Evaluation of the Total-Evaporation Method for Mass Spectrometric Analysis of Uranium and Plutonium Safeguards Samples: Report of Phase I

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EVALUATION OF THE TOTAL-EVAPORATION METHOD FOR MASS SPECTROMETRIC ANALYSIS OF URANIUM AND PLUTONIUM SAFEGUARDS SAMPLES: REPORT OF PHASE I

by

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ABSTRACT

The total-evaporation thermal ionization mass spectrometric method for the isotopic analysis of uranium and plutonium was developed by group CST-1 at Los Alamos National Laboratory (LANL) and has been used for several years.[1] This analytical method offers significantly better precision and accuracy than conventional techniques. A two-phase collaboration was initiated to assist the International Atomic Energy Agency (IAEA) in implementing this technique at their Safeguards Analytical Laboratory (SAL) in Seibersdorf, Austria. In Phase I, portions of SAL samples that were prepared and analyzed at SAL using their conventional techniques were shipped to LANL and analyzed using the total-evaporation method. Four analyses were made of each of twelve uranium and twelve plutonium samples. The precision of these analyses bettered the IAEA goal of ± 0.05% by a factor of two. After an SAL review of the data from both LANL and SAL in 1992 additional measurements were made at LANL to try to resolve the discrepancies between the mean values. These measurements supported the total-evaporation results and indicated the possibility of a problem with collector calibration and fractionation control at SAL. In Phase II of this work, which has not yet been completed, the effect of impurities on the total-evaporation method will be investigated and a five-isotope uranium mixture will be prepared to assist in collector calibration and testing.

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I. INTRODUCTION

The use of the total-evaporation method for isotopic analysis with multicollector mass spectrometers has been proposed to improve the precision and accuracy of mass-spectrometric measurements of uranium and plutonium at SAL. To establish whether this technique would work satisfactorily on SAL samples, the following plan was proposed and implemented.

Phase I: Ship portions of samples of both uranium and plutonium that were prepared and analyzed at SAL using their standard techniques to LANL for analysis using the total-evaporation procedure. Compare the LANL results with the SAL results.

Phase II: Depending on the results of Phase I, explore methods to overcome the problems that might cause divergent analytical results (such as the effects of impurities). Also in this phase, investigate the suitability of the internal calibration procedure (double-spike method).

A copy of the task statement appears as Appendix B.

II.   EXPERIMENTAL

A. Mass Spectrometer

A standard commercial instrument was used (VG Isotopes model VG 354 of 1986 vintage). This instrument has five Faraday collectors, four of which are adjustable, and a Daly ion-counting system. The operating software for the instrument had been previously modified at LANL to perform analyses in the total-evaporation/integration mode.

B.   Filament Assemblies

The filament holders were reusable metal blocks suitable for the NBS-type triple-filament geometry. The filament assemblies were fabricated at LANL using zone-refined rhenium ribbon and were not degassed prior to use with the total-evaporation method.

C. Collector Setup

The collectors were adjusted to accommodate the three sample types. The axial collector (Ax) is fixed, while the two low-mass collectors (L2 and L1) and two high-mass collectors (H2 and H1) are adjustable.

1. Uranium.	collector:	L2	L1	Ax	H1		H2
	isotope:	233	234	235	236		238
2. Pu with ^{244}Pu.	collector:	L2	L1	Ax	H1		H2
	isotope:	239	240	241	242		244
3. Pu without ^{244}Pu.	collector:	L2	L1	Ax	H1	H2	
	isotope:	238	239	240	241	242	

Note: the plutonium standards CRM-128 and NBS-947 were analyzed with both the second and third collector arrangements.

D. Sample Dissolution

1. Uranium.   One ml of 1 M HNO_3 was added to the sample vial. There was no further treatment. The estimated concentration of uranium was 0.5 mg/ml.

2. Plutonium. Two drops of 8M HNO_3 were added to the sample vial. The solution was evaporated on a hot plate, and the residue taken up in 0.1 ml of 1M HNO_3. The estimated concentration of plutonium was 50 µg/ml.

E. Filament Loading

For the plutonium samples a nominal 0.5 µl drop of solution was placed on one sample filament using a micro-syringe with a disposable tip. The solution was evaporated by passing a current of 1.2 A through the filament. The filament was then covered with a beaker and the filament current increased until the filament first became visibly red (at about 700-800°C). The filament current was then immediately reduced to zero. Because of the high specific activity of plutonium, the sample load was limited to 20-30 ng, which yielded good results. The alpha activity from this amount of plutonium is typically 3000-18 000 dis/min, depending primarily on the ^{238}Pu content. The alpha activity loaded onto the filament, monitored with a simple survey meter, was arbitrarily limited to about 8000 dis/min, so some of the loads were probably less than 20 ng.

Because uranium's specific activity is lower, a sample sufficient to yield 30 to 60 V/min of intensity (typically 200-300 ng) was loaded for the uranium samples. Otherwise the procedure was the same.

The instrument time required per sample was not a strong function of the amount of sample loaded until the sample size exceeded about 300 ng. For loads less than this, the analysis time was 25 to 35 minutes, essentially independent of the sample size.

III.   RESULTS AND DISCUSSION

The data of the Phase I analyses are listed in Tables 1-4 in Appendix A. No attempt was made to analyze all of the samples in an uninterrupted sequence. The runs were made over a period of several months as the workload of our group permitted. The date of each analysis is indicated, in the format *mm/dd/yy.* A total of 24 samples were submitted, 12 of uranium and 12 of plutonium. Duplicate measurements were performed on each sample, a total of four measurements on each. This resulted in 96 analyses. In addition, uranium and plutonium standards (U-500, U-010, U-030, IRM-199, NBL CRM-128, and NBS-947) were analyzed, for a total of 43 standard analyses. Copies of the standard certificates are included in Appendix C.

No corrections, relative to reference materials, have been applied to the data. The relative gains of the measuring channels were determined using the standard built-in current source at the start of each analysis. The relative efficiency of each collector had been previously determined, independent of standards, using techniques that have been described.[1] Results are presented as atom ratios, with respect to ^{238}U or ^{239}Pu. The column labeled *V-MIN* reports the total integrated intensity for each loading. That is, for each measurement period (5 sec or .083 min) the product of the total intensity of all isotopes (in V with a 1×10^{11} Ω input resistor) and the integration period (in min) is formed and summed over the entire analysis. While a statistical evaluation of the data is to be done at SAL, a few observations may be made.

- For uranium ratios greater than about 0.03 the average precision (RSD for four analyses) is about 0.006%.

- For smaller ratios, the precision is controlled by amplifier noise, and is typically 2–5 ppm of the major isotope.

- The plutonium samples exhibit slightly poorer precision, possibly due to the smaller sample loadings. For the three samples containing ^{244}Pu the average precision of the ^{244}Pu/^{239}Pu ratio is 0.017%, and for the samples with ^{242}Pu/^{239}Pu ratios greater than 0.05 the average precision was about 0.015%. The ^{240}Pu/^{239}Pu ratios were very reproducible, as was expected with a difference of only one mass unit. The worst case was 0.014% for sample 12704A, with 0.005% being typical.

Figure 1 presents the range of precision for the major isotope ratios over the four determinations for each sample and reference material. As might be expected, the reproducibility of measurements from the samples is somewhat poorer than it is for measurements from the high-purity reference materials. Nonetheless, the reproducibility of sample measurements still betters the IAEA target value of ± 0.05% by a factor of two.
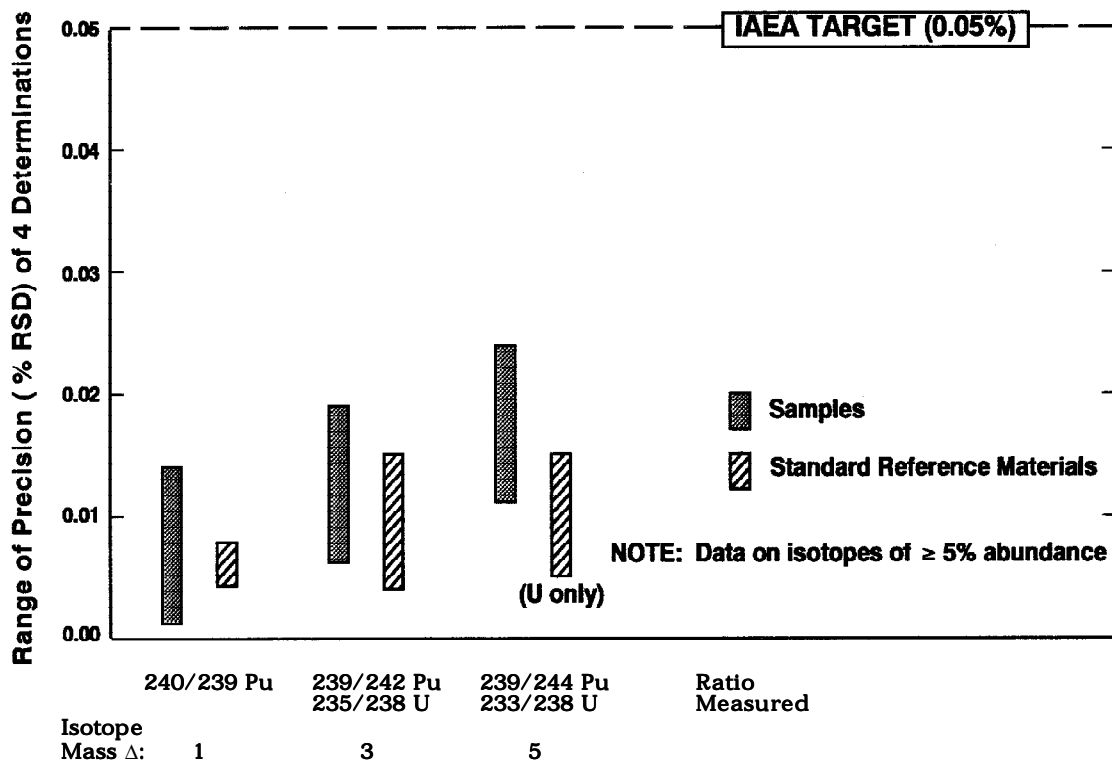

Fig. 1. Precision obtained at LANL using the total-evaporation technique on IAEA-prepared samples.

Because the samples were analyzed more than a year after separation, the ingrowth of ^{241}Am produces poor precision in the ^{241}Pu/^{239}Pu ratios. This is evident also in the NBS-947 material, which was purified several months prior to these analyses (on 10 October 1991). The ^{241}Pu/^{239}Pu ratios should be excluded or treated separately to make sense of the data. Similarly, it may be possible to draw conclusions about residual uranium in the plutonium fractions by looking at the precision of the ^{238}Pu/^{239}Pu ratios. Samples 12704A, 12705A, and 12706A exhibit somewhat poorer precision for this ratio. This may be related to the amount of uranium in the original sample (presumably the sample did contain uranium at some point) and the efficiency of the separation.

The behavior of the ^{241}Pu/^{239}Pu ratio (when ^{241}Am is present) may be of interest in understanding the evaporation and ionization characteristics of mixtures of elements. At first glance it would appear that small amounts of americium should not affect the precision of the measurement, because of the use of total evaporation. One expects the accuracy of the ratio to be degraded because of the different ionization efficiencies of plutonium and americium. The observed variability, which is fairly large, may be due to changes in the relative ionization efficiencies from run to run or within a run, to physical separation of the elements on the filament, or to other unknown mechanisms.

IV.   ADDITIONAL ANALYSES PERFORMED IN PHASE I

In August 1992 the Principal Investigator visited SAL to review and discuss the preliminary results of Phase I with SAL personnel and to determine if further work was required. A report of this visit is included as Appendix D. The following conclusions were reached.

• The run-to-run precision obtained at LANL using the total-evaporation method meets the SAL goal of 0.05% or better for all isotopes present as at least 2% of the sample.

• Significant deviations exist between the mean values observed by SAL and LANL for several of the samples. These deviations approach 0.5% and are most obvious in ratio pairs with large mass differences, such as ^{233}U/^{238}U and ^{244}Pu/^{239}Pu.

To complete Phase I, LANL agreed to reanalyze three samples, 12701A, 12702A, and 12703A. For these plutonium samples, the deviations between the two Laboratories' results were fairly large. The samples were reanalyzed using single collector peak-jumping techniques (not the total-evaporation method) to look for anomalies in the multicollector data. Two different instruments and two different techniques were used.

• For peak jumping, using the axial Faraday collector on the VG-2 multicollector instrument, relatively large (100 to 200 ng) samples were loaded. No attempt was made to control or reproduce fractionation. Three to six blocks of ten ratios each constituted a run. The loadings were reanalyzed until the required intensity (500 mV) could not be obtained. These data are listed in Table 5 in Appendix A.

• We also employed peak jumping with a single-filament (graphite) ion-counting technique on instrument VG-1. This is our standard technique for analyzing routine plutonium samples. The data are not as precise as from Faraday measurements, but are corrected for fractionation effects relative to plutonium isotopic standard CRM-128. Five filament loadings of each sample and fifteen loadings of CRM-128, nominally 2 ng each, were analyzed. The sample data are listed in Table 6 and the CRM-128 data in Table 7 in Appendix A.

A. Discussion

In Figs. 2, 3, and 4, the deviations of the Faraday peak-jumping and SAL data from the LANL total-evaporation data are plotted as a function of the mass difference of the various ratios. If mass-dependent fractionation was the only difference between these data sets then the data points for a particular run should lie on a straight line passing through the origin. The LANL peak-jumping data show fair agreement with the total-evaporation results, although there are deviations outside the precision of the measurements. The $^{240}Pu/^{239}Pu$ ratio generally is low by 0.03 to 0.05%, indicating that the total-evaporation result may be high. This would suggest a slight error in calibration of the collector on which the ^{240}Pu is measured. For the SAL data, there appears to be an offset relative to the total evaporation data as well as fractionation differences. The offset could be caused by an error in the calibration of the collector used to measure the reference isotope ^{239}Pu.
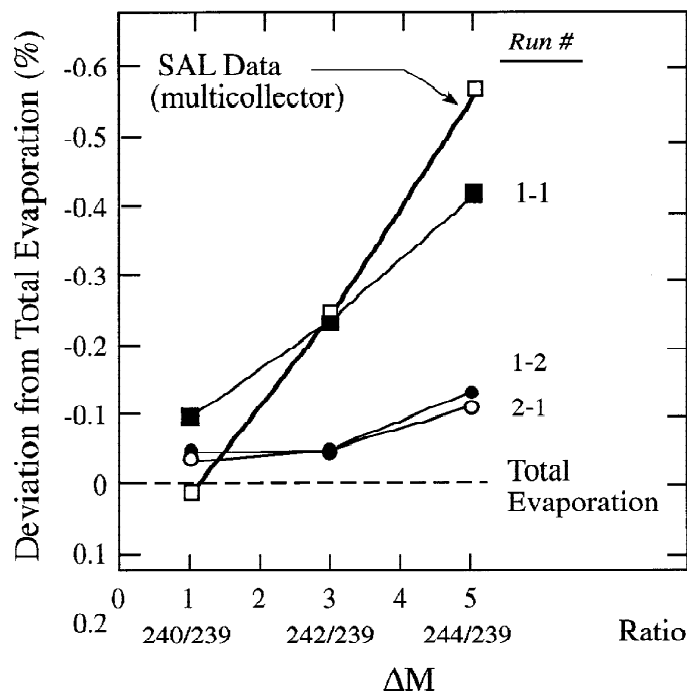
Fig. 2. Deviations of LANL peak-jumping and SAL multicollector data from LANL total-evaporation data (sample 12701A, ^{239}Pu ref).

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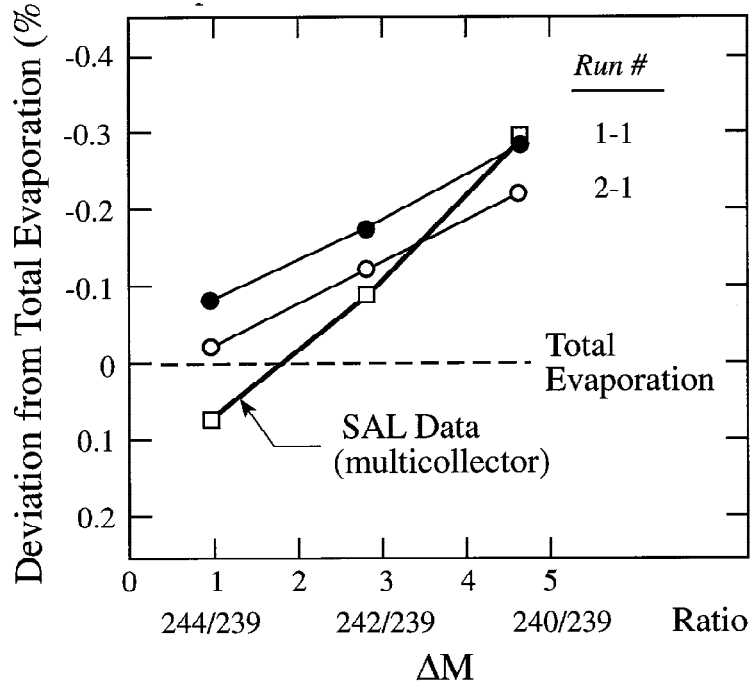
Fig. 3. Deviations of LANL peak-jumping and SAL multicollector data from LANL total-evaporation data (sample 12702A, ^{239}Pu ref).
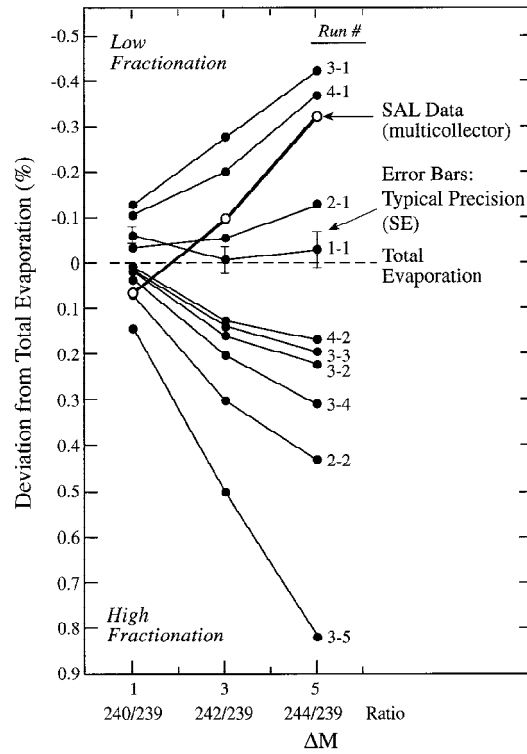
Fig. 4. Deviations of LANL peak-jumping and SAL multicollector data from LANL total-evaporation data (sample 12703A, ^{239}Pu ref).

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In Figs. 5, 6, and 7 the same data are plotted, except that the data are renormalized using ^{242}Pu as the reference isotope to help to identify individual collector anomalies. The deviations calculated in this manner are listed in Table 8. The LANL peak-jumping vs. total-evaporation data still look reasonable. The SAL data, however, show fairly large deviations from linearity for the ^{239}Pu/^{242}Pu and ^{240}Pu/^{242}Pu ratios. This further suggests a problem with the ^{239}Pu (and possibly the ^{240}Pu) collectors.
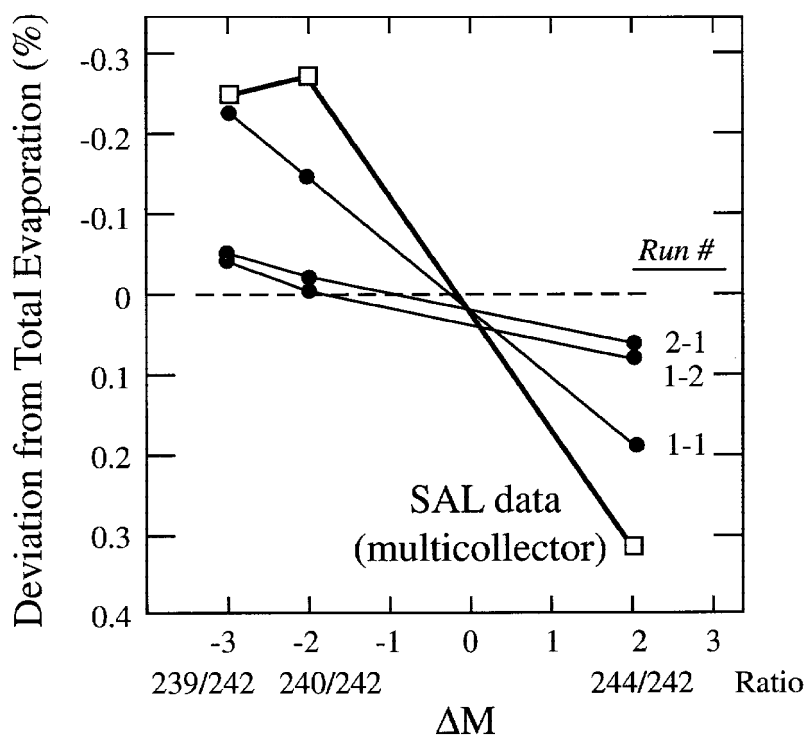
Fig. 5. Deviations of LANL peak-jumping and SAL multicollector data from LANL total-evaporation data (sample 12701A, ^{242}Pu ref).
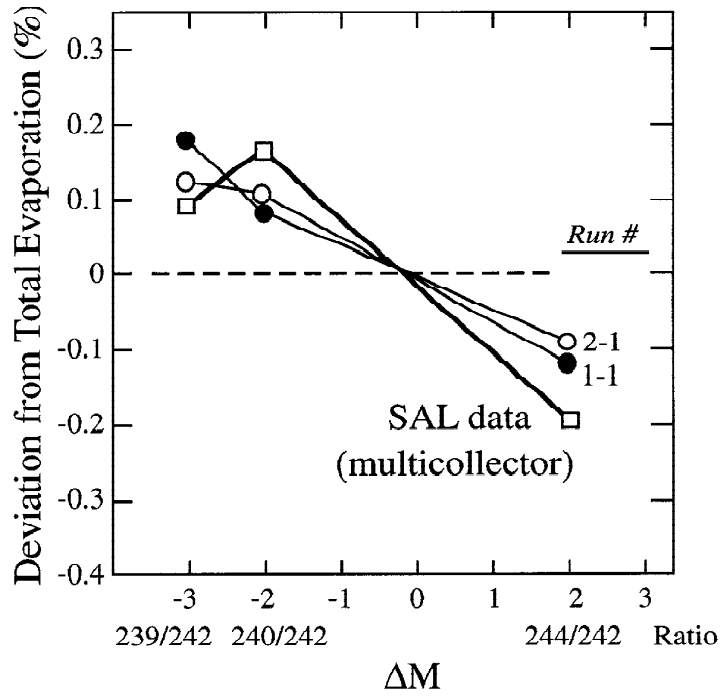
Fig. 6. Deviations of LANL peak-jumping and
SAL multicollector data from LANL total-
evaporation data (sample 12702A, ^{242}Pu ref).
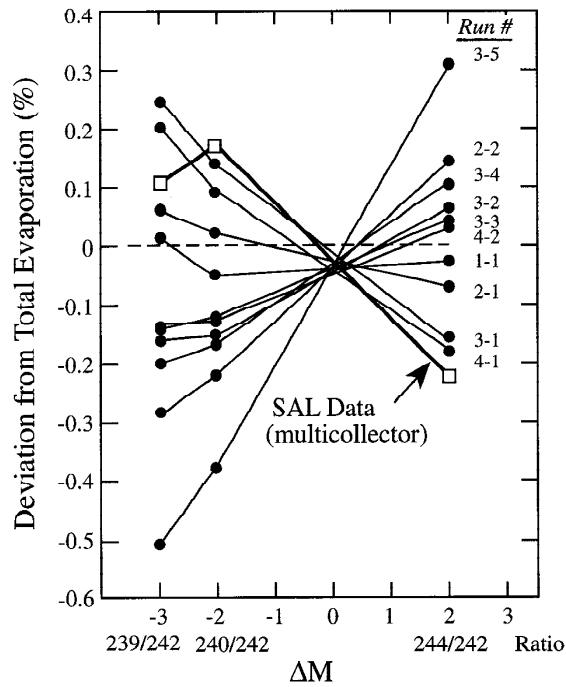
Fig. 7. Deviations of LANL peak-jumping and
SAL multicollector data from LANL total-
evaporation data (sample 12703A, ^{242}Pu ref).

In Figs. 8, 9, and 10 the deviations of the single-filament ion-counting data and SAL data from the total evaporation data are plotted for the $^{240}Pu/^{239}Pu$, $^{242}Pu/^{239}Pu$, and $^{244}Pu/^{239}Pu$ ratios. The ion-counting data support the total-evaporation data within the precision of the measurements. These data are listed in Table 6 in Appendix A.
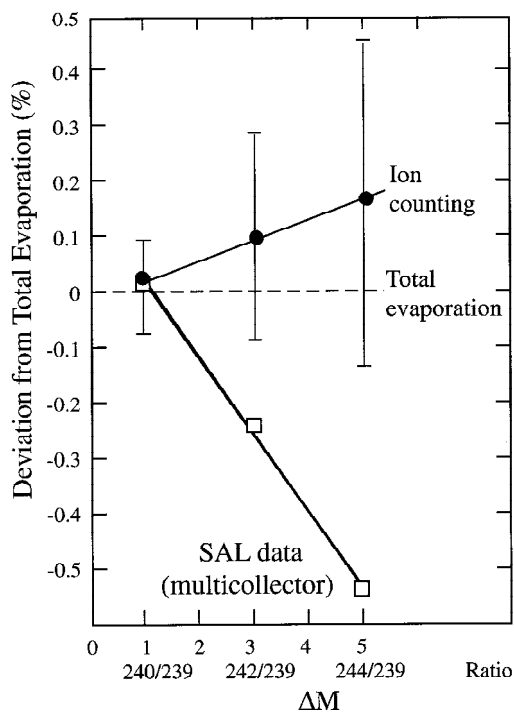
Fig. 8. Deviations of LANL single-filament ion-counting data and SAL multicollector data from LANL total-evaporation data (sample 12701A).
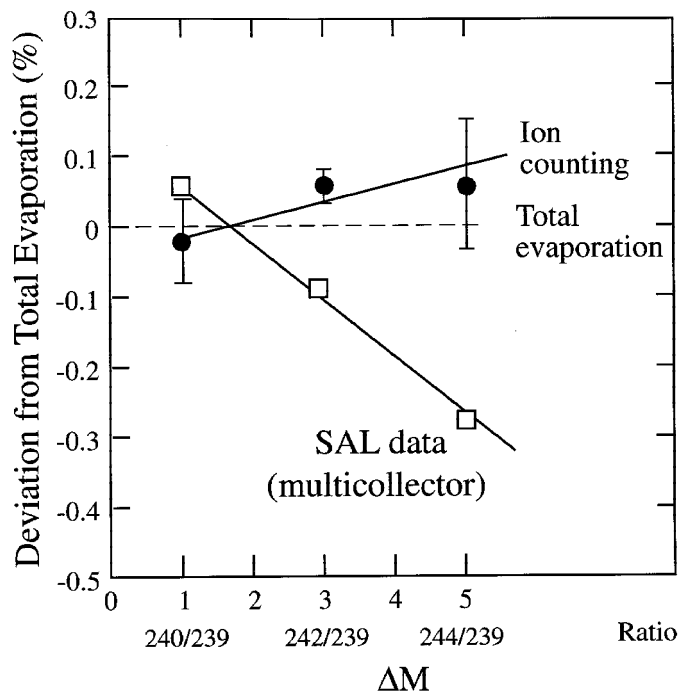
Fig. 9. Deviations of LANL single-filament ion-counting data and SAL multicollector data from LANL total evaporation data (sample 12702A).

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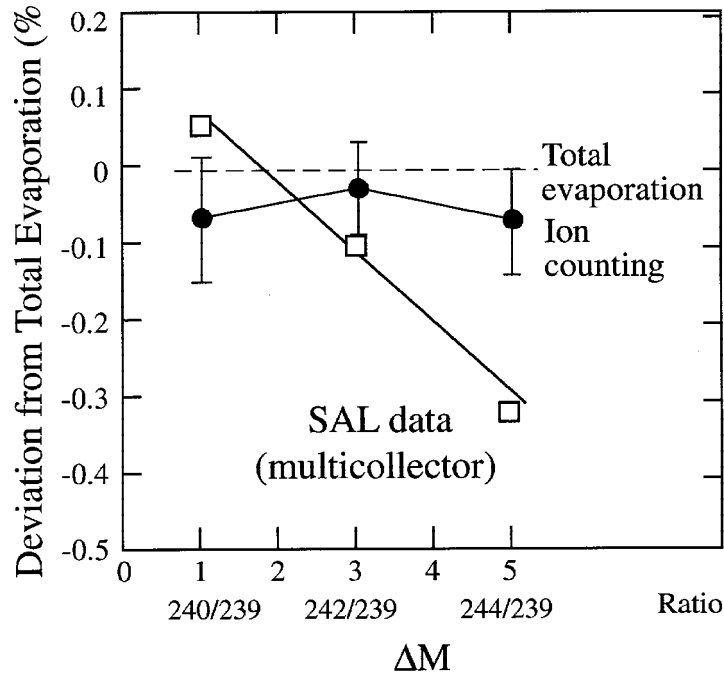
Fig. 10. Deviations of LANL single-filament ion-counting data and SAL multicollector data from LANL total-evaporation data (sample 12703A).

As pointed out earlier, the CRM-128 and NBS-947 standards were both analyzed at LANL using two different collector arrangements. This gave us a means of confirming the relative calibration of four of the collectors. Looking at the data in Tables 1 and 2 for CRM-128, we find the following.

- The ^{242}Pu/^{239}Pu ratio from H1/L2 is 1.000983 ± 0.000151 (Table 1).

- The ^{242}Pu/^{239}Pu ratio from H2/L1 is 1.001112 ± 0.000071 (Table 2). Deviation = 0.013%.

Similarly, for NBS-947we find the following.

- The ^{240}Pu/^{239}Pu ratio from L1/L2 is 0.241217 ± 0.000011 (Table 1).

- The ^{240}Pu/^{239}Pu ratio from Ax/L1 is 0.241216 ± 0.000017 (Table 2). Deviation = <0.01%.

The agreement of these results indicates that the relative gains of the L2/L1/Ax collectors and the H2/H1 collectors are good to about 0.01%. Unfortunately, it is not possible to get a good check of the H1/Ax calibration from this data because the isotope involved is ^{241}Pu (which is fairly small in NBS-947). In addition, this was not a recent separation and hence the precision on the ratio measurements was compromised by the ingrowth of ^{241}Am.

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B. Conclusions

A comparison of the reproducibility of samples vs. reference materials indicates no significant degradation due to sample preparation. The high precision obtained in analyzing the SAL samples using the total-evaporation technique indicates that existing SAL chemical purification procedures provide suitable samples and that the total-evaporation technique yields reproducible analyses with less than half the IAEA allowable error. Implementation of the total-evaporation method should permit SAL to reduce the overall uncertainty of mass spectrometric measurements to less than 0.1%.

The discrepancies observed in the multicollector data from the two Laboratories appear to have two components, one due to mass-dependent fractionation and one due to collector calibration anomalies. Total evaporation should reduce errors due to fractionation to a very low level. However, a new method or standard material is needed to assure that each collector is properly calibrated and functioning normally. Investigation of collector calibration methods and the effects of impurities on the total-evaporation method are planned for Phase II of this work.

REFERENCES
1. E. L. Callis and R. M. Abernathey, *Int. Journal Mass Spec. Ion Processes*, **103**, 93105 (1991).

Appendix A

ISPO A.169

Tables 1-8

TABLE 1. ISPO A.169 Plutonium Data: 244 Traced

SAMPLE NO	RUN #	DATE	V-MIN		240/239	241/239*	242/239	244/239
12701A	1	2/13/92	10.9		0.467837	0.069185	1.188452	0.453034
	2	2/13/92	9.5		0.467875	0.069019	1.188481	0.453053
	3	2/14/92	23.7		0.467865	0.069517	1.188853	0.453274
	4	2/14/92	20.8		0.467846	0.069321	1.188697	0.453148
			Mean		0.467856	0.069261	1.188621	0.453127
			SD		0.000017	0.000211	0.000190	0.000110
			RSD%		0.0037	0.3045	0.0159	0.0242
12702A	1	2/13/92	18.4		0.462499	0.069259	1.070442	0.406987
	2	2/13/92	20.8		0.462531	0.068878	1.070367	0.406911
	3	2/14/92	19.6		0.462504	0.068603	1.070239	0.406868
	4	2/14/92	20.6		0.462540	0.068678	1.070398	0.406950
			Mean		0.462519	0.068855	1.070362	0.406929
			SD		0.000020	0.000294	0.000087	0.000051
			RSD%		0.0043	0.426	0.0082	0.0126
12703A	1	2/13/92	12.8		0.492467	0.069895	1.735277	0.666371
	2	2/13/92	8.4		0.492499	0.069987	1.735607	0.666577
	3	2/14/92	19.6		0.492418	0.069801	1.735269	0.666400
	4	2/14/92	9.6		0.492468	0.069837	1.735434	0.666478
			Mean		0.492463	0.069880	1.735397	0.666457
			SD		0.000033	0.000081	0.000159	0.000092
			RSD%		0.0068	0.116	0.0092	0.0138
CRM-128	1	2/13/92	11.4		0.000699	0.000719	1.001008	0.000010
	2	2/13/92	7.3		0.000683	0.000724	1.001143	0.000003
	3	2/14/92	15.4		0.000681	0.000739	1.000778	0.000009
	4	2/14/92	11.2		0.000700	0.000723	1.001001	0.000011
			Mean		0.000691	0.000726	1.000983	0.000007
			SD		0.000010	0.000009	0.000151	0.000007
			RSD%		1.469	1.208	0.0151	97.1
	Certified-Decay Corrected				-	-	1.000830	-
					-	-	± 0.000260	-
NBS-947	1	2/13/92	11.6		0.241227	0.022808	0.015567	0.000006
	2	2/13/92	15.4		0.241206	0.022786	0.015577	0.000001
	3	2/14/92	14.5		0.241225	0.022775	0.015568	0.000001
	4	2/14/92	25.1		0.241210	0.022774	0.015561	0.000002
			Mean		0.241217	0.022786	0.015568	0.000003
			SD		0.000011	0.000016	0.000007	0.000002
			RSD%		0.0044	0.0693	0.0424	95.2
	Certified-Decay Corrected				0.241220	0.022460	0.015600	
					± 0.000290	± 0.000050	± 0.000050	

*The precision of the [241]Pu measurements is degraded due to ingrowth of [241]Am in the samples since separation.

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TABLE 2. ISPO A.169 Plutonium Data: Untraced

SAMPLE NO	RUN #	DATE	V-MIN	238/239	240/239	241/239*	242/239
12704A	1	2/27/92	2.8	0.011191	0.317049	0.075848	0.03787S
	2	2/27/92	5.0	0.011214	0.316991	0.076118	0.037892
	3	2/28/92	3.8	0.011240	0.316944	0.075691	0.037883
	4	2/28/92	7.3	0.011172	0.316975	0.075325	0.037867
		MEAN		0.011204	0.316990	0.075746	0.037879
		SD		0.000029	0.000044	0.000331	0.000011
		RSD%		0.2622	0.0139	0.4372	0.0283
12705A	1	2/27/92	1.9	0.015866	0.350924	0.096981	0.052596
	2	2/27/92	3.3	0.015860	0.350900	0.096722	0.052589
	3	2/28/92	2.6	0.015820	0.350854	0,096554	0.052581
	4	2/28/92	2.2	0.015791	0.350891	0.096849	0.052605
		MEAN		0.015834	0.350892	0.096777	0.052593
		SD		0.000035	0.000029	0.000183	0.000010
		RSD%		0.2231	0.0083	0.1894	0.0194
12706A	1	2/27/92	12.1	0.002163	0.301187	0.032216	0.011274
	2	2/27/92	7.3	0.002157	0.301168	0.032120	0.011265
	3	2/28/92	7.9	0.002118	0.301164	0.032126	0.011272
	4	2/28/92	14.4	0.002119	0.301200	0.032136	0.011280
		MEAN		0.002139	0.301180	0.032150	0.011273
		SD		0.000024	0.000017	0.000045	0.000006
		RSD%		1.13	0.0056	0.139	0.0549
12707A	1	2/28/92	9.4	0.015511	0.371777	0.090571	0.056091
	2	2/28/92	17.9	0.015506	0.371767	0.090211	0.056087
	3	3/02/92	11.5	0.015517	0.371773	0.090505	0.056085
	4	3/02/92	10.0	0.015508	0.371771	0.090434	0.056079
		MEAN		0.015511	0.371772	0.090430	0.056086
		SD		0.000005	0.000004	0.000157	0.000005
		RSD%		0.0309	0.0011	0.1731	0.0089
12708A	1	2/28/92	14.4	0.015502	0.371757	0.090236	0.056082
	2	2/28/92	12.8	0.015515	0.371718	0.089903	0.056068
	3	3/02/92	12.4	0.015520	0.371737	0.090221	0.056070
	4	3/02/92	20.6	0.015526	0.371745	0.090169	0.056067
		MEAN		0.015516	0.371739	0.090132	0.056072
		SD		0.000010	0.000016	0.000156	0.000007
		RSD%		0.0658	0.0044	0.1725	0.0124

*The precision of the [241]Pu measurements is degraded due to ingrowth of [241]Am in the samples since separation.

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TABLE 2. ISPO A.169 Plutonium Data: Untraced (continued)

SAMPLE NO	RUN #	DATE	V-MIN	238/239	240/239	241/239*	242/239
12709A	1	2/28/92	16.5	0.015520	0.371748	0.089933	0.056074
	2	2/28/92	23.4	0.015546	0.371778	0.090468	0.056084
	3	3/2/92	19.4	0.015516	0.371730	0.090448	0.056064
	4	3/2/92	13.6	0.015518	0.371791	0.090771	0.056082
			MEAN	0.015525	0.371762	0.090405	0.056076
			SD	0.000014	0.000028	0.000348	0.000009
			RSD%	0.0908	0.0075	0.3845	0.0162
12710A	1	3/2/92	11.6	0.000576	0.132124	0.007933	0.002057
	2	3/2/92	21.9	0.000578	0.132124	0.007918	0.002056
	3	3/3/92	14.2	0.000583	0.132129	0.007967	0.002055
	4	3/3/92	11.6	0.000584	0.132127	0.0 7933	0.002052
			MEAN	0.000580	0.132126	0.007938	0.002055
			SD	0.000004	0.000002	0.000021	0.000002
			RSD%	0.6656	0.0019	0.2613	0.1051
12711A	1	3/2/92	32.5	0.000572	0.132133	0.007965	0.002055
	2	3/2/92	17.0	0.000579	0.132136	0.007966	0.002056
	3	3/3/92	6.5	0.000583	0.132129	0.007941	0.002059
	4	3/3/92	14.3	0.000568	0.132130	0.007940	0.002054
			MEAN	0.000576	0.132132	0.007953	0.002056
			SD	0.000007	0.000003	0.000014	0.000002
			RSD%	1.17	0.0024	0.182	0.105
12712A	1	3/2/92	12.2	0.000594	0.132116	0.007899	0.002061
	2	3/2/82	19.0	0.000576	0.132124	0.007940	0.002057
	3	3/3/92	9.2	0.000588	0.132136	0.007933	0.002053
	4	3/3/92	13.8	0.000586	0.132114	0.007936	0.002055
			MEAN	0.000586	0.132123	0.007927	0.002057
			SD	0.000007	0.000010	0.000019	0.000003
			RSD%	1.28	0.0076	0.238	0.166

*The precision of the [241]Pu measurements is degraded due to ingrowth of [241]Am in the samples since separation.

TABLE 2. ISPO A.169 Plutonium Data: Untraced (continued)

SAMPLE NO	RUN#	DATE		V-MIN	238/239	240/239	241/239*	242/239
CRM-128	1	2/27/92		13.8	0.000069	0.000695	0.000728	1.001125
	2	2/27/92		9.2	0.000074	0.000653	0.000731	1.001207
	3	3/3/92		11.5	0.000051	0.000679	0.000733	1.001063
	4	3/3/92		10.2	0.000050	0.000667	0.000724	1.001051
			MEAN		0.000061	0.000674	0. 000729	1.001112
			SD		0.000012	0.000018	0.000004	0.000071
			RSD%		20.2	2.65	0.537	0.0071
	Certified-Decay Corrected				-	1.000830	-	-
					-	± 0.000260	-	-
NBS-947	1	2/27/92		12.2	0.003363	0.241223	0.022770	0.015567
	2	2/27/92		8.2	0.003385	0.241234	0.022787	0.015576
	3	3/3/92		13.8	0.003366	0.241214	0.022787	0.015570
	4	3/3/92		7.2	0.003363	0.241193	0.022738	0.015562
			MEAN		0.003369	0.241216	0.022771	0.015569
			SD		0.000011	0.000017	0.000023	0.000006
			RSD%		0.3145	0.0072	0.1015	0.0376
	Certified-Decay Corrected				0.003330	0.241220	0.022460	0.015600
					± 0.000070	± 0.000290	± 0.000050	± 0.000050

*The precision of the ^{241}Pu measurements is degraded due to ingrowth of ^{241}Am in the samples since separation.

TABLE 3. ISPO A.169 Uranium Data

SAMPLE NO	RUN #	DATE	V-MIN	233/238	234/238	235/238	236/238
12713A	1	9/18/91	45.3	0.330278	0.009083	0.004042	0.325689
	2	9/18/91	54.9	0.330332	0.009080	0.004037	0.325714
	3	9/23/91	26.0	0.330358	0.009068	0.004041	0.325732
	4	9/24/91	41.3	0.330298	0.009087	0.004045	0.325691
			MEAN	0.330317	0.009080	0.004041	0.325707
			SD	0.000036	0.000008	0.000003	0.000020
			RSD%	0.0108	0.0902	0.0818	0.0063
12714A	1	9/18/91	36.0	0.296687	0.008168	0.004000	0.292646
	2	9/18/91	22.8	0.296699	0.008159	0.003995	0.292664
	3	9/23/91	66.3	0.296692	0.008154	0.004002	0.292669
	4	9/23/91	41.5	0.296726	0.008151	0.004007	0.292671
			MEAN	0.296701	0.008158	0.004001	0.292663
			SD	0.000017	0.000007	0.000005	0.000011
			RSD%	0.0059	0.0912	0.124	0.0039
12715A	1	9/18/91	31.2	0.486163	0.013333	0.004179	0.478838
	2	9/19/91	31.5	0.486139	0.013333	0.004181	0.478805
	3	9/23/91	28.2	0.486198	0.013328	0.004171	0.478827
	4	9/23/91	28.1	0.486187	0.013317	0.004190	0.478839
			MEAN	0.486172	0.013328	0.004180	0.478827
			SD	0.000026	0.000008	0.000008	0.000016
			RSD%	0.0054	0.0566	0.187	0.0033

TABLE 3. ISPO A.169 Uranium Data (continued)

SAMPLE NO	RUN #	DATE	V-MIN	233/238	234/238	235/238	236/238
12716A	1	9/19/91	58.0	0.000001	0.000319	0.036746	0.000021
	2	9/19/91	60.9	0.000001	0.000317	0.036744	0.000014
	3	9/23/91	79.5	0.000002	0.000314	0.036743	0.000021
	4	9/23/91	19.5	0.000009	0.000310	0.036748	0.000027
			MEAN	0.000003	0.000315	0.036745	0.000021
			SD	0.000004	0.000004	0.000002	0.000005
			RSD%	158	1.24	0.0060	25.6
12717A	1	9/19/91	54.8	0.000006	0.000321	0.036751	0.000020
	2	9/19/91	60.4	0.000001	0.000316	0.036745	0.000018
	3	9/23/91	52.1	0.000001	0.000310	0.036747	0.000023
	4	9/23/91	88.4	0.000003	0.000316	0.036748	0.000019
			MEAN	0.000002	0.000316	0.036748	0.000020
			SD	0.000003	0.000005	0.000002	0.000002
			RSD%	132	1.43	0.0068	10.8
12718A	1	9/19/91	85.4	0.000006	0.000315	0.036746	0.000020
	2	9/19/91	41.6	0.000000	0.000318	0.036751	0.000018
	3	9/23/91	30.1	0.000006	0.000309	0.036747	0.000020
	4	9/23/91	60.4	0.000001	0.000318	0.036746	0.000018
			MEAN	0.000003	0.000315	0.036748	0.000019
			SD	0.000004	0.000004	0.000002	0.000001
			RSD%	137	1.35	0.0065	6.08

TABLE 3. ISPO A.169 Uranium Data (continued)

SAMPLE NO	RUN #	DATE	V-MIN	233/238	234/238	235/238	236/238
12719A	1	9/13/91	47.5	0.000006	0.000081	0.007729	0.000471
	2	9/13/91	63.4	0.000004	0.000075	0.007727	0.000469
	3	10/8/91	22.1	0.000003	0.000083	0.007729	0.000469
	4	10/8/91	67.8	0.000000	0.000080	0.007724	0.000471
			MEAN	0.000003	0.000080	0.007727	0.000470
			SD	0.000003	0.000003	0.000002	0.000001
			RSD%	76.9	4.27	0.0306	0.246
12720A	1	9/13/91	21.1	0.000003	0.000074	0.007577	0.000268
	2	9/13/91	21.9	0.000008	0.000073	0.007572	0.000255
	3	10/8/91	52.7	0.000000	0.000076	0.007571	0.000253
	4	10/8/91	50.2	0.000002	0.000070	0.007572	0.000255
			MEAN	0.000003	0.000073	0.007573	0.000258
			SD	0.000003	0.000003	0.000003	0.000007
			RSD%	105	3.41	0.0358	2.68
12721A	1	9/13/91	62.8	0.000002	0.000061	0.007266	0.000007
	2	9/18/91	83.8	0.000001	0.000056	0.007264	0.000004
	3	10/8/91	69.4	0.000001	0.000056	0.007261	0.000005
	4	10/8/91	127.2	0.000000	0.000058	0.007258	0.000000
			MEAN	0.000001	0.000058	0.007262	0.000004
			SD	0.000001	0.000002	0.000004	0.000003
			RSD%	81.6	4.09	0.0482	73.6

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TABLE 3. ISPO A.169 Uranium Data (continued)

SAMPLE NO	RUN #	DATE	V-MIN	233/238	234/238	235/238	236/238
12722A	1	9/13/91	21.9	0.000002	0.000134	0.007561	0.000034
	2	9/13/91	1 7. 1	0.000000	0.000134	0.007564	0.000041
	3	10/8/91	49.8	0.000001	0.000131	0.007558	0.000032
	4	10/8/91	69.3	0.000003	0.000136	0.007562	0.000036
			MEAN	0.000002	0.000134	0.007561	0.000036
			SD	0.000001	0.000002	0.000003	0.000004
			RSD%	86.1	1.54	0.0331	10.8
12723A	1	9/13/91	25.7	0.000005	0.000132	0.007565	0.000035
	2	9/13/91	47.8	0.000001	0.000133	0.007567	0.000035
	3	10/8/91	28.6	0.000003	0.000135	0.007574	0.000038
	4	10/8/91	44.4	0.000000	0.000134	0.007569	0.000044
			MEAN	0.000002	0.000134	0.007569	0.000038
			SD	0.000002	0.000001	0.000004	0.000004
			RSD%	98.5	0.967	0.0510	11.2
12724A	1	9/13/91	34.7	0.000004	0.000131	0.007564	0.000036
	2*	9/13/91	11.1	0.000013	0.000129	0.007581	0.000037
	3	10/8/91	42.4	0.000004	0.000141	0.007566	0.000036
	4	10/8/91	23.9	0.000003	0.000130	0.007571	0.000036
	5	10/8/91	40.8	0.000002	0.000135	0.007566	0.000034
			MEAN	0.000003	0.000134	0.007567	0.000036
			SD	0.000007	0.000005	0.000003	0.000001
			RSD%	245	3.72	0.0395	2.82

* Total signal less than optimum: max intensity = 3 V. Values not used in the MEAN or SD calculations.

TABLE 4. Uranium Standards Analyzed in Conjunction with ISPO A.169 Samples

SAMPLE NO	RUN #	DATE	V-MIN	233/238	234/238	235/238	236/238
NBS-500	1	9/11/91	28.0	0.000006	0.010424	1.000153	0.001545
	2	9/11/91	63.1	0.000007	0.010418	0.999932	0.001539
	3	9/11/91	33.6	0.000008	0.010420	1.000077	0.001534
	4	9/11/91	29.8	0.000009	0.010440	1.000030	0.001538
	5	9/11/91	34.5	0 000003	0.010435	1.000080	0.001534
			MEAN	0.000007	0.010427	1.000054	0.001538
			SD	0.000002	0.000010	0.000081	0.000005
			RSD%	34.9	0.0924	0.0081	0.294
			Certified values	NA	0.010422	0.999700	0.001519
			Uncertainty	NA	± 0.000019	± 0.001000	± 0.000006
			Measured/Certified	NA	1.000518	1.000355	1.012508
NBS-U010	1	9/23/91	48.3	0.000003	0.000055	0.010142	0.000071
	2	9/23/91	20.1	0.000003	0.000049	0.010154	0.000074
	3	9/23/91	18.1	0.000001	0.000055	0.010141	0.000067
	4	9/23/91	35.1	0.000010	0.000056	0.010148	0.000083
	5	9/26/91	29.5	0.000002	0.000057	0.010145	0.000074
	6	9/26/91	34.4	0.000003	0.000061	0.010146	0.000075
	7	9/26/91	24.3	0.000001	0.000054	0.010131	0.000068
	8	9/26/91	47.3	0.000000	0.000059	0.010140	0.000074
			MEAN	0.000001	0.000056	0.010143	0.000073
			SD	0.000004	0.000004	0.000007	0.000005
			RSD%	298	6.41	0.0662	6.76
			Certified values	NA	0.0000547	0.010140	0.0000688
			Uncertainty	NA	± 0.0000005	± 0.000010	± 0.0000007
			Measured/Certified	NA	1.019196	1.000333	1.064680

TABLE 4. Uranium Standards Analyzed in Conjunction with ISPO A.169 Samples (continued)

SAMPLE NO	RUN #	DATE	V-MIN	233/238	234/238	235/238	236/238
NBS-U030	1	9/26/91	36.5	0.000004	0.000198	0.031430	0.000219
	2	9/26/91	29.1	0.000001	0.000198	0.031429	0.000212
	3	9/26/91	40.5	0.000000	0.000198	0.031435	0.000212
	4	9/26/91	47.1	0.000003	0.000198	0.031436	0.000216
			MEAN	0.000002	0.000198	0.031433	0.000215
			SD	0.000002	0.000000	0.000004	0.000003
			RSD%	91.3	0.0000	0.0112	1.58
			Certified values	NA	0.0001960	0.031430	0.0002110
			Uncertainty	NA	± 0.0000010	± 0.000031	± 0.0000010
			Measured/Certified	NA	1.010204	1.000080	1.017773
IRM-199	1	9/10/91	41.3	1.000011	0.002050	1.000376	0.000264
	2	9/10/91	27.8	0.999961	0.002064	1.000281	0.000276
	3	9/10/91	37.2	1.000033	0.002062	1.000329	0.000261
	4	9/10/91	46.7	0.999920	0.002036	1.000278	0.000256
	5	9/10/91	50.5	0.999999	0.002055	1.000315	0.000261
	6	9/11/91	77.9	1.000027	0.002053	1.000347	0.000265
	7	9/11/91	44.7	1.000075	0.002059	1.000362	0.000256
	8	9/11/91	56.1	1.000011	0.002055	1.000332	0.000261
	9	9/11/91	30.5	1.000018	0.002054	1.000355	0.000261
	10	9/11/91	21.5	1.000033	0.002045	1.000351	0.000258
			MEAN	1.000009	0.002053	1.000333	0.000262
			SD	0.000042	0.000008	0.000033	0.000006
			RSD%	0.0042	0.4003	0.0033	2.21
			Certified values	1.00001	0.002051	1.00015	0.000246
			Uncertainty	± 0.0003	± 0.00001	± 0.0002	± 0.00001
			Measured/Certified	0.999999	1.001121	1.000183	1.064634

TABLE 5. Comparison of Peak-Jumping (LANL) and SAL Multicollector Results with LANL Total-Evaporation Results (^{239}Pu Reference)

SAMPLE NO.	DATE	LOADING RUN NO.	OBSERVED RATIOS, PEAK-JUMPING AXIAL COLLECTOR			DATA PLOTTED IN FIGURES 2,3,4 DEVIATION FROM LANL TOTAL EVAPORATION %		
			240/239	242/239	244/239	240/239	242/239	244/239
12701A	9/25/92	1-1	.46739 ± .008	1.18587 ± .11	.45128 ± .022	−.100	−.232	−.409
		1-2	.46769 ± .011	1.18803 ± .014	.45254 ± .015	−.035	−.050	−.130
	10/8/92	2-1	.46771 ± .011	1.18803 ± .03	.45261 ± .036	−.031	−.050	−.114
SAL Data Multicollector			.46794	1.18567	.45058	+.018	−.249	−.565
12702A	9/25/92	1-1	.46212 ± .009	1.06852 ± .012	.40579 ± .013	−.086	−.172	−.281
	10/8/92	2-1	.46239 ± .007	1.06903 ± .015	.40604 ± .027	−.028	−.125	−.219
SAL Data Multicollector			.46284	1.06942	.40576	+.069	−.088	−.288
12703A	9/30/92	1-1	.492164 ± 015	1.73518 ± .036	.666211 ± .040	−.061	−.013	−.037
	9/30/92	2-1	.492274 ± .010	1.73437 ± 0.16	.665574 ± .026	−.038	−.059	−.133
		2-2	.492793 ± .009	1.74040 ± .016	.669322 ± .016	+.067	+.288	+.430
	9/30/92	3-1	.491823 ± .009	1.73075 ± .023	.663632 ± .034	−.130	−.269	−.426
		3-2	.492499 ± .009	1.73811 ± .012	.667905 ± .020	+.007	+.156	+.217
		3-3	.492553 ± .005	1.73733 ± .005	.667712 ± .007	+.018	+.134	+.188
		3-4	.492633 ± .010	1.73877 ± .020	.668464 ± .032	+.035	+.194	+.301
		3-5	.493146 ± .014	1.74408 ± .015	.671892 ± .020	+.138	+.500	+.816
	11/25/92	4-1	.49193 ± .008	1.73190 ± .016	.663990 ± .026	−.108	−.202	−.372
		4-2	.49250 ± .005	1.73762 ± .009	.667614 ± .012	+.008	+.128	+.174
SAL Data Multicollector			.49279	1.73361	.66430	+.066	−.103	−.325

Note: Errors listed are internal precision (percent standard error) based on 30-50 ratios.

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TABLE 6. LANL Single Filament/Ion Counting: Average of Five Filament Loadings

SAMPLE	238/239	240/239	241/239	242/239	244/239
12701A	.003949	.467946	.069296	1.18981	.45384
SD	.000019	.000395	.000178	.002261	.001354
% RSD	.48	.08	.28	.19	.30
TOTAL EVAP.	NA	.46790	(.6930)*	1.18858	.45311
SAL RESULTS	.00395	.46794	.06919	1.18567	.45058

DEVIATIONS FROM LANL TOTAL EVAPORATION

	238/239	240/239	241/239	242/239	244/239
LANL ION COUNTING		+ .010%	- .006%	+ .10%	+ .16%
SAL		+ .009%	- .160%	- .25%	- .56%

SAMPLE	238/239	240/239	241/239	242/239	244/239
12702A	.003824	.46245	.06926	1.0710	.40715
SD	.000018	.000265	.000130	.00024	.00036
% RSD	.47	.06	.21	.02	.09
TOTAL EVAP.	NA	.46256	(.06890)*	1.07033	.40691
SAL RESULTS	.00385	.46284	.06906	1.06942	.40576

DEVIATIONS FROM LANL TOTAL EVAPORATION

	238/239	240/239	241/239	242/239	244/239
LANL ION COUNTING		- .024%	+ .52%	+ .06%	+ .059%
SAL		+ .060%	+ .23%	- .085%	- .28%

SAMPLE	238/239	240/239	241/239	242/239	244/239
12703A	.004503	.49218	.07008	1.7348	.66596
SD	.000040	.00037	.00010	.00097	.00045
% RSD	.90	.08	.16	.06	.07
TOTAL EVAP.	NA	.49251	(.06990)*	1.7353	.66644
SAL RESULTS	.00449	.49279	.07012	1.7336	.66434

DEVIATIONS FROM LANL TOTAL EVAPORATION

	238/239	240/239	241/239	242/239	244/239
ION COUNTING		- .067%	+ .26%	- .029%	- .072%
SAL		+ .057%	+ .31%	- .098%	- .316%

Ratios corrected for decay to 1/11/90; analysis dates 11/25/92 to 12/1/92; average of five filament loadings. Deviations plotted in Figs. 8, 9, and 10.

* 241 TOTAL EVAP. not decay corrected (because both americium and plutonium are measured).

TABLE 7. CRM-128 Analyzed Concurrently with Samples 12701A, 12702A, and 12703A (Single-Filament Ion-Counting Technique)

DATE	RUN NO.	CORRECTED 242/239
11/30/92	1	1.00198
11/30/92	2	1.00138
11/30/92	3	1.00132
11/30/92	4	1.00078
11/30/92	5	0.99993
11/30/92	6	0.99987
11/30/92	7	1.00045
11/30/92	8	1.00296
11/30/92	9	1.00127
11/30/92	10	1.00093
12/1/92	11	1.00322
12/1/92	12	0.99842
12/1/92	13	1.00084
12/1/92	14	0.99988
12/1/92	15	<u>1.00068</u>
	MEAN	1.00093
	STD. DEV.	0.00122
	% RSD	0.12
	CERTIFIED VALUE	1.00085 ± .0003
	DEVIATION FROM CERTIFIED	+ .008%

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TABLE 8. Deviations of LANL Peak-Jumping Results and SAL Multicollector Results from LANL Total-Evaporation Results (^{242}Pu Reference)

SAMPLE	DATE	RUN NO.	239/242	240/242	244/242
12701A	09/25/92	1-1	+.233	+.135	-.176
		1-2	+.050	+.015	-.079
	10/08/92	2-1	+.050	+.020	-.063
	SAL (Multicollector)		+.250	+.267	-.316
12702A	09/25/92	1-1	+.172	+.086	-1.08
	10/08/92	2-1	+1.25	+.097	-.095
	SAL (Multicollector)		+.089	+.160	-.200
12703A	09/30/92	1-1	+ .012	- .048	- .024
		2-1	+ .059	+ .021	- .073
		2-2	- .288	- .221	+ .141
		3-1	+ .268	+ .138	- .157
		3-2	- .156	- .149	+ .061
		3-3	- .135	- .115	+ .053
		3-4	- .194	- .161	+ .108
		3-5	- .500	- .363	+ .313
	11/25/92	4-1	+ .202	+ .093	- .169
		4-2	- .128	- .122	+ .045
	SAL (Multicollector)		+ .103	+ .171	- .222

Note: same data as Table 5, recalculated using ^{242}Pu as the reference isotope.

Appendix B

ISPO A.169

Task Statement

TASK AREA A - Measurement Technology

89/SAL02 (A. 169)

Subtask: Advanced Methods in Surface Ionization Spectrometry

Contractor: LANL

Problem: The multidetector mass spectrometers used in the Safeguards Analytical Laboratory (SAL) permit the measurement of isotopic ratio measurements with excellent internal precision (< 0.1% for the major ratios). Accuracies and external precisions do not match the instrument capability due to problems in the handling of the sample. These problems include reproducibility of the sample loading technique on the sample filaments for insertion into the mass spectrometer and matching the chemical separation technique to the sample loading technique.

Objective: Assist SAL to improve the accuracy and precision of isotopic analysis of uranium and plutonium measurements made by thermal-ionization mass spectrometers.

Activities:

Phase I:

a.   In consultation with the IAEA, develop a detailed work plan.

b.   Evaluate the performance of the total evaporation method on actual samples supplied by SAL. Prepare a report for IAEA evaluation.

Phase II:

c.   If the results of activity b. indicate possible negative impact from impurities, explore techniques to overcome this problem.

Schedule & Milestones:

Phase I

1.   Start task   - May 1990

2.   Complete (a)   - July 1990

3.   Complete (b)   - December 1990

Phase II

1. Complete (a)   - To be determined (TBD)

Funding:

        Phase I   1990 - $80,000

        Phase II   1991 - TBD

89/SAL02   (15)

DISCUSSION

1. IAEA Requirements

The IAEA has stated that the precision and accuracy (0.1% and 0.5% respectively) of their mass spectrometric measurement of plutonium isotopes is at present sufficient to satisfy requirements for existing facilities. However, unless improvements are made, it will not be adequate in verifying inventories for larger plants. A significant portion of the 0.5% total error is due to the mass spectrometry (0.2-0.3%). Hence, improvement in the mass spectrometry measurement would both lower the total error and be an incentive for reducing the sampling and chemical errors.

2. Preliminary Work Plan

Phase I

(a) Prepare a Detailed Work Plan

In consultation with the IAEA Task Officer, prepare a detailed work plan for Phase I. Include in the work plan an experimental plan for testing the total-evaporation method using samples from SAL.

(b) Evaluate the Total-Evaporation Method

Determine the optimum sample size and loading procedures for the total-evaporation method. Analyze samples provided by SAL as outlined in the experimental plan. Compare results obtained by the total-evaporation method with those obtained by SAL using their standard procedures. Decide if there is sufficient evidence of a problem with impurities to continue to Phase II. Provide an interim report.

<u>Phase II</u>

(c)   Explore Techniques to Improve the Total-Evaporation Method

Identify any impurities which affect the performance of the total-evaporation method. Devise methods to overcome these problems and improve the chemical separations. Investigate the suitability of internal calibration procedures (double-spike method) on actual SAL samples. Compare these results with those obtained from the same samples run to exhaustion using the total-evaporation method and SAL's standard method. Provide a report of the results.