is intimately related to the accuracy. In general, the double-spike analysis will be as accurate as it is precise. The precision for Faraday multi-collection can be predicted from the $^{235}U$ signal to noise ratio using Figure 10.

Direct comparison of the double-spike method with the TIMS total evaporation method indicates that the precision of the total evaporation method should be slightly better. However, the bias for the total evaporation method is much greater than for the double-spike method, and it is probable that real-world analyses by total evaporation will be much less reproducible.

The main drawback of the double-spike method for TIMS analyses is the requirement for an un-spiked analysis of the sample. Given the possibility of unparalleled accuracy and high precision that can be obtained with the double-spike using simultaneous multi-collection methods, the additional effort involved in splitting samples and making separate analyses may be worthwhile.

Finally, it is worthwhile repeating the caveat that the precision and accuracy for double-spiked analyses that have been calculated from these simulations only indicate the potential of the method. They do not necessarily represent the true analytical reproducibility. That reproducibility cannot be modeled with computer simulations; it must be determined by analyses.