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## Evaluation of Uranium and Plutonium Internal Standards

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OPERATED BY  
MARTIN MARIETTA ENERGY SYSTEMS, INC.  
FOR THE UNITED STATES  
DEPARTMENT OF ENERGY

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D. H. Smith  
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## ABSTRACT

Two internal standards have been synthesized and evaluated for application in mass spectrometric analysis of uranium. Each standard is a mixture of highly enriched  $^{233}\text{U}$  and  $^{236}\text{U}$ . One is used to refine  $^{235}\text{U}/^{238}\text{U}$  ratio measurements and the other for isotope dilution applications. An internal standard consisting of a mixture of  $^{242}\text{Pu}$  and  $^{244}\text{Pu}$  has been characterized for use in plutonium analyses. Precisions obtainable on pulse-counting instruments have been improved to about 0.1%.

## INTRODUCTION

Thermal ionization mass spectrometry is subject to a number of biases which must be corrected for if analyses of high accuracy are to be obtained. Among these are some that are relatively predictable: conversion efficiency at the first dynodes of electron multipliers varies with mass, as does the extraction efficiency of the drawing out potential field of the ion source (lighter ions are more readily extracted than heavier). There are, however, a number of biases that are unique for each sample and which are usually corrected for only on an average basis. The two most important are filament-source geometry and sample-filament chemistry. The first of these arises from the fact that, in thermal ionization, a new filament must be brought into position for each sample; the most common devices for accomplishing this are a sample insertion probe or a carousel.<sup>1</sup> With present technology, it is impossible to obtain exact reproducibility on the scale necessary for application of a truly constant bias correction. Detailed configuration of the filament or filaments, its position relative to the ion source, and the location of the sample on the filament are some of the obvious factors affecting bias due to geometry.

Sample-filament chemistry is, if anything, more difficult to control than geometrical factors. Many vagaries can be traced to interactions of the sample with the surface, which is usually rhenium for a single filament system. The chemical form of the sample must be rigorously controlled; this is not as easy as it may first appear because many elements are sensitive to excess oxygen, tending to leave the surface as molecular oxide species rather than the desired metal ions.

Since nitric acid is a common dissolution medium, it is not possible to eliminate prior to loading the excess oxygen provided by the nitrate. Evaporation as oxide species has profound effects on observed isotopic ratios by complicating the fractionation process. In the case of uranium,  $UO$  and  $UO_2$  are both more volatile than the metal. It is virtually impossible to control evaporation of oxide species in a fashion reproducible enough for analytical use and impossible to eliminate the oxygen that causes the problem.

Various means have been tried over the years to counteract this problem. The most successful has been to use a multiple-filament arrangement. In this technique the uranium sample is carefully oxidized after it has been loaded on its filament. In the mass spectrometer, the sample is evaporated as  $UO$  or  $UO_2$  and impinged on a second, hot ( $\sim 2100^\circ C$ ), filament where both fragmentation of molecular species and production of  $U^+$  occur. The crucial factor in this kind of analysis is to have the vast majority of the sample evaporate as a single species; which species seems to be of less importance.

However, multiple filament arrangements require samples of a microgram or so, and there are numerous applications where such quantities are inconvenient or impossible to obtain. For samples of a nanogram or less, single-filament thermal ionization is necessary, with all the attendant woes of non-reproducible filament chemistry. Samples prone to leave the filament as volatile oxides, such as uranium and plutonium, are reduced on the filaments before analysis by heating in benzene vapor or by adding a small amount of sucrose to the filament. Neither technique is fully effective in eliminating evaporation as oxides.

Some progress has recently been made in regulating surface interactions. The resin bead sample loading technique, in which uranium and plutonium are loaded onto the filament on anion resin beads, provides a reducing environment in intimate contact with the sample and significantly reduces evaporation as oxide species.<sup>2,3</sup> Ion microprobe studies reveal that the bead also seems to serve as a reservoir of sample, feeding it to the ionization region in a controlled manner.<sup>4</sup> Addition of an overcoat of rhenium slurried in a sucrose solution

enhances ion emission and also provides better control of evaporation,<sup>5</sup> as does electrodeposition of a layer of rhenium over the sample.<sup>6,7,8</sup>

For both single and multiple filament configurations, the normal procedure is to arrive at a bias correction per mass applicable to all samples. This bias correction is determined by repetitive analyses of a certified standard whose isotopic composition is known to a high degree of accuracy; this standard is usually NBS U-500, where the ratio of  $^{235}\text{U}$  to  $^{238}\text{U}$  is close to one. The correction factor necessary to convert the measured value of the ratio to the theoretical is then the bias correction required for that analysis. Several replicate analyses (we use at least six) are performed, the average of the bias correction obtained from them, and its value used in all subsequent analyses of routine samples.

The idea of applying an internal standard is that, if one knows the value of one isotopic ratio extremely well, comparison of the measured with the known value allows calculation of the bias correction applicable to the specific filament and operating conditions in question. Vagaries in fractionation will, in theory, automatically be corrected for, and a more accurate analysis will result. To apply this technique obviously requires at least three isotopes: two for the internal standard ratio and at least one for the sample. Bias correction is assumed to vary linearly with mass over the relative small range required for a single element, which is a valid approximation. It is known not to be linear over extended mass ranges.

Application of internal standards to thermal ionization mass spectrometry was first suggested by Dietz et al.<sup>9</sup> It has been applied for many years in strontium analyses, where the natural abundance ratio of isotopes 86 and 88 provide a built-in internal standard for calculating the bias to be applied to determine the abundance of the radiogenic nuclide,  $^{87}\text{Sr}$ .<sup>10</sup> It has been applied to molybdenum, nickel,<sup>11</sup> and other elements as well as to uranium.<sup>9,12,13</sup> The theory behind its application has been extensively treated by Dodson.<sup>14,15</sup>

This paper presents more extensive results with regard to the application of internal standards to uranium isotopic analyses than have

been available previously and should allow a realistic appraisal of its value over widespread isotopic and concentration ranges. We also report the first development of a plutonium internal standard, and we point out the area limiting further advance.

#### CALCULATIONAL CONSIDERATIONS

Because of the small size of the samples being analyzed, pulse-counting detection systems are used on all three mass spectrometers employed in this work; these multi-stage instruments have been previously described.<sup>16,17</sup> Previous work using internal standards addressed the case of analogue, as opposed to digital, output.<sup>11,13</sup> Although algebraic solutions of the simultaneous equations involved are possible, an iterative approach is generally used. Results for bias corrections obtained iteratively were identical to those obtained analytically in an independently developed computer program.<sup>18</sup>

Pulse counting yields output in digital form and simplifies to some extent treatment of the data by allowing corrections to be made directly to the counts collected for any given mass. The equations involved have been solved for the general case and are applicable to any element. In these equations, subscripts a and b represent the internal standard isotopes and c the analyte isotope; subscripts t, s, and m refer respectively to the tracer (spike or the internal standard), unspiked sample, and mixture of sample and spike; C refers to counts and R to isotopic ratios. Thus,  $R_{acs}$  refers to the isotopic ratio of isotope a to isotope c in the unspiked sample. For the case of uranium,  $a=233$ ,  $b=236$ , and  $c=238$ . To derive the necessary equations, which are completely general, we need to correct for the contribution of the spike (internal standard) to the sample mass (mass c) and for the contribution of the sample to the spike masses (a and b). Algebraically, we need to calculate  $C_{st}$ ,  $C_{at}$ , and  $C_{cs}$ . It is thus necessary to know the isotopic composition of the spike and the sample prior to analyzing the mixture.

We start by defining the number of counts for a given isotope in the mixture of spike and sample as the sum of its constituents. We have chosen mass "b" here, but mass "a" could obviously be substituted and equivalent results obtained.

$$C_{bm} = C_{bs} + C_{bt} \quad (1)$$

$$C_{cm} = C_{cs} + C_{ct} \quad (2)$$

But we know that

$$C_{bs} = C_{cs} R_{bcs} \quad (3)$$

and

$$C_{ct} = C_{bt} R_{cbt} \quad (4)$$

Thus, by substitution, one obtains:

$$C_{bm} = C_{cs} R_{bcs} + C_{bt} \quad (5)$$

and

$$C_{cs} = C_{cm} - C_{bt} R_{cbt} \quad (6)$$

Hence

$$C_{bm} = (C_{cm} - C_{bt} R_{cbt}) R_{cbt} + C_{bt} \quad (7)$$

Thus, the number of counts of two internal standard isotopes corrected for the contribution of the sample are calculated from the following equations:

$$C_{at} = \frac{C_{am} - R_{acs} C_{cm}}{1 - R_{acs} R_{cat}}, \quad (8)$$

$$C_{bt} = \frac{C_{bm} - R_{bcs} C_{cm}}{1 - R_{bcs} R_{cbt}}. \quad (9)$$

The counts of the analyte isotope due to the sample can then be calculated from either  $C_{at}$  or  $C_{bt}$ :

$$C_{cs} = C_{cm} - C_{at} R_{cat} \quad \text{or}$$

$$C_{cs} = C_{cm} - C_{bt} R_{cbt}. \quad (10)$$

To calculate the bias correction per mass,  $f$ , necessary to apply to the data, the following equation is used:

$$f = \left( \frac{R_{abt}}{C_{at}/C_{bt}} - 1 \right) / (M_b - M_a), \quad (11)$$

where  $M_x$  is the relevant isotopic mass.

In the iterative scheme, the various corrected counts are estimated using equations 8-10 and an approximate bias correction calculated using equation 11. The new values of counts calculated by applying this bias correction are then inserted into equations 8-10 and the process repeated until successive values of a test ratio ( $^{235}\text{U}/^{238}\text{U}$  if refinement of that ratio is required;  $^{233}\text{U}/^{238}\text{U}$  or  $^{236}\text{U}/^{238}\text{U}$  for isotopic dilution work) agree to within 1 ppm. This usually takes three or four iterations and is accomplished automatically in the computer programs that process the data.<sup>19,20</sup> The iterative protocol is outlined in Table 1.

Table 1. Iterative Computational Procedure

- 
1. Correct all mass positions for deadtime and background.
  2. Correct relevant mass positions for contributions from second component: major spike components for sample contribution; sample peaks for spike contribution.
  3. Calculate bias correction per mass and apply to counts at all mass positions.
  4. Check test ratio for convergence; return to step 2 if test fails, otherwise proceed to further calculations.
- 

## EXPERIMENTAL

Synthesizing two uranium spikes was necessary because of the scarcity of high purity  $^{236}\text{U}$ . Isotope dilution procedures require about 1 mg of spike per sample, and the total U.S. supply of  $^{236}\text{U}$  of greater than 99% purity is only about 50 mg. Enough high purity  $^{236}\text{U}$  was obtained for use in refinement of  $^{235}\text{U}/^{238}\text{U}$  ratios. In this case, sample and spike were equilibrated on a glass microscope slide; only a few nanograms of spike were consumed for each sample. To reduce uncertainty in the correction of  $^{235}\text{U}$  for contribution from the spike, sample-spike ratios of between 5- and 20-to-one were used.

Isotope dilution work, where the  $^{235}\text{U}$  need not be monitored as the isotopic composition of the sample is known, presents less stringent demands for isotopic purity of the spike components. There is a relatively abundant supply of  $^{236}\text{U}$  of about 89% isotopic purity, and we obtained some for this purpose. Equilibration in this case is done in vials containing sample solution and about one milligram of mixed spike in dilute  $\text{HNO}_3$  so that the spike-sample mixture yields a  $^{233}\text{U}/^{238}\text{U}$  ratio of about one.

The two components ( $^{233}\text{U}$  and  $^{236}\text{U}$ ) were mixed to give a ratio of about one in each spike. The isotopic compositions of the individual components and of the two resulting internal standards are given in Table 2.

Table 2. Isotopic Composition of Uranium Internal Standards

Isotope	233	234	235	236	238	233/236
High Purity Spike						
233 Component	99.925	0.0317	0.0032	0.0014	0.038	
236 Component	0.0108	0.0008	0.201	99.674	0.113	
Mixture	46.935	0.0155	0.1084	52.864	0.0771	0.88785
Low Purity Spike						
233 Component	99.528	0.185	0.062	0.015	0.209	
236 Component	0.000	0.119	9.25	89.27	1.32	
Mixture	47.899	0.153	4.903	46.250	0.795	1.03566

These spikes were first isotopically calibrated by using the well-known  $^{235}\text{U}/^{238}\text{U}$  ratio of NBS U-500 as the internal standard to determine the  $^{233}\text{U}/^{236}\text{U}$  ratio; the  $^{235}\text{U}/^{238}\text{U}$  ratios in the spikes were then established by analyzing the spikes alone and using the known  $^{233}\text{U}/^{236}\text{U}$  ratios as internal standard ratios. Results of these analyses are given in Table 3. The precisions quoted are standard deviations calculated from the formula

$$s = \left[ \sum_{i=1}^n [(x - x_i)^2 / (n - 1)] \right]^{1/2}, \text{ where } x_i$$

are the individual values and  $x$  the average of  $n$  determinations.

Table 3. Calibration of Uranium Internal Standards

	$^{233}\text{U}/^{236}\text{U}$	$^{235}\text{U}/^{238}\text{U}$	$^{238}\text{U}/^{233}\text{U}$
High Purity	0.88785+0.00070	0.002051+0.000003	0.001458+0.000030
Low Purity	1.03566+0.00022	0.10196 +0.00005	0.01657 +0.00003

The concentration of the low purity spike was determined by calibration with gravimetrically prepared solutions of NBS U-950 (natural uranium). Knowledge of the concentration of the high purity spike was unnecessary.

#### RESULTS AND DISCUSSION

The effect of the high purity internal standard was evaluated by processing the data from replicate analyses of two samples using both the bias correction calculated on the basis of the internal standard and the average bias correction in routine use for the instrument in question. Thus the data for each sample were identical for the two processings; only the calculational procedure was changed. Both samples were equilibrated with the spike in solution before loading on the filaments. The results obtained are given in Table 4. Table 5 contains detailed results for NBS010.

Table 4. Comparison of Results with and without Use of an Internal Standard

Sample	Analyses	Without	Bias	With	Bias
		$^{235}\text{U}/^{238}\text{U}$	Correction % Mass	$^{235}\text{U}/^{238}\text{U}$	Correction % Mass
NBS U010	6	0.012172 <u>+0.000043</u>	0.296	0.012192 <u>+0.000009</u>	0.234
SALE H-66	6	0.025770 <u>+0.000053</u>	0.296	0.025702 <u>+0.000029</u>	0.384

Significant improvement in precision was noted for each sample. Neither of the two  $^{235}\text{U}/^{238}\text{U}$  values can be compared directly to the accepted one for the sample in question since each reflects a contribution from the spike. Tables 4 and 5 also list the average bias correction per mass applied in each case. The value applied when no internal standard calculations were done (0.296%) was derived initially by analyzing NBS-U500 and then by refining through routine checks against NBS-U010. The average values reported in Table 4 for the internal

Table 5. NBS U 010 with and without Internal Standard Calibration

	<u>Regular (without)</u>			
	<u>233/238</u>	<u>235/238</u>	<u>236/238</u>	<u>BC/mass</u>
1	0.87763	0.012215	0.98781	0.296
2	0.87912	0.012197	0.98929	
3	0.87282	0.012133	0.98661	
4	0.86603	0.012106	0.98327	
5	0.87644	0.012205	0.98751	
6	0.87592	0.012176	0.98723	
Avg.	0.87466	0.012172	0.98695	
S.D.	0.00472	0.000043	0.00201	
RSD, %	0.5	0.4	0.2	
	<u>Internal Standard (with)</u>			
	<u>233/238</u>	<u>235/238</u>	<u>236/238</u>	<u>BC/mass</u>
1	0.87652	0.012206	0.98732	0.321
2	0.87758	0.012183	0.98851	0.335
3	0.87793	0.012182	0.98891	0.179
4	0.87752	0.012188	0.98844	0.033
5	0.87720	0.012199	0.98808	0.267
6	0.87686	0.012195	0.98770	0.266
Avg.	0.87727	0.012191	0.98816	0.234
S.D.	0.00052	0.000009	0.00058	0.113
RSD, %	0.06	0.08	0.06	48.

standard calculations were based on the averages obtained from the six samples (See Table 5) which are themselves averages of the ten individual determinations which comprise an analysis. Each one thus represents about 60 individual determinations.

The variation from sample to sample (and sometimes from run to run) of this bias correction per mass graphically illustrates the power of the internal standard. Even though great care is exercised to take data under as nearly identical conditions as possible, we have observed the bias correction per mass to vary from more than 0.5% per mass to negative values. Table 6 tabulates the variation of bias correction within a single analysis.

One of the critical parameters in normal isotopic analyses is to be sure data are taken on approximately the same portion of the isotopic fractionation curve for each sample. This is usually estimated on a time vs temperature coordinate system and is at best only a crude approximation. To investigate the effect of the internal standard on this parameter, we performed repetitive analyses on the same filament loading. The results are shown in Table 7, where concentration results for SALE sample H-66 are reported. Each point listed represents the average of at least 15 runs, more than enough for a normal complete analysis. The effect of the internal standard is obvious; only near the end, after more than 4 hours of operation at over 1750°C, does it fail to produce an accurate result. Fractionation at this point is severe and ion counting rates are quite low. It thus appears that the requirement to take data at highly reproducible time-temperature points is not as stringent when an internal standard is used; this is a powerful advantage.

One of the interesting observations made in the course of these experiments is that the mass spectrometric analysis may not always be the limiting factor in the accuracy of a measurement. Two SALE H-66 samples were prepared in parallel; all analytical steps, including weighing, dissolution, and spiking, were carried out independently. The uranium concentrations determined are given in Table 8. Note that no concentration for preparation 1 is as high as the lowest for preparation 2; the two data sets have no overlap. It seems reasonable to conclude

Table 6. Variation of Bias within a Single Analysis

Run	Bias (% Mass)
1	0.644
2	0.454
3	0.462
4	0.632
5	0.521
6	0.837
7	0.633
8	0.530
9	0.543
10	0.500
Avg.	0.576
S.D.	0.115

Table 7. Uranium Results from a Single Resin Bead Run to Exhaustion (SALE H-66)

Run	Avg. Bias 238/233	Corr. Int. Std. 238/233	Avg. Bias Corr. Wt. %	Int. Std. Wt. %
1	0.6342	0.6352	87.82	87.96
2	0.6403	0.6341	88.66	87.80
3	0.6372	0.6341	88.23	87.80
4	0.6417	0.6338	88.86	87.77
5	0.6380	0.6342	88.34	87.81
6	0.6476	0.6342	89.68	87.82
7	0.6386	0.6340	88.43	87.79
8	0.6203	0.6339	85.93	87.81
9	0.6388	0.6347	88.46	87.89
10	0.6354	0.6345	87.97	87.85
11	0.6350	0.6348	87.93	87.90
Avg.	0.6370	0.6343	88.21	87.84
S.D.	0.0067	0.0004	0.92	0.06
%RSD	1.05	0.07	1.05	0.07

that uncertainties in weighing, pipetting, etc., attendant upon sample preparation are the source of this phenomenon. Under normal conditions, this fact would not have been observed: the precision for all seven analyses is  $\pm 0.05\%$ .

A systems calibration check was made by analyzing replicate loadings of a series of NBS standards. The results are given in Table 8. All samples were equilibrated with the high purity spike on glass microscope slides. The dimples in the slides were used to hold the solutions; their volumes were 30-40  $\mu\text{L}$ . This allowed mixing about 30  $\mu\text{L}$  of sample with about 10  $\mu\text{L}$  of spike solution. Efforts to achieve equilibration in the filaments failed. The volume of each filament is about 1  $\mu\text{L}$ , and, due to the canoe shape,<sup>21</sup> capillary action drew the bulk of the solution to the two ends. This seemed to prevent adequate mixing of successive 1  $\mu\text{L}$  loadings of sample and spike in about 20% of the cases. To reduce corrections to the 235 mass position, an approximate 10:1 sample to spike ratio was used. It should be noted that, for the NBS-U500 standard, this ratio requires a correction to the 235 position of about 1%.

The results listed in Table 9 deserve some comment. We consistently obtained precisions of about  $\pm 0.1\%$ , and at higher enrichments (5% or more), we were consistently better than that figure except for NBS-U970; our relatively poor results ( $\pm 0.3\%$ ) for this standard are unexplained. In the third column of the table, we list the values obtained by dividing the measured 235/238 ratio by the certified values; they are thus a measure of our accuracy. We were accurate to  $\pm 0.1\%$  or better in all cases but one; NBS-U750 stubbornly refused to conform. The original set of six measurements and a second set of six gave results that were statistically indistinguishable; the results in the table reflect all twelve measurements. Our precision on the 235/238 ratio was  $\pm 0.04\%$ , and we are 0.17% high for the average value. We have no explanation of this unless the certified value is slightly in error.

The low purity spike was evaluated using SALE samples. Results are given in Table 10. Again, the power of the technique is evident, with relative standard deviations of better than 0.1%. The poorer precision reported for the 300 series sample undoubtedly reflects its known lack of the desired homogeneity.

Table 8. Analyses of SALE H-66: Two Preparations  
(Concentrations in % U)

Replicate	Prep 1	Prep 2
1	87.738	87.823
2	87.744	87.803
3	87.742	87.813
4		87.836
Avg.	87.741	87.819
S.D.	0.003	0.014
RSD, %	0.003	0.016

Table 9. Systems Calibration

Standard	Pct. 235	5/8 Meas.-5/8 Theo.	% RSD
005	0.4895	0.9999	0.10
950	0.720	1.0000	0.14
010	1.0037	0.9992	0.11
020	2.038	1.0008	0.14
030	3.046	0.9999	0.11
050	5.010	1.0008	0.03
100	10.190	1.0001	0.05
200	20.013	1.0001	0.08
500	49.696	1.0002	0.07
750	75.357	1.0017	0.04
930	93.336	1.0004	0.08
970	97.663	1.0009	0.31
Avg.		1.0003	0.11

Table 10. Quantitative Results of SALE Samples

H-66		300 Series	
Analysis	Pct. U	Analysis	Pct. U
1	87.80	1	88.06
2	87.75	2	88.10
3	87.78	3	87.97
4	87.79	4	88.09
5	87.70	5	88.15
6	87.74	6	88.15
		7	88.19
Avg.	87.76	8	87.98
S.D.	0.04	9	87.97
Pct RSD	0.04	10	88.04
Reference	87.78	11	88.06
Avg/Ref	0.9998	12	88.09
		13	88.00
		14	88.02
		Avg.	88.06
		S.D.	0.07
		Pct RSD	0.08
		Reference	88.08
		Avg/Ref	0.9998

In addition to the uranium internal standards, we have synthesized, characterized, and put into use one of plutonium. The isotopes chosen for internal standard use were 242 and 244. The composition of the enriched isotopes and the resulting mixture are given in Table 11 and typical results in Table 12.

Table 11. Pu Internal Standard

	238	239	240	241	242	244
High 242	0.0004	0.0048	0.0518	0.0246	99.853	0.0648
High 244	0.0015	0.0409	0.0863	0.0008	0.911	98.960
Mix	0.00056	0.02258	0.06813	0.00892	50.0343	49.8655

Table 12. Typical Results Using the Pu Internal Standard

	238/239	240/239	241/239
NBS 947*, certified	0.00358	0.24139	0.03469
NBS 947, measured	0.00359	0.24133	0.03468
Std. Dev.	0.00002	0.00020	0.00004
RSD, %	0.6	0.08	0.12

Corrected to February 15, 1983

We had no test sample for plutonium analogous to the uranium ones provided by SALE, but external precision of measurements of unknown samples was about what we obtained for total uranium: better than +0.1%.

Widespread application of a plutonium internal standard is precluded by the lack of availability of <sup>244</sup>Pu. It is very expensive to produce, and, at the time of writing (August, 1985), the outlook for further production is bleak.

It is particularly disappointing that this is the case because this technique would have a profound effect on safeguards. With the latest state-of-the-art isotope ratio mass spectrometers, precisions of better than  $\pm 0.01\%$  have been attained.<sup>13</sup> Table 13 lists results obtained using our new Vacuum Generators VG-354 isotope ratio mass spectrometer. A prospective uranium internal standard made of a mixture of enriched  $^{233}\text{U}$  and  $^{236}\text{U}$  was analyzed in replicate, and NBS U-500 was used as the internal standard. The two ratio columns contain values for the mixture of the proposed spike and NBS U-500 and those with the contribution of the NBS standard stripped away; it is this second value that would be used as the internal standard ratio. Precisions of  $\pm 0.005$  percent were obtained and are comparable to many titrimetric techniques; it is the possibility of obtaining such high quality analyses from microgram-sized samples (as opposed to milligram-sized) that is so attractive to safeguards. The international program, administered by the International Atomic Energy Agency (IAEA) from Vienna, analyzes several thousand samples a year. The cost savings that could be realized by a drastic reduction of sample size is enormous.

Table 13. Internal Standard Analysis Using VG-354

Position	Mixture	Sample
	233/236	233/236
1	0.888260	0.889491
2	0.888146	0.889377
3	0.888174	0.889405
4	0.888209	0.889440
5	0.888161	0.889393
6	0.888213	0.889444
7	0.888254	0.889486
Avg.	0.888202	0.889434
S.D.	0.000044	0.000044
RSD, %	0.005	0.005

There is currently under way a joint experiment involving the IAEA, ORNL, the French nuclear laboratory at Saclay, and the French reprocessing facility at LaHague. ORNL's participation is funded by the International Safeguards Project Office under ISPO Task A-126. Samples of spent reactor fuel were taken at LaHague and spiked with an internal standard composed of a mixture of uranium ( $^{233}\text{U} + ^{236}\text{U}$ ) and plutonium ( $^{242}\text{Pu} + ^{244}\text{Pu}$ ). A reference sample was processed in parallel with the spent fuel samples. Samples were shipped to the various laboratories both on resin beads and as residues of dried solutions. Results from the two techniques will be compared, as will results obtained using the internal standards to those obtained using an average bias correction. It is hoped that, since internal standard calculations correct each instrument to the same ratio, the results using the new technique will clearly demonstrate its superiority. One possible limitation on precision was encountered in the fact that the  $^{242}\text{Pu}/^{244}\text{Pu}$  ratio was about 2. Our technique of analyzing plutonium and uranium sequentially from a single resin bead demands that we analyze plutonium at temperatures low enough to limit uranium contribution of the 238 mass position to manageable levels. In practice, we analyze plutonium at count rates of 100,000 per second for the most abundant isotope. At a count rate of 50,000 per second for  $^{244}\text{Pu}$ , internal precision for a typical single run is limited to  $\pm 0.14\%$ ; for an entire analysis of ten runs it would be  $\pm 0.04\%$  based on counting statistics of  $^{244}\text{Pu}$  alone. Doubling the count rate reduces these levels to  $\pm 0.10\%$  and  $\pm 0.03\%$ , respectively. At our normal counting rate for uranium of 300,000 per second, the values are  $\pm 0.06\%$  and  $\pm 0.02\%$ . For these samples, we are thus operating in a range where we are close to being count-rate limited in our precision and any increase in count rate will be reflected directly in an improvement in precision.

Because the scarcity of suitable enriched isotopes precludes widespread application of the internal standard technique in the most straightforward manner, it is desirable to explore alternatives. One idea worth investigating involves spiking concentrated spent fuel solutions with a mixture of uranium and plutonium comprised of a single

enriched isotope of each element. These two isotopes would serve as isotope dilution markers and could be relatively abundant (and hence relatively inexpensive) isotopes.  $^{235}\text{U}$  and  $^{240}\text{Pu}$  suggest themselves for this role. Other possibilities are  $^{234}\text{U}$  (rare and expensive) and  $^{239}\text{Pu}$  (plentiful but the most abundant isotope in spent fuel).  $^{238}\text{Pu}$  and  $^{241}\text{Pu}$  are unsuitable because of their short half lives. Internal standards would then be added at the analytical laboratory and would serve solely to calibrate the instrument. In this manner, a minimum of the isotopes in short supply would be used; it is possible that each filament could be spiked individually, thus reducing the amount of each isotope to either a microgram or a nanogram per filament, depending upon instrumentation.

There are two drawbacks to such a plan. The first is that, for each sample, three analyses will be required instead for two. These will be the unspiked sample, the sample plus isotope dilution spike, and the sample plus isotope dilution spike plus internal standard. The second drawback is that a much larger correction for the contribution of sample to the isotope dilution mass position will have to be made than was previously required. Uranium composition in spent fuels has a  $^{235}$  content of about 1% and should thus not impose insuperable difficulties. On the other hand,  $^{240}\text{Pu}$  often reaches 20% abundance, and satisfactory correction for its contribution is problematic. A series of experiments to evaluate this procedure is being planned and should be carried out.

#### CONCLUSIONS

Application of internal standards clearly leads to significantly enhanced precision and will be of enormous benefit to programs such as safeguards where highly precise results are required. Attaining precisions of 0.1% has been long-sought goal of mass spectrometrists in small sample analysis. While we cannot claim to have reached this point yet, it does seem to be within reach for the first time. A big step could be made toward it if  $^{236}\text{U}$  and  $^{244}\text{Pu}$  in greater than 99.9%

purity were to become available in sufficient quantities. It would save enormous time (to say nothing of tedium) if a single internal standard could serve both to refine  $^{235}\text{U}/^{238}\text{U}$  measurements and in isotopic dilution. The ineluctable barrier of precision in most of this work is about 0.04%, which is imposed by counting statistics. Our goal is to approach this barrier as closely as possible.

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