Use of IsoProbe for Uranium and Plutonium Analysis in Environmental Samples

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Progress Report

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in Environmental Samples**

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Introduction:
The ability to detect and isotopically characterize uranium and plutonium in environmental samples is of primary importance in the search for nuclear proliferation. The utility of isotope ratio measurements for environmental monitoring is limited by sample preparation costs, measurement precision, and sensitivity. This is particularly true for wide-area monitoring where the number of samples required varies inversely with obtainable precision and sensitivity. This report summarizes an initial evaluation of the applicability of a new technique, magnetic-sector, multicollector, inductively-coupled-plasma mass spectrometry, to environmental sample analysis. This technique is embodied at Lawrence Livermore National Laboratory in the form of a commercially available instrument, the IsoProbe, manufactured by Micromass, LTD. (United Kingdom). Ours is the second of the current generation of such instruments installed in the United States and the first within the Department of Energy complex.

Inductively-coupled plasma mass spectrometry (ICPMS) using quadrupole mass filters has existed for roughly 15 years. Magnet sector instruments have also existed for about half that time and multicollector instruments have existed for nearly as long. Among the things that make the new generation of instruments, and the IsoProbe in particular, unique are (1) the use of a gas-collision cell to reduce the energy spread of the ions and to remove ions associated with the plasma gas and (2) the introduction of multiple electron-multiplier detection systems. The net effect of these features is to increase sensitivity and precision.

Historically uranium and plutonium isotopic compositions have been determined by thermal ionization mass spectrometry (TIMS). While requiring extensive sample preparation, no other technique matched its precision and sensitivity for such measurements. The purposes of this project are to evaluate whether the IsoProbe can replace TIMS for environmental monitoring analyses, whether it can extend the state-of-the-art to higher precision, and whether costs savings can be achieved at the same time.

Configuration of the LLNL IsoProbe:
As currently configured, sample can be introduced into the plasma by conventional solution nebulization (~1 ml/min), micro-nebulization with desolvation (~0.1 ml/min), or laser ablation (direct sampling of solids). Ions generated in the plasma pass through a hexapole collision cell where they are thermalized (energy spread reduced) and then through a sector magnet. Ion beam detection is through 9 Faraday cups, 7 electron multipliers, and a Daly detector equipped with an energy filter to increase abundance sensitivity. The collector slit on the "axial" (middle) detector is also adjustable to achieve higher resolution on this central detector, which can be either a moveable Faraday or the Daly. The Daly detector is fixed in the axial position. The Faradays and electron multipliers can be adjusted along the focal plane to properly position them for simultaneous collection of multiple peaks.

Personnel:
The principle operator is Ross Williams. The responsible person is Ian Hutcheon. The contact for this project is Price Russ.

Status of the Instrument:
The IsoProbe was physically installed in the laboratory in November 1999. It was activated by factory trained personnel in February and March 2000. Initial performance evaluations have been made using conventional and micro-nebulization, Aridus system (Cetac Technologies), have been made. As expected the Aridus system not only uses less sample but also yields more ions per atom consumed. At this time laser ablation has not been used. All of the detection options have been tested and found to operate, but some details of inter-calibration and stability have not been fully evaluated.

As can be expected with a new technology, a number of issues had to be addressed during the initial period of operation. Most were minor and attributable to "the learning curve". One problem is significant and as yet not fully resolved. This is the presence of background peaks at every mass, Figure 1. These peaks, which are of the order of 10^{-16} - 10^{-15} amps in intensity, almost certainly arise from interactions in the hexapole drift tube region and vary in intensity with plasma conditions and extraction voltage. While they limit detection limits and require the subtraction of "on-peak" backgrounds, their intensity is reasonably stable under fixed operating conditions. Therefore, it is possible to obtain high-precision isotope ratios using the Faraday detectors. On-peak backgrounds are determined by multiple analyses of a blank. Typically blank measurements bracket each group of five samples. We are currently working with the manufacturer to understand these peaks and find a way to eliminate them.

Preliminary Uranium and Plutonium Studies:
In evaluating whether the IsoProbe and similar technology can improve the quality of uranium and plutonium isotopic measurements in environmental samples and whether it can accomplish this while also reducing costs requires evaluating a variety of parameters. These include
- Sensitivity for U and Pu.
- Precision and accuracy of $^{238}U/^{235}U$ determinations using externally determined bias factors.
- Precision and accuracy of $^{238}U/^{235}U$ determinations using the double spike technique to correct for bias.
- Precision of minor isotope determinations.
- Background
- Interferences
- Limits on ^{236}U determinations and how the energy filter and high-resolution options effect the ability to detect this isotope.
- Use of multiple electron multipliers for isotopic ratio determinations at low intensity. This is particularly important for plutonium, which usually occurs at much lower concentrations than uranium.
- Use of simplified chemical preparation.

- Simultaneous measurement of U and Pu isotopes using a combination of Faraday and multiplier detectors.

One also needs to evaluate different methods of sample introduction. This is not as simple as determining the sensitivity change for different sampling techniques. For example using the Aridus sampling system increases sensitivity by an order of magnitude, but it also exacerbates the background peak problem mentioned earlier.

To date we have investigated the instrument's performance for natural uranium and investigated the detection limit for plutonium. The preliminary results for these studies will be presented here.

Uranium:

For uranium we have attempted to compare the precision and sensitivity of IsoProbe analyses to TIMS performance. For TIMS our typical sample load is 50 - 100 ng and an analysis using pulse counting detection extends over several hours. With the IsoProbe and the Aridus nebulizer, 1 ml of solution will generate ions for roughly 10 minutes and a uranium concentration of 40 ppb will produce an ion beam $> 10^{-10}$ amps for ^{238}U. Such a signal will saturate the Faraday detectors so the concentration must be kept below 40 ppb. For the work to be described, the uranium concentration was about 30 ppb and the total uranium consumed per analysis was <40ng. In addition to the 10 minute analysis time, a ten minute wash-out was used between samples for a total time per analysis of 20 minutes.

A natural uranium sample, NIST SRM 4321C (equivalent to NBS960 and NBL CRM 112-A), was analyzed 16 times per day on each of three days spread over a eight day period. In order to assess the extent and variability of mass bias the sample was spiked with the LLNL ^{236}U/^{233}U double spike. The spike level was selected such that ^{236}U/^{235}U was ~2.5. This value was used so that the error in the spike determinations would be less than that in the ^{235}U measurements while using a minimal amount of the spike. Because the double spike is unlikely to be used in all real world samples and to extract as much data as possible from the data set, ^{238}U/^{235}U was evaluated both considering and ignoring the double spike. ^{234}U was also measured but with the Daly detector rather than a Faraday channel.

Before discussing the results it is useful to establish a reference point for performance. Figure 2 shows ^{238}U/^{235}U results for a suite of soil samples measured by TIMS using the double spike. For samples of <100ng uranium, this plot reasonably represents the state-of-the-art for TIMS. The typical mass fractionation correction applied was ~0.0005 per mass unit.

Figures 3 - 5 are the ^{238}U/^{235}U results for each of the three days. The ratios plotted have not been corrected for mass bias. Note that the vertical scale in Figures 3 - 5 is one third that of Figure 2. Several conclusions can be quickly drawn. Obviously, the mass bias is much larger than the fractionation observed in TIMS. There was essentially no change in bias between days one and two but it was significantly different on day three. The

difference on day three was the use of a different extraction potential. The data scatter beyond the reported uncertainty for each analysis, but there is no trend in the variation during the course of the analyses on a given day. Although the data scatter beyond the reported uncertainty, the total range of observed values for any given day is smaller than in the double-spike corrected TIMS data shown in Figure 2. Under fixed operating conditions, if one determines the bias from only one analysis of a standard, $^{238}U/^{235}U$ can be determined in samples to better than ±0.1% (1 std. dev.) for samples containing less than 50 ng of uranium.

The results of using the double spike to correct for bias are shown in Figures 6 - 8. The correction was made using the average ratios for the 30 data collections for each sample. The double spike corrected $^{238}U/^{235}U$ values scatter less than the uncorrected values. It is important to note that this reduction could not have been achieved with an external standard. The average of all 48 determinations is 137.84 ± 0.05 (1 σ). This is in good agreement with the usually accepted value of 137.88. (Deleting the three most deviant points would not change the average but would reduce the standard deviation to 0.03.) The relative standard deviation of 0.04% is a substantial improvement in the state-of-the-art for samples of a few tens of nanograms. In spite of this, a closer inspection of the data reveals several problems that need to be addressed. The values measured in this study suggest that there is a slight bias with respect to the nominal value. This could be a calibration problem with the double spike, the nominal value may be incorrect, or there may be some other factor. The scatter of the data are also larger than can be explained by the statistics of the individual analyses.

To investigate the variations among analyses, we plotted the individual $^{238}U/^{235}U$ and $^{236}U/^{233}U$ values in the order they were collected to look for variations that the bias correction would not address. The results for a subset of the data are shown in Figure 9. It is clear that even though the bias is not discernibly changing over the course of the set of analyses it is varying within the time frame of a single analysis. The changes in bias do not, however, correspond to changes of the sample. As a result of this observation, the data were reprocessed making the bias correction for each measurement of $^{238}U/^{235}U$ from the simultaneously measured $^{236}U/^{233}U$. The results are shown in Figures 10 - 12. The effect of making the bias correction on the individual ratios is to reduce the calculated uncertainty of each point. It does not change the average values for $^{238}U/^{235}U$ but does reveal a residual analysis-to-analysis variation that is limiting the precision of the technique. This variation is not understood but likely related to the background peaks. We are continuing to investigate this issue.

The ability to determine $^{234}U/^{235}U$ using the Daly for the ^{234}U measurements was also investigated. The results are plotted in Figures 13 -15. The average for all determinations is 0.00726 ± 0.00004 (1 σ) in good agreement with the nominal value of 0.00730 (± 1%). There does however seem to be a difference between the results for the first two sets of data and the third one. Again this may have to do with the background peaks. Detector gain factors may also be important. In any case one can determine $^{234}U/^{235}U$ to within 1% in a near-normal sample. The statistical uncertainties for each determination is typically 0.1% (2 σ mean) compared to about 0.8% for similar samples by TIMS as measured in

our laboratory. If we can improve the "external" precision of the $^{234}U/^{235}U$ determinations, we will achieve a substantial improvement over TIMS in the ability to determine this ratio.

With the double spiked samples it is impossible to estimate the ability of the system to detect ^{236}U at environmental levels. With the energy filter and high resolution (~1500) option to improve abundance sensitivity, it should be possible to achieve a dynamic range of 10^9 and an abundance sensitivity of ~10^8. Unfortunately at this time the ubiquitous on-mass background peaks severely limit the ability to measure minor peaks. To put some limits on the ability to measure minor isotopes in the presence of the background, $^{236}U/^{235}U$ was measured in a set of 6 natural uranium samples where there should be no ^{236}U. The precision with which "0" can be measured qualitatively establishes a detection limit for minor isotopes. It can also help understand the scatter to be expected in other measurements. The results for the six determinations are shown in Figure 16. While two standard deviations of the mean of each value is typically 0.00002 or $2x10^{-7}$ of the total uranium, the standard deviation of the six measurements is 0.0001 - 5 times the apparent uncertainty. Based on these data it is unreasonable to expect to detect, much less quantify, peaks with < 1 ppm abundance. A variation in the background of $1x10^{-4}$ relative to ^{235}U would explain the 1% variation observed in $^{234}U/^{235}U$. It would also explain half of the scatter seen in $^{238}U/^{235}U$ (if the 3 most deviant point are excluded).

One should note that there are two components to this problem. One is the variability of the background peaks in time. The other has to do with the counting statistics uncertainty in their measurement. If the total background could be reduced to the dark current of the detector, the internal precision would be much less than the $2x10^{-7}$ value given above. The fact that the internal precisions are much better than the external does imply that the background peaks are relatively constant on the time scale of the measurements (10 minutes).

Plutonium Detection Limit:
A detection limit study for plutonium was done by standard additions using NBS SRM 948 using the Daly detector. Blanks, 10, 20, 40 and 80 fg/g (ppq) standards were analyzed. Figure 17, the blank subtraction plot for ^{239}Pu illustrates the magnitude of the on-peak backgrounds and their variability. Blanks were analyzed before and after the standards and the drift was assumed to be linear with time for the purposes of correction.

The uncertainties plotted and propagated in the calculations are one standard deviation on 30 measurements. These uncertainties are conservative because they are greater than the theoretical 2-sigma uncertainties from counting statistics for an integration time of 5 seconds, and are also greater than the 2-sigma of the mean for the 30 measurements. Blank corrected ^{239}Pu count rates are different from zero for all standards.

A regression analysis was used to calculate the uncertainties on the slope and intercept of the regression line using the analytical uncertainties on both "X" and "Y" values. For ^{239}Pu, the minimum detectable level, 8 ppq, is taken as the negative of the intercept of the minimum slope with the X-axis. That is, if this minimum slope is taken to be a

calibration (response) curve originating at the origin, then only signals from ^{239}Pu samples greater than or equal to 8 ppq will have count rates statistically different from zero. For a 10 minute analysis using 1 ml of solution, this corresponds to the consumption of 8 femtograms of Pu.

These data indicate that without further background reduction, ^{240}Pu /^{239}Pu ratios could be measured in 0.1 pg Pu with a precision of only about 75%. The measured ^{240}Pu /^{239}Pu ratio for the 80 fg sample was 0.126 ±0.093 compared to the certified value of 0.086. Investigation of the precision obtainable for plutonium isotopics in the picogram range is a high priority. Efforts will continue to determine the factors contributing to the high backgrounds.

Summary:
Preliminary studies using uranium and plutonium standards support the concept that the IsoProbe and similar technologies can effectively compete with and likely supplant TIMS as the preferred technique for isotopic determinations. Before this can happen additional work is required to understand the background peaks observed in the IsoProbe, the system must be more fully characterized, and the level of sample preparation needed will have to be evaluated.
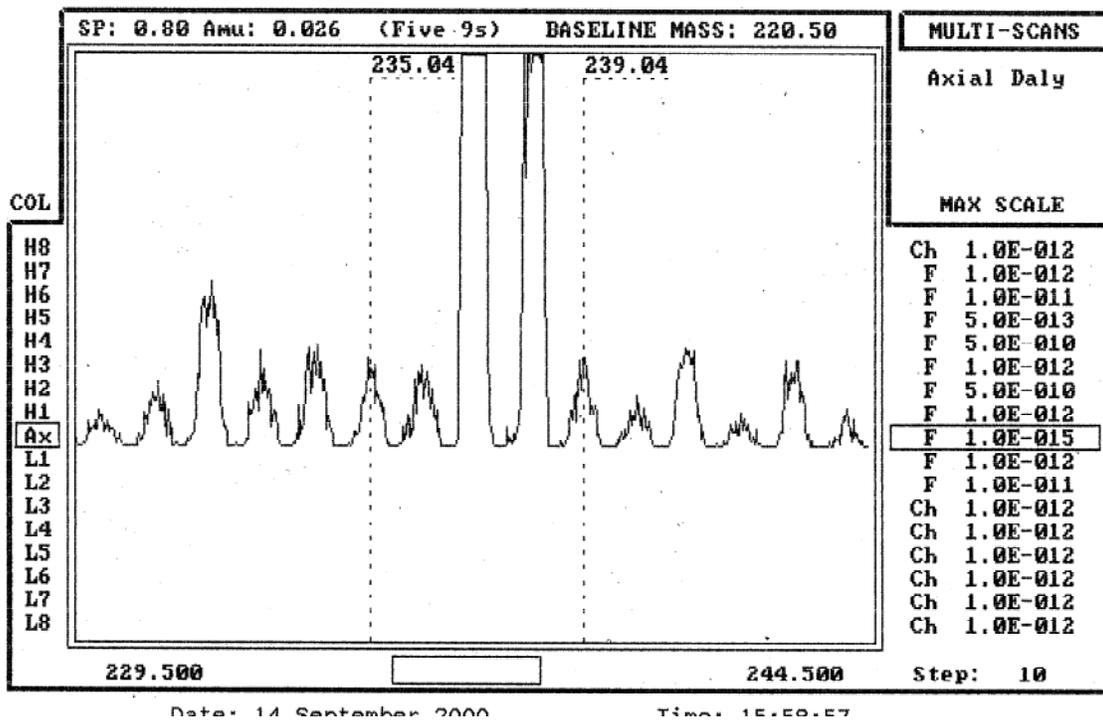
IsoProbe scan showing background peaks at all masses. The peak at 238 is uranium contamination. The one at 237 is $AuAr^+$. (The hexapole rods are gold plated.)

Figure 1
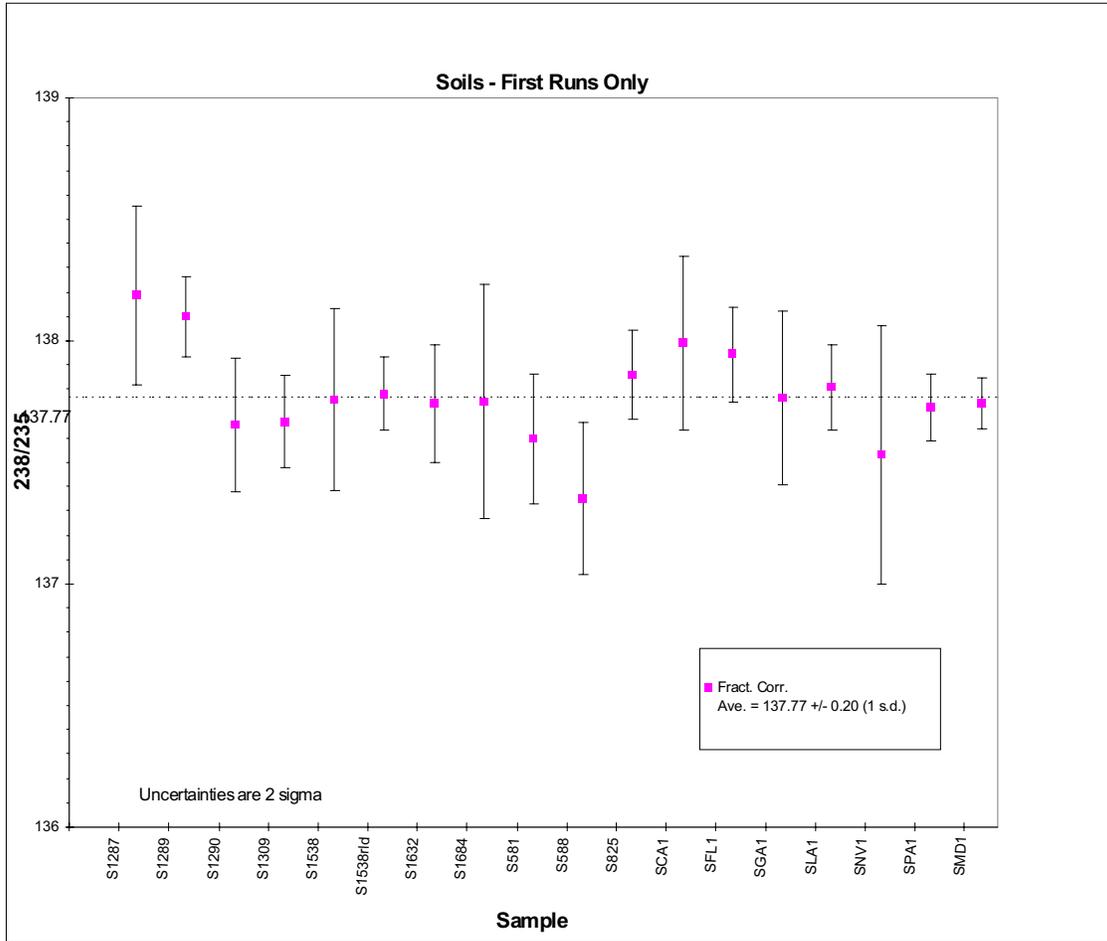
TIMS results for a series of soils

Figure 2
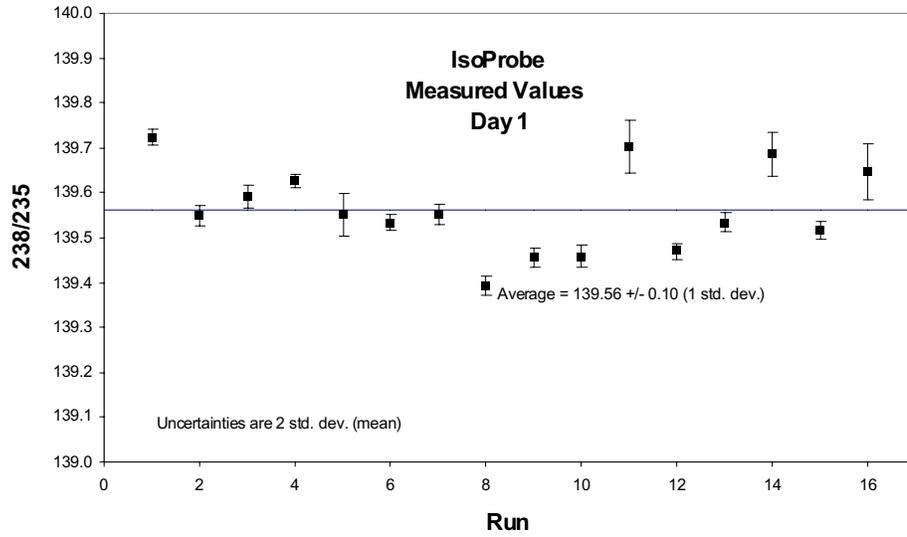
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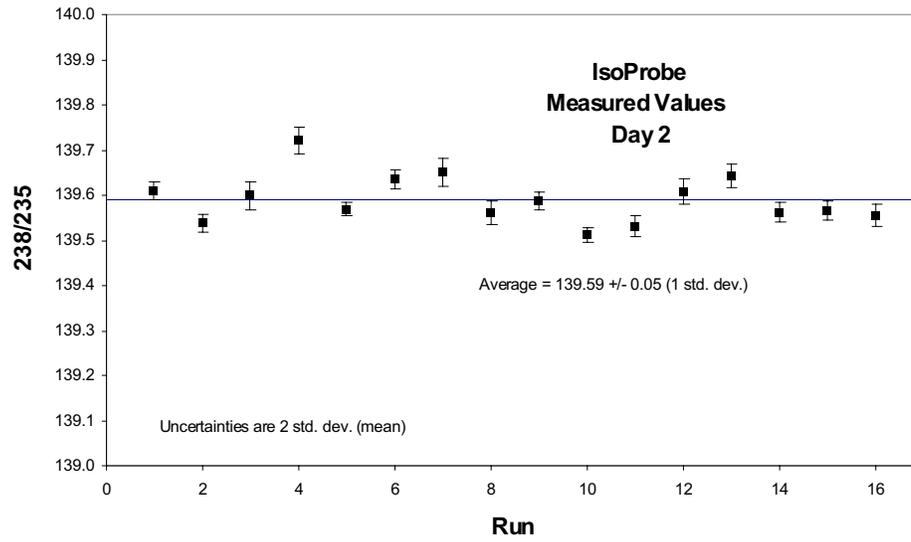
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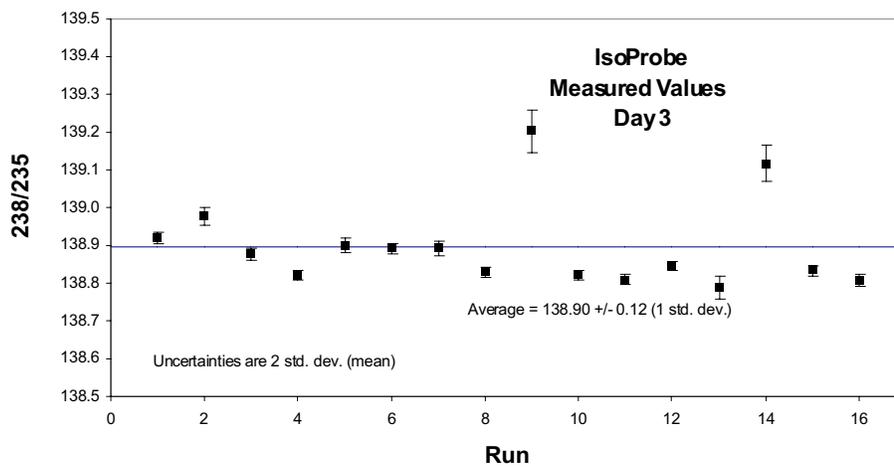
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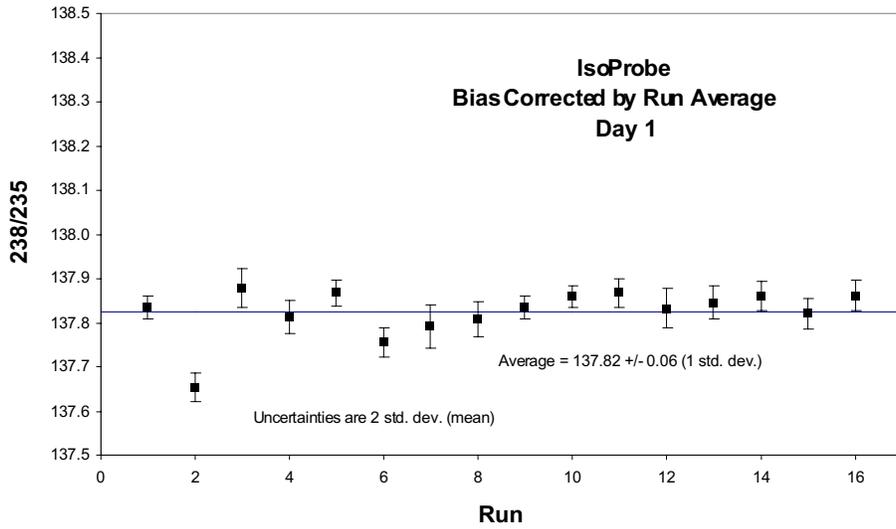
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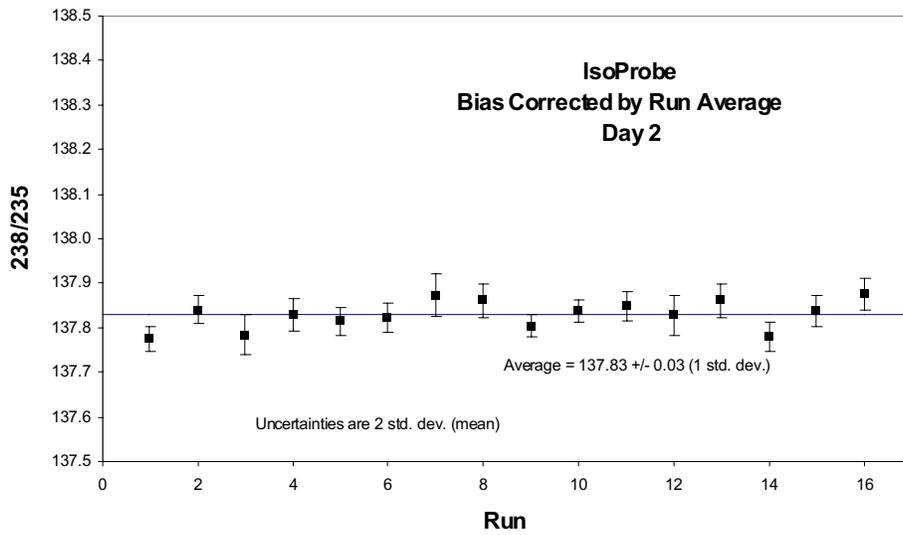
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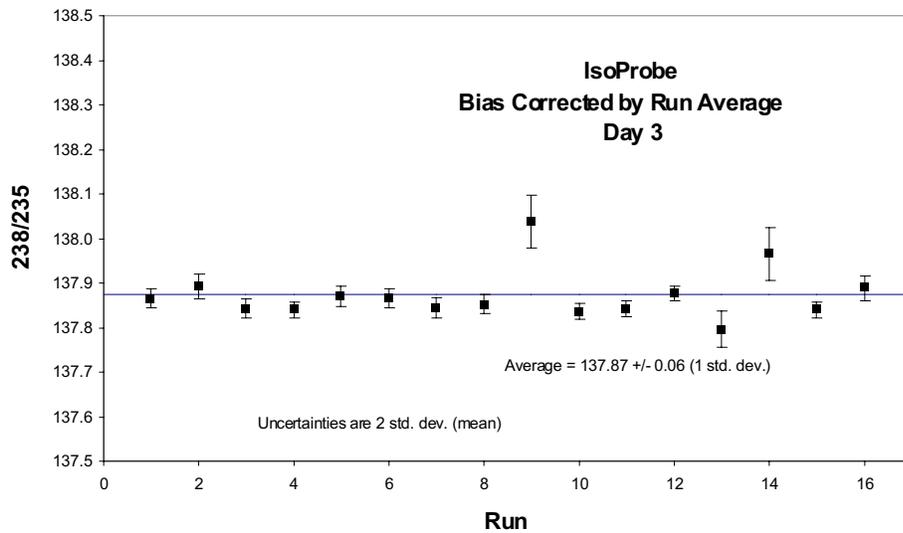
Figure 8
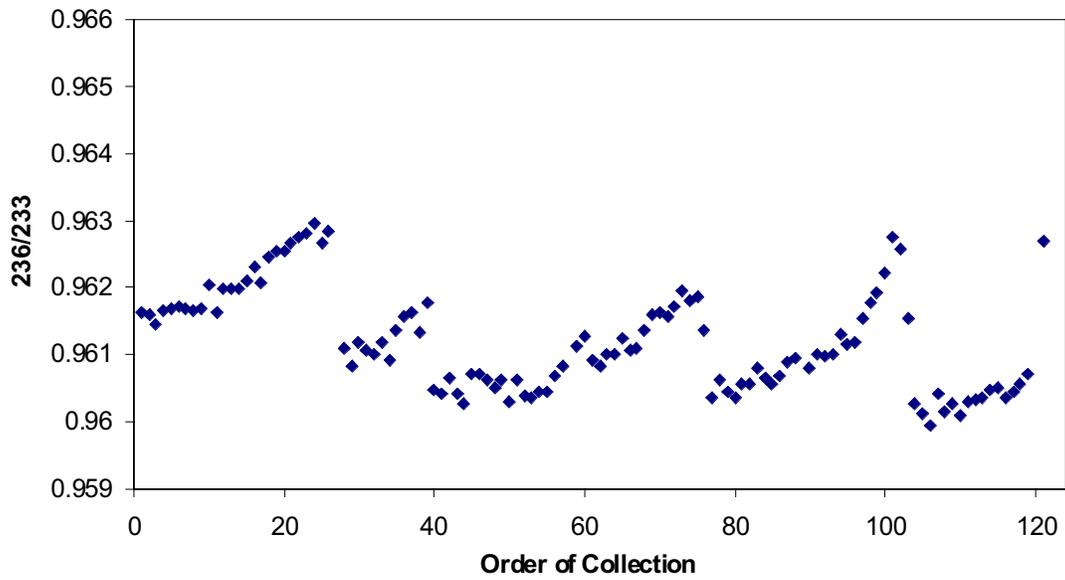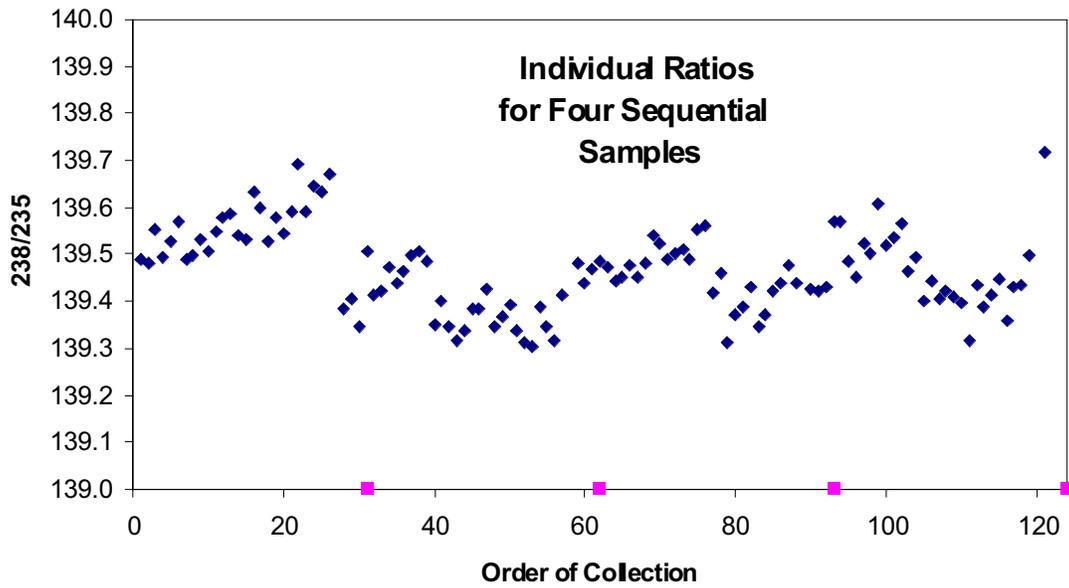
Figure 9

Sample changes occurred at the points indicated by the squares along the abscissa in the upper plot. The time elapsed between samples would be approximately equivalent to 30 points.
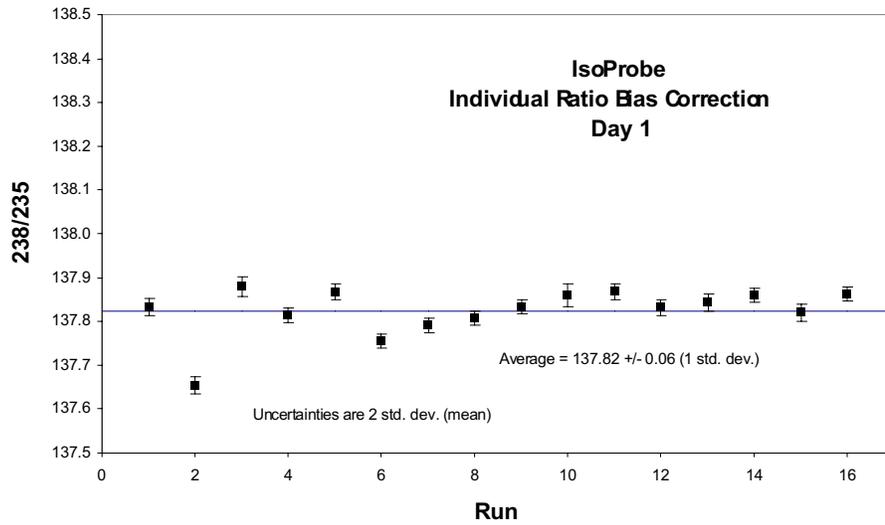
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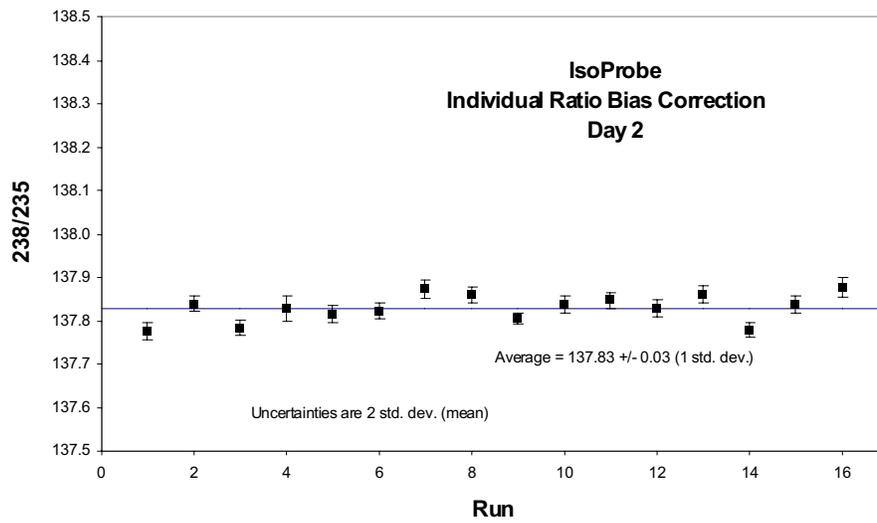
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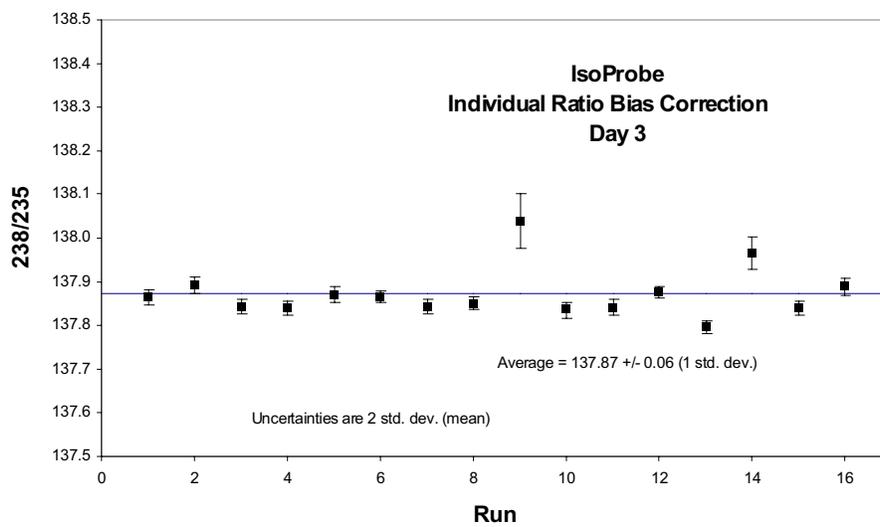
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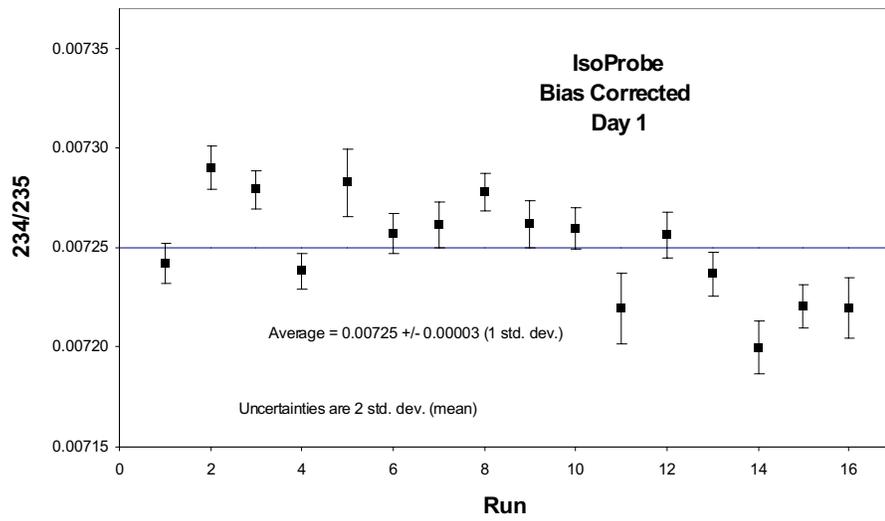
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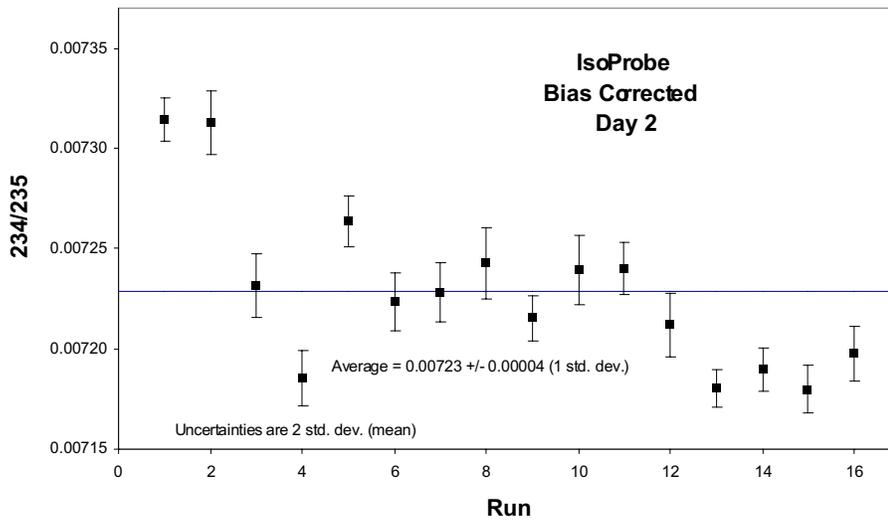
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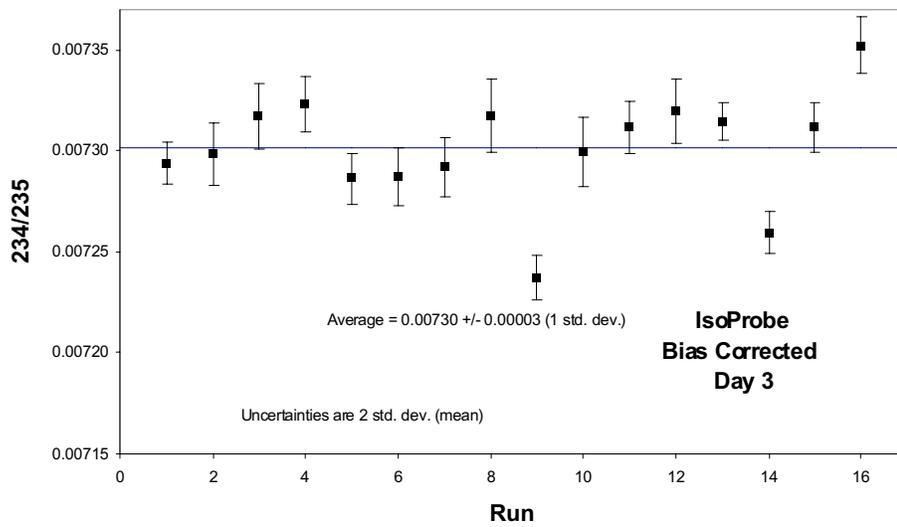
Figure 15
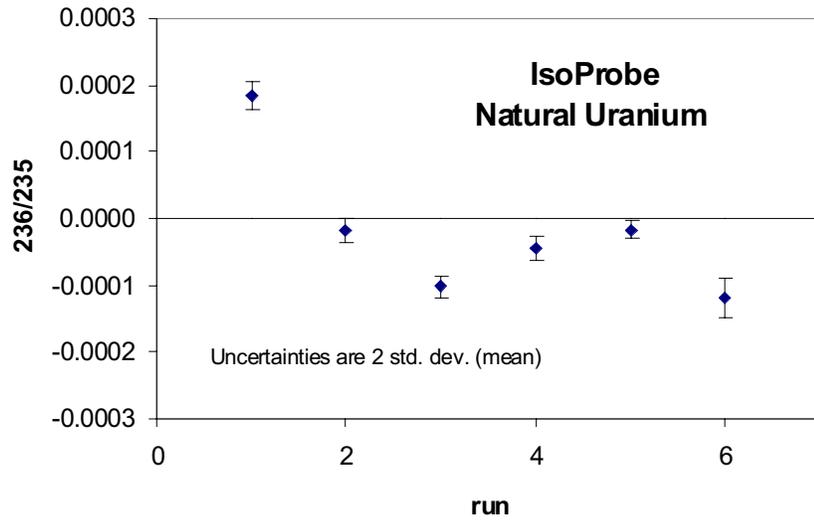
Figure 16

^{239}Pu Standard Additions - Blank Subtraction
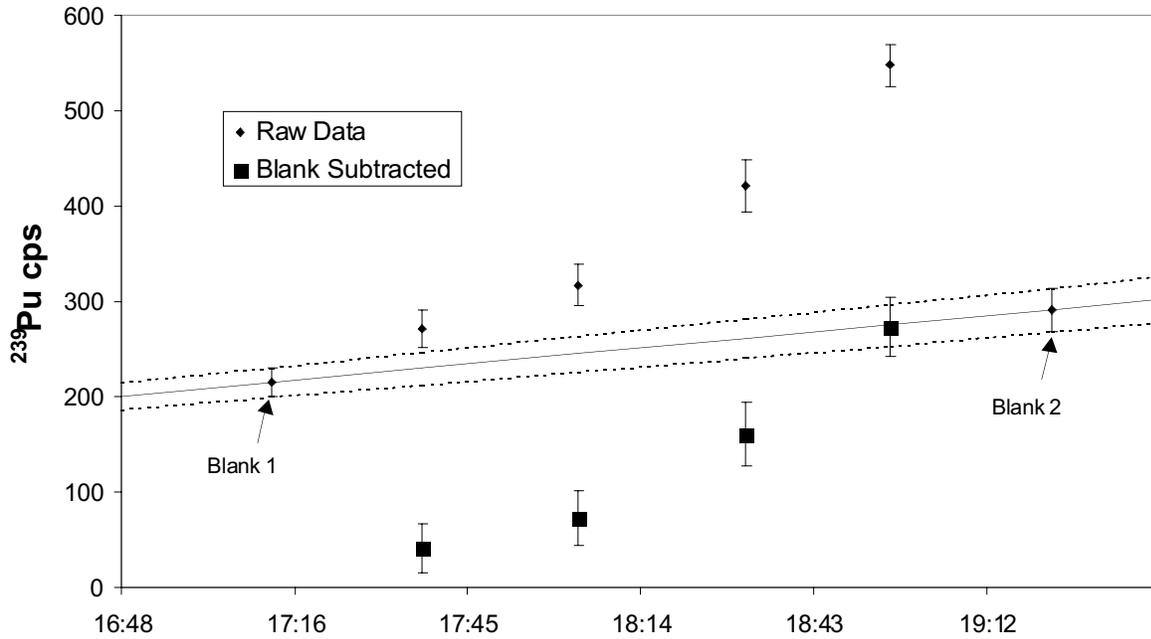
Figure 17

^{239}Pu Standard Additions

Figure 18