CONF-890565--3

LA-UR -89-1684

LA-UR--89-1684

DE89 013444

Received

JUN 07 1989

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TITLE HIGH PRECISION ISOTOPIC ANALYSES OF URANIUM AND PLUTONIUM BY TOTAL SAMPLE VOLITILIZATION AND SIGNAL INTEGRATION

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SUBMITTED TO 11th Symposium on Safeguards and Nuclear Material Management
LUXEMBOURG, May 30 - June 1, 1989

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HIGH PRECISION ISOTOPIC ANALYSES OF URANIUM AND PLUTONIUM BY TOTAL SAMPLE VOLATILIZATION AND SIGNAL INTEGRATION

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ABSTRACT

Techniques have been developed which permit rapid, high-precision analyses of uranium and plutonium by multiple-filament thermal ionization mass spectrometry utilizing a commercial multicollector instrument. The salient feature of the method is volatilization of the entire sample while simultaneously integrating the signal from each isotope, thus virtually eliminating the effects of isotope fractionation in the evaporation process. The method permits the analysis of samples much smaller than required for conventional techniques using Faraday collectors and is expected to have application in the analysis of many elements in addition to uranium and plutonium. Run-to-run reproducibilities of ~0.02% (RSD) have been obtained for isotope ratios of uranium and plutonium.

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1. INTRODUCTION

Conventional thermal ionization techniques rely on the use of rigidly controlled experimental conditions such as sample size, purity, chemical form, heating pattern, as well as other parameters to attempt to reproduce fractionation behavior and biases observed due to the evaporation process.[1] Sample evaporation is generally believed to follow the Rayleigh distillation law in which the lighter isotopes are preferentially evaporated.[2] Observed ratios, in general, change throughout the analysis, producing a fractionation curve. To obtain a stable ion beam for single collector measurements and to reduce the rate of fractionation, only a small percentage, typically 1% to 50%, of the sample is actually evaporated. Unfortunately, unless a known isotopic ratio is present in the sample, either inherent or added, one has no way of knowing at a given point in the analysis, the corresponding position on the fractionation curve.[3] The use of an internal normalizing ratio, when available, or an added double-spike can improve reproducibility dramatically.[4,5] However, not all elements are amenable to these techniques and the double-spike method generally requires an additional analysis of the unspiked material.

A direct outcome of Rayleigh distillation is that if all atoms are evaporated, and all, or a fixed fraction, of them collected, no bias is introduced in the evaporation process.[6] While this has been known for many years, application to single collector measurements has been difficult. Problems include the necessity of obtaining a stable ion beam and uncertainties in the amount of sample evaporated but not measured during the analysis and the unknown amount of material remaining on the filament at the termination of the analysis.

The availability of multicollector instrumentation, however, eliminates most of the problems in applying the total evaporation method. Some advantages are: a stable ion beam in no longer required because all isotopes are collected simultaneously and more intense ion beams can be obtained as a result, and the duty cycle, the fraction of time that the ion beams are actually being collected, is nearly 100%.

Accordingly, techniques and software were developed to exploit the advantages of the multicollector system. Similar techniques have been simultaneously developed by others.[7]

2. EXPERIMENTAL

Apparatus

A commercial mass spectrometer, (VG Isotopes, Winsford, England, Model VG-354) equipped with five adjustable Faraday collectors and a Daly detector ion-counting system was employed in this work. Demountable triple filament assemblies and filaments of high purity rhenium were used. The instrument is equipped with a 16 sample turret and is fully automated, except for collector positioning.

Reagents

Uranium and plutonium isotopic standards U-500, U-900, U-100, U-[illegible], NBS-946, NBS-947, NBS-948 (US National Bureau of Standards) and CRM 128 (New Brunswick Laboratory, US DOE) were converted to the nitrate form and diluted to nominal concentrations of 0.5 mg/ml (U) and 0.0[illegible] mg/ml (Pu) in $1\underline{M}$ HNO_3. The plutonium standards, except for CRM-128, were purified by ion exchange to remove ^{241}Am ingrowth.

Analysis Procedure

The standard instrument operating software was modified to permit analyses in the total evaporation integration mode. These modifications were made with the goal of minimizing sample evaporation during the initial stages of peak location and focusing, and of rapidly raising the intensity level to as large a value as practical after starting the integration. Details of the procedure are as follows. While holding the sample filament current at zero, the ionizing filament is brought to operating temperature by monitoring the ^{187}Re intensity. The [illegible] peaks are next located and the total beam intensity is set to 10^{-14} A using the ion-counting system. Use of the ion-counting system at this stage, while not essential, minimizes the consumption of sample before initiation of the integration. After the peaks have been located and focusing has been completed, the Daly system is turned off, Faraday amplifier zeros are measured, and the integration/current ramp is started. Before each 5-second integration period, the sample filament current is incremented in steps of 20 to 100 mA, depending on the present beam intensity. The maximum beam intensity is controlled roughly between 6 X 10^{-11} and 7 X 10^{-11}A by suspending the current ramp when the intensity is within these limits. Because all isotopes are collected simultaneously, a stable ion beam is not required. The integration/current ramp continues until sample exhaustion ($<10^{-13}$ A intensity). A second set of amplifier zeros is measured at the end of the analysis and averaged with the first set.

Individual ratios are calculated and printed for each 5-second integration period. The final ratios, however, are based on the summations of the individual DVM readings, corrected for amplifier zeros, which are proportional to the integrated intensities.

3. RESULTS AND DISCUSSION

A typical intensity profile and current ramp for a plutonium sample is shown in Fig. 1. Note that the intensity rises rapidly and is maintained at a high level, in this case 3 X 10^{-11}A, yielding a high signal/noise ratio, and then drops rapidly on exhaustion of the sample. The jagged nature of the profile in the mid portion is due to the step wise incrementation of the filament current. The rapid drop in intensity on sample exhaustion is important in reducing the effect of the termination intensity level on the integrated ratios.

Integration times are generally about 10 minutes, but [illegible], depending on the quantity of sample loaded. Overhead activities such as turret positioning, ionizing filament warm-up, focusing, and channel [illegible] calibration bring the total analysis time to about [illegible] minutes.

A fractionation plot for a uranium ([illegible]) sample and a theoretical curve, based on a simple fractionation model, are shown in Fig. [illegible] [illegible] the rapid drop in the observed ratios early in the analysis to a value very near the true ratio and then the slow change until >95% sample consumption. The difference between the theoretical and observed curves is probably due to the assumption of complete mixing of the residual sample in the model. In the total evaporation procedure, the sample is volatilized very rapidly and hence mixing probably only occurs in the top few monolayers of sample. This view is reinforced by the behavior at the end of the analysis when only a few monolayers are present, in which a rapid drop in the ratio is observed, more in line with the model.

The fact that even extreme variations in the observed fractionation behavior during the analysis can be overcome by total integration is demonstrated in Fig 3, a plot of the results of a Sr analysis. In contrast to the behavior of U or Pu, which usually exhibit a single peak in the intensity profile and a monotonically decreasing ratio (light/heavy ratios are plotted), Sr exhibits two, possibly three, distinct peaks as the filament temperature is ramped with a corresponding variation in the observed 86/88 ratio. This behavior is apparently due to the presence of multiple chemical species which volatilize at different temperatures. In spite of the volatilization of different species, however, the integrated ratio is very near ([illegible]) the certified value for this standard.

Results obtained on uranium and plutonium standards which indicate the very low biases observed with the technique are shown in Table 1. These data have been corrected only for the amplifier gain, determined with a built-in current source, and the relative collector efficiency, discussed later. The observed values are all well within the uncertainty limits of the standards, indicating that, within these uncertainty limits, "true" or unfractionated ratios are obtained.

The extremely high precision attainable on replicate plutonium and uranium analyses is shown in Tables 2 and 3, respectively. [illegible] precision (RSD) for the major isotope ratios is typically [illegible]. While these data represent short term (1 week) variation, measurements made over periods of several months show only slightly expanded [illegible] RSD precision limits.

The precision of minor isotope measurements is determined primarily by the noise level and drift of the amplifiers, and the maximum intensity level that can be tolerated on the major isotope. Observed values are typically ± 2 to ± 3 ppm abundance for integrated intensities in the 10-50 V-min(Volt-minutes) range. The loading of larger samples would probably not reduce these values significantly.

In the case of ^{238}Pu measurements, the contribution due to ^{238}U from filament materials or the sample itself must be considered. Data on NBS-947 indicates a contribution of about ± 10 ppm abundance from these sources.

The amount of sample loaded was 10-20ng Pu and 100-200 ng U. With 10^{11} Ω input resistors, these sample sizes yielded integrated intensities of about 10 V-min for plutonium and 50 V-min for uranium. The total analysis time for samples of this size is typically 30 minutes. As indicated in Tables 2 and 3, the total integrated intensity for a given size sample may vary considerably, particularly for uranium. This affect may be due to the sensitivity of the uranium ionization to oxygen pressure in the source region.

Using conventional techniques, where only a portion of the sample is evaporated, care must be exercised to control the amount of sample loaded because the fractionation behavior is affected. This can be difficult or impractical in real-world situations where the precise amount of sample may not be known. In Table 4 are shown the effects of a sample size variation of a factor of 10 for uranium using the total evaporation procedure. While there is a discernible effect, on the order of 0.02%, it is small compared to what one would expect using conventional techniques. In addition, the integrated intensity becomes a valuable diagnostic tool for rejection of analyses which yield integrated intensities far outside the norm. With conventional techniques, one often has little indication of problems based on the analysis data alone.

In general, the precision of replicate plutonium analyses is somewhat better than uranium. This is thought to be due to the fact [illegible], the volatilization of Pu from the filament is more nearly complete. After analysis, several U and Pu sample filaments were dissolved and analyzed by isotope dilution to determine the residual sample [illegible] filament. Residual Pu was less than 1% while uranium averaged at [illegible]. The larger uranium residual may be due to diffusion of U into the filament material at the somewhat higher temperatures required for U volatilization.

Secondly, the production rate of uranium oxide ions may vary during the analysis, and hence alter the fraction of sample molecules converted to U^+ ions and collected. The production of plutonium oxide ions appears to be insignificant.

Another interesting difference in the behavior of U and Pu is that uranium volatilizes quite differently from filaments which have been previously degassed. On undegassed filaments, both elements exhibit a relatively rapid drop in intensity as the sample is exhausted, the desired behavior. On degassed filaments, however, uranium exhibits a long, relatively low intensity tail, which may last many minutes even at filament currents of 4A (≈1900°C). An explanation of this behavior is not readily apparent.

Collector Calibration

The standard VG software provides for determination of the collector efficiency, which may be defined as the ratio of the gains measured with the current source to those measured with an actual ion beam, by sequentially measuring an ion beam, such as ^{187}Re and ^{133}Cs, on each of the collectors. Because this is essentially a peak switching technique, and subject to beam instabilities, long data acquisition times are often required to obtain adequate precision. In addition, the standard procedure was not fully automated. A fully automated procedure was developed which allowed the acquisition of large amounts of data in a more convenient manner. The collector efficiencies determined in this manner, using a ^{238}U ion beam, varied from +.00[illegible] to +.01[illegible], with respect to the axial collector, with a precision of about .00[illegible], based on [illegible] filament loadings.

To check the validity of the efficiencies measured in this manner, a series of measurements were made using the total evaporation [illegible] procedure in which a one mass unit separation ratio, [illegible], was measured on each of the four pairs of adjacent collectors [illegible] Ax, Ax H1, H1 H[illegible]

Unfortunately, identical results were not obtained on each pair of collectors, the differences indicating errors on the order of .01 in the efficiency factors.

Accordingly, a method was sought for calibrating the collectors in the simultaneous collection mode to resolve this discrepancy. Because no standards are available having ratios certified to the accuracy levels required (<.01%), a procedure was sought which would be independent of the true value of the ratio being measured. An inspection of the possibilities of using a one mass unit separation ratio such as Pu 240/239, reveals an unsolvable system since for N collectors, only N-1 equations can be written, and the number of unknowns is N (i.e., the relative gain of N-1 collectors plus the unknown ratio). Similarly for other isotope mixtures, the number of unknowns is always one more than the number of independent equations that can be written for a fixed collector arrangement.

However, for adjustable collector systems, calibration is possible using a mixture of isotopes such as U-233-235-238 without any knowledge of the actual isotope ratios or fractionation during the analyses by repositioning the collectors. Consider the arrangements shown in Fig.4:

For position 1 we have

$$r_1 = \frac{F1}{F4} R_1 (1-\alpha_1)^5 \qquad \text{eq 1}$$

$$r_2 = \frac{1}{F_4} R2 (1 - \alpha_1)^3 \qquad \text{eq 2}$$

where r1,r2 = observed ratios, corrected for amplifier gains

F_1, F_4 = collector efficiency factors, L2 and H.

R1, R2 = True ratios 233/238 and 235/238, in sample

α_1 = Fractionation factor for 1 AMU for the analysis

For position 2

$$r_3 = \frac{F1}{F4} \cdot R1 \ (1-\alpha_2)^5 \qquad \text{eq 3}$$

$$r_4 = \frac{F2}{F4} R2 \ (1-\alpha_2)^3 \qquad \text{eq 4}$$

where r_3, r_4 = observed ratios

F_2 = Collector efficiency factor, L1

α_2 = Fractionation factor for second analysis

By combining eq 1 and eq 3 we have

$$\frac{r_1}{r_3} = \left(\frac{1-\alpha_1}{1-\alpha_2}\right)^5 \quad \text{or} \quad \left(\frac{1-\alpha_1}{1-\alpha_2}\right)^3 = \left(\frac{r_1}{r_3}\right)^{3/5} \qquad \text{eq 5}$$

combining eq 2 and 4 we have

$$\frac{r2}{r4} = \frac{1}{F_2} \cdot \left(\frac{1+\alpha_1}{1+\alpha_2}\right)^3 \qquad \text{eq 6}$$

Combining eq 5 and 6 and solving for F_2 we have

$$F_2 = \frac{r_4}{r_2}\left(\frac{r_1}{r_3}\right)^{3/5} \qquad \text{eq 7}$$

For statistical analysis of multiple runs at the two positions the terms can be regrouped as

$$F_2 = \frac{r_1{}^{3/5}}{r_2} \cdot \frac{r_4}{r_3{}^{3/5}} \qquad \text{eq 8}$$

because the expressions in brackets should be constant from run to run for a given collector arrangement.

Similar rearrangements can be devised for determining the remaining efficiency factors F_1, F_3 and F_4.

A comparison of the efficiencies determined in this manner with those determined by peakswitching a single ion beam is shown in Fig 5. While the differences are not large (.002 to .01%), they are sufficient to account for the variations observed when measuring a given isotope ratio on different pairs of collectors.

4. CONCLUSIONS

The combination of multicollector instrumentation and techniques which permit total sample volatilization has been found to provide significant improvements in analysis precision and sample through-put. The insensitivity of the method to sample size and drying procedures allows the relaxation of controls normally applied in order to achieve high precision and accuracy. The method should be applicable to many elements in addition to those studied so far, which include U, Pu, Am, Eu and Sr. It appears that the method is capable of producing near-absolute measurements based on uranium and plutonium standard data. Unfortunately, an order-of-magnitude improvement in reference material uncertainties will be required to evaluate the method fully.

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Fig 1: A typical intensity profile and current ramp for a plutonium sample.

Fig 2: Observed and theoretical fractionation curves (U500)

Fig 3: Intensityprofile, fractionation curve, and current ramp for a strontium sample.

Fig 4: Example of collector calibration (L1/Ax) by repositioning of L2 and H2 collectors.

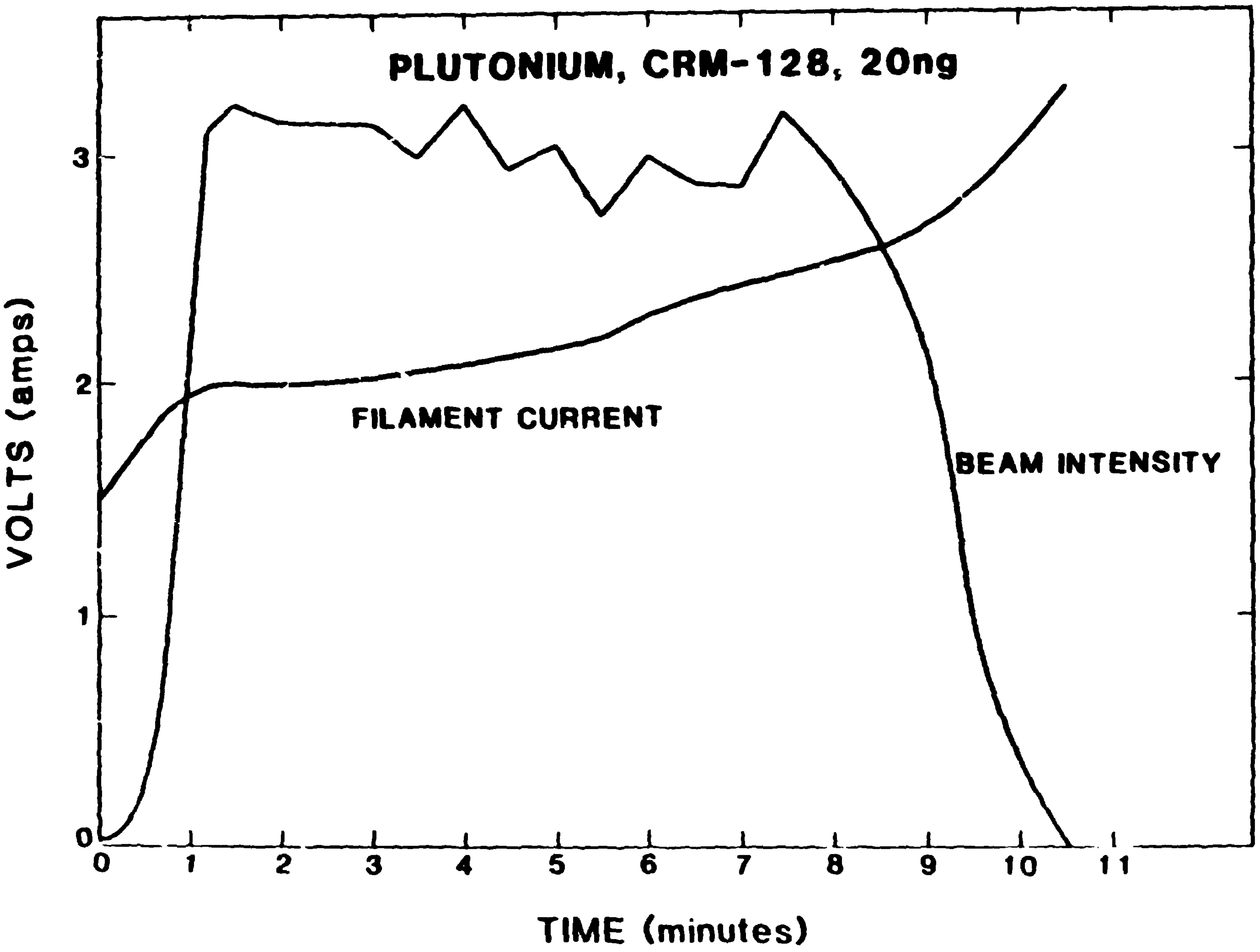
Fig 5: Comparison of collector efficiencies, determined by single ion beam switching and collector repositioning.

Table 1: Observed versus certified values for several uranium and plutonium standards

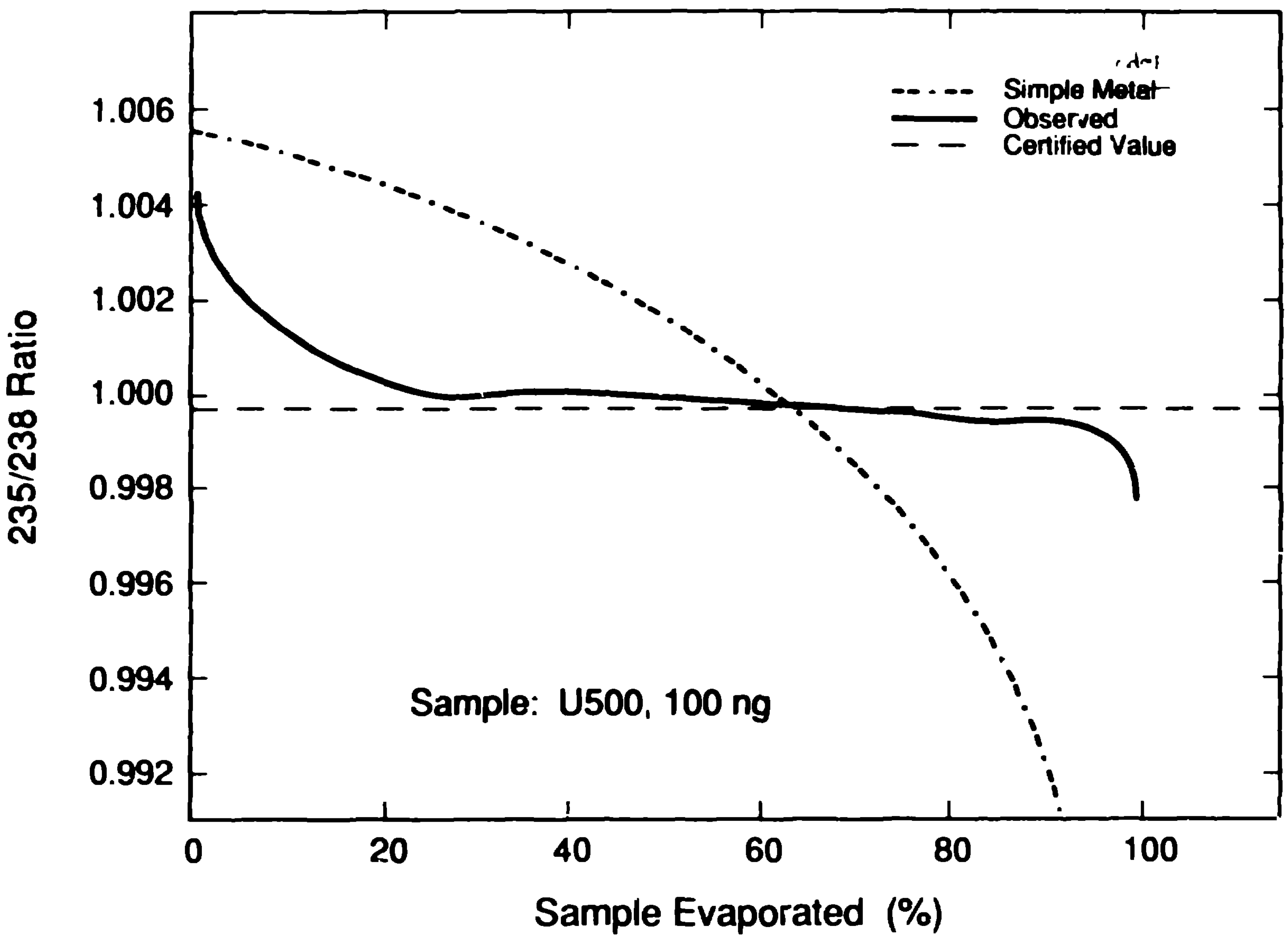
Table 2: Replicate analyses of NBS-947 plutonium standard demonstrating the high precision obtainable, 10-20 ng Pu loaded.

Table 3: Replicate analyses of U-500 uranium standard, 100-200 ng U loaded.

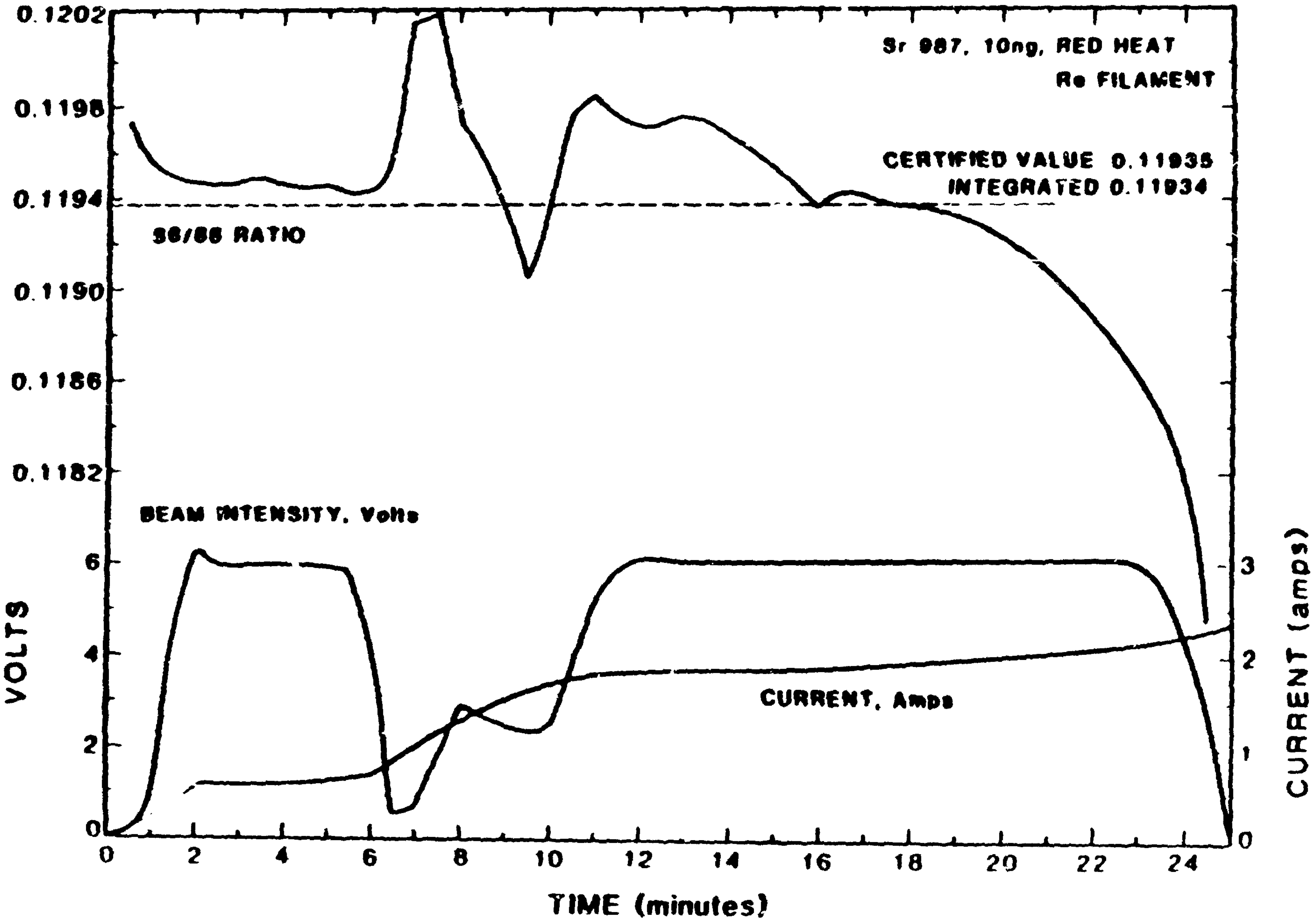
Table 4: Effect of sample size on observed 235/238 ratio for NBS-U500 standard.


PLUTONIUM, CRM-128, 20ng
VOLTS (amps)
0
1
2
3
FILAMENT CURRENT
BEAM INTENSITY
0
1
2
3
4
5
6
7
8
9
10
11
TIME (minutes)

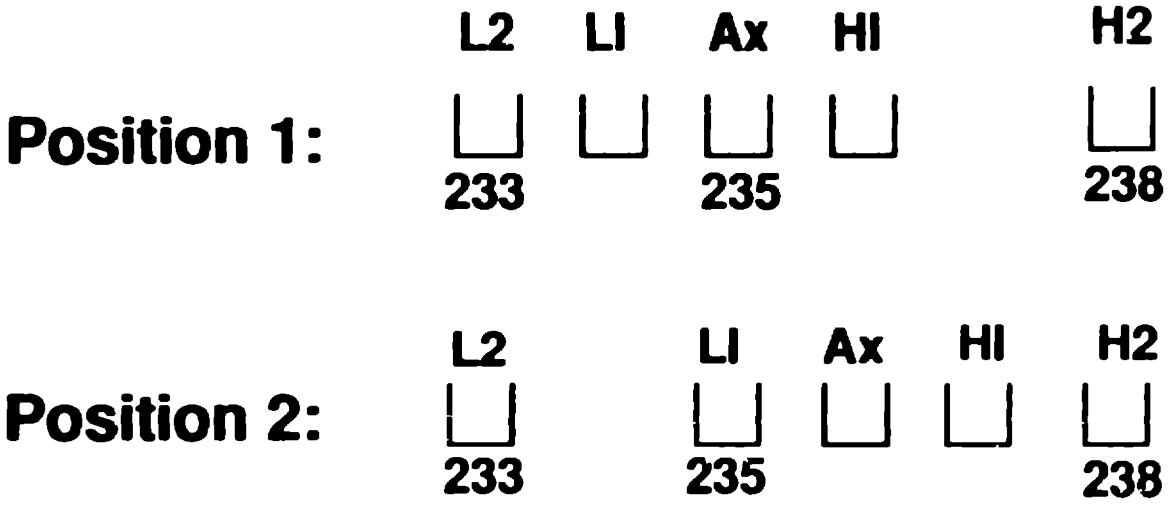
C. S VG-4899


Simple Metal
Observed
Certified Value
Sample: U500, 100 ng
235/238 Ratio
1.006
1.004
1.002
1.000
0.998
0.996
0.994
0.992
0
20
40
60
80
100
Sample Evaporated (%)

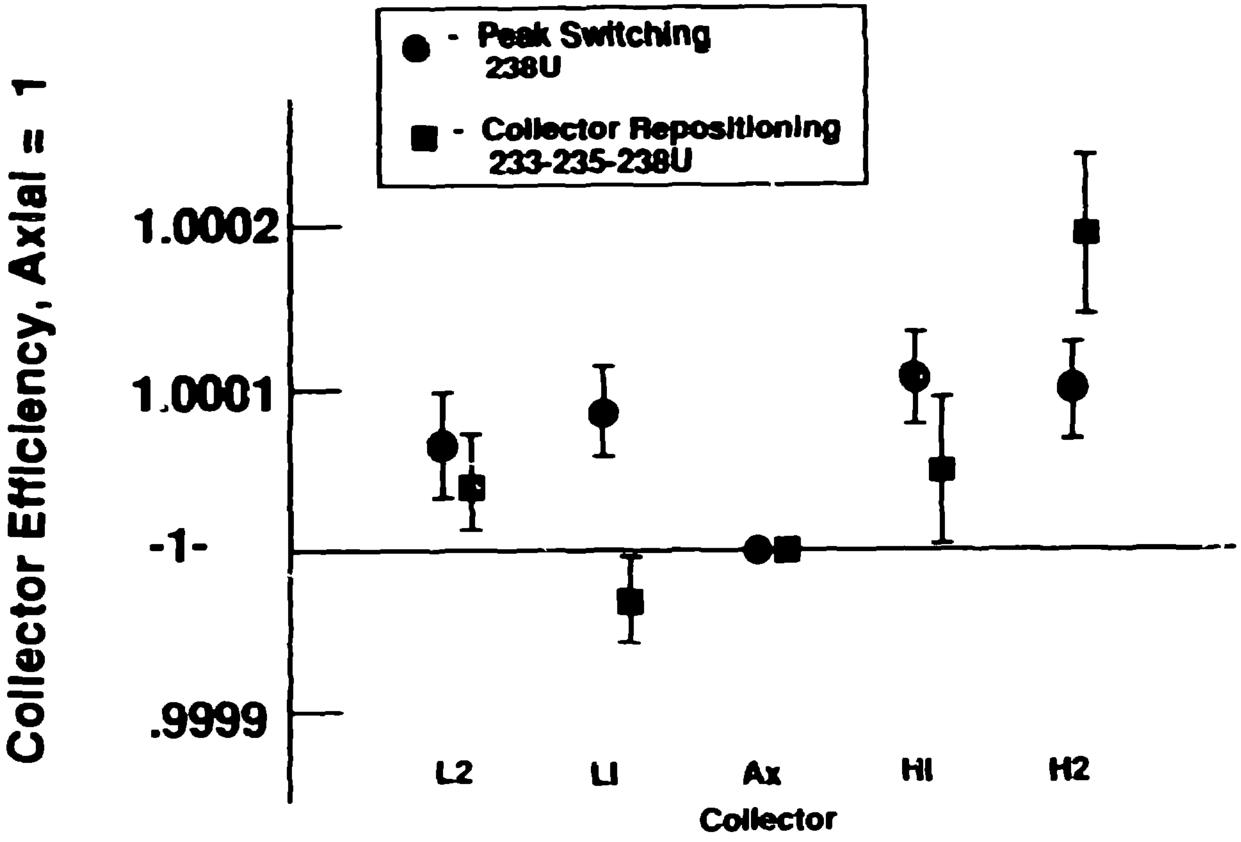
CLS-89-4900A


0.1202
0.1198
0.1194
0.1190
0.1186
0.1182
6
4
2
0
VOLTS
Sr 987, 10ng, RED HEAT
Re FILAMENT
CERTIFIED VALUE 0.11935
INTEGRATED 0.11934
86/88 RATIO
BEAM INTENSITY, Volts
CURRENT, Amps
3
2
1
0
CURRENT (amps)
0
2
4
6
8
10
12
14
16
18
20
22
24
TIME (minutes)

CLS-88-4858



Example of collector calibration (LI/Ax) by repositioning of L2 and H2 collectors.



Collector Efficiency by Different Methods

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OBSERVED VS CERTIFIED VALUES FOR URANIUM AND PLUTONIUM STANDARDS

Standard	Element	Ratio	Observed Value	Deviation from Certified	Uncertainty of Certified Value
NBS-946	Pu	240/239	0.144963	-0.019%	± 0.14%
NBS-947	Pu	240/239	0.241278	+0.003%	± 0.14%
NBS-948	Pu	240/239	0.086353	+0.049%	±0.14%
CRM-128	Pu	242/239	1.00096	+0.022%	±0.026%
NBS-U500	U	235/238	0.99985	+0.015%	±0.1%
NBS-U900	U	235/238	10.3785	+0.034%	±0.1%
NBS-U100	U	235/238	0.113642	+0.037%	±0.1%
NBS-U020	U	235/238	0.020812	+0.010%	±0.1%
NBS-U010	U	235/238	0.010144	+0.040%	±0.1%

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ANALYSES OF NBS-947

20 ng Pu Loaded

Run	V-Min	238	239	240	241	242
1	10.6	.2659	77.6597	18.869	2.0331	1.2244
2	13.2	.2667	77.6601	18.8159	2.0331	1.2243
3	10.3	.2658	77.6616	18.8164	2.0324	1.2239
4	6.2	.2662	77.6586	18.8164	2.0349	1.2240
5	9.7	.2645	77.6590	18.8191	2.0331	1.2243
6	9.4	.2655	77.6582	18.8172	2.0343	1.2248
7	14.5	.2653	77.6617	18.8158	2.0330	1.2242
8	12.5	.2650	77.6583	18.8194	2.0330	1.2242
MEAN		.2656	77.6597	18.8171	2.0334	1.2242
STD DEV		7	14	14	8	3
RSD		±.26%	±.0018%	±.0074%	±.039%	±.025%
CERTIFIED VALUE		.264	77.66	18.816	2.034	1.226

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ANALYSES OF NBS - U500

100-200 ng Uranium Loaded

Run	V-Min	Atom Ratios 234/238	Atom Ratios 235/238	Atom Ratios 236/238
1	32.5	.010413	.999801	.001528
2	80.1	.010411	.999743	.001520
3	142.5	.010426	.999756	.001520
4	75.0	.010437	.999622	.001522
5	13.4	.010414	.999892	.001532
6	65.9	.010437	.999850	.001529
7	32.3	.010428	.999796	.001516
8	58.0	.010427	.999733	.001511
9	37.6	.010424	.999762	.001531
10	14.3	.010427	.999773	.001520
MEAN	55.4	.010424	.999768	.001523
STD DEV	38.6	± 9	± 68	± 7
CERTIFIED VALUE		.010422	.9997	.001519

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Ng U Loaded	Integrated Intensity, V-min	Observed 235/238 Ratio
20	10.0	.99982
50	17	.99985
100	45	.99975
200	103	.99962

Variation of observed 235/238 ratio with sample size for NBS U-500 standard.
Certified value = .9997. (Mean of 2 determinations at each level.)