A Survey of Uranium and Thorium Background Levels in Water, Urine, and Hair and Determination of Uranium Enrichments by ICP-MS

Amir H. Mohagheghi[*1], Sonoya T. Shanks[1], Joseph A. Zigmond[1], Gary L. Simmons[1], and Sandra L. A. Ward[2]. [1]Sandia National Laboratories, P.O.Box 5800, Albuquerque, NM 87185. [2]New Mexico State University, P.O.Box 8001, Las Cruses, NM 88003.

Abstract

Sandia National Laboratories collects bioassay samples to monitor individuals for possible exposure to uranium and thorium as part of ongoing medical surveillance of employees. The current analytical methods involve separation chemistry and alpha spectrometry for isotopic measurements or Kinetic Phosphorescence Analysis for total uranium. There are several areas where this monitoring can be improved (e.g. analysis times and accurate isotopic ratio measurements). In addition, in case of accidents or exposure to people who are not routinely monitored, the optimum window for collecting bioassay samples may be missed. An example of this scenario is the recent concern over the exposure of civilians to Depleted uranium from military ammunition in Kosovo and Kuwait. For these cases, hair may be an alternative bioassay. Analytical procedures utilizing an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) have been developed that have simplified sample processing and improved the isotopic ratio measurements. The focus of this study is to survey the background levels for U-235, U-236, U-238, and Th-232 isotopes in hair, urine, and drinking water which could be used to determine action levels for follow-up monitoring. In addition, variations of U-238 to U-235 mass ratio for the background samples are measured. The analytical procedures, achieved detection limits, observed background distributions, and the results of uranium isotope ratio tests are presented.

Introduction

One of the challenges of monitoring personnel for possible exposure to uranium and thorium is the presence of naturally occurring levels of uranium and thorium in collected bioassay samples. Given the fluctuations in background levels, a positive determination of possible low level exposure to man made radioisotopes becomes difficult. In case of chronic or acute exposure to people who are not routinely monitored, the optimum window for collecting urine samples may be missed. An example of this scenario is the recent concern over the

exposure of civilians to Depleted uranium from military ammunition in Kosovo and Kuwait. In addition, background levels vary significantly from one person to the next and also change for the same individual on a time scale as short as a day. This variance is affected by several factors including food and drink sources, metabolism, physical activity, illness, and age. Establishing comprehensive background distributions that take into account all the important parameters is a massive task and is beyond the scope of this study. However, even a limited knowledge of the background variations will be a valuable aid in determining action levels for follow up studies.

In case of uranium monitoring, isotopic information may be used to determine uranium's origin (Depleted or Enriched). The main issue with the current method (chemical separation followed by alpha spectroscopy) is that the U-238 to U-235 ratio is not generally well determined due to relative weakness of the U-235 signal and the overlap in energy between U-235 alpha particles and alpha particles from other uranium isotopes. While these problems can be overcome by taking a large aliquot, improving chemical yields, long count times, and careful spectral analysis, the analysis time and costs can become prohibitive. In addition, thorium analysis will require an additional analytical procedure that is performed separately.

Amid the issues with the current analytic methods are several areas where bioassay monitoring can be improved. In the case of accidents or exposure to people who are not routinely monitored, the optimum window for collecting urine samples may be missed. It is important to note from the time an intake occurs either, through inhalation and/or ingestion, the majority of uranium that enters the body is excreted from the body in the first 24-hours. The majority of that uranium is excreted through the feces, a small amount through the urine, and some through the hair follicles and other paths. The body also has a retention factor for uranium, which drops rapidly. For some people this could happen over the course of a few days.

Therefore the optimum time frame for collecting urine samples varies from a couple of days to less than 24 hours.

Another area needing improvement is the determination of background levels, i.e. levels of uranium and thorium radionuclides naturally present in the body. Background levels vary from one person to the next and also change on a time scale as short as a day. This is due to change in food and drink sources, geographic location, metabolism, physical fitness, illnesses, and age among many other factors. In order to make a diagnosis on an individual/s who may have a possible intake, the knowledge of background levels and the concurrent variance is an integral part to assessing an exposure.

Study Goals

Issues with the current method of isotopic detection and methods in monitoring have prompted a pilot study to investigate alternate methods of uranium and thorium isotopic detection by employing an ICP-MS unit. The ICP-MS method is rapid and inexpensive relative to alpha spectrometry and provides accurate isotopic data for long lived radioisotopes. The proposed solution to develop and test new analytical methods for isotopic detection, using the ICP-MS method is: 1) Investigate the use of hair for exposure monitoring. Hair retains the history of uranium intake much longer than urine or feces does, and is therefore an alternate method of in vitro monitoring for individuals who cannot be reached during the optimum time frame once a suspected intake has occurred. 2) Determine preliminary background distribution of U-235, U-236, U-238 and Th-232 isotopes in hair, urine, and drinking water. 3) Termination of exposure source. Determining the source of exposure, be it occupational or natural, is revealed through the ratio of U-238 to U-235 (i.e. natural, depleted, or enriched uranium). 4) Investigate

the existence of any correlation for each isotope between hair, urine, and water. Water may play a significant role in uranium and thorium intake.

Methodology

Specimen Collection

Collection of hair, urine, and drinking water specimens were taken from a control group consisting of people aged 18 years and older who were either employees of Sandia National Laboratories or family members of employees. It was the original goal to recruit a control group of 100 people, between July and August 2001, however only 70 people volunteered. Out of those seventy participants, the total number of specimens donated was 202 samples: 70 water samples, 70 urine samples, and 62 hair samples. Collection kits, along with instructions on specimen collection, were issued to all participating individuals. Inside the kits were two 50 ml plastic bottles, for urine and water collection, and a 3"x5" plastic baggy for hair collection. Participants were instructed to refrigerate urine and water samples and to return them within three days, from time of collection, in order to maintain sample integrity. Returned samples were stored in a refrigerated area while waiting analysis. Instructions, assigned to hair samples, were to collect a handful of hair or the equivalent of a small lock of hair in the case someone couldn't donate a handful. Four weeks was allotted for hair collection to give time for people to collect their hair from haircuts or hairbrushes. One individual who did not have hair on his head, he was allowed to donate arm and leg hair instead.

Several of the participants' homes were located in the Albuquerque region and the surrounding areas. This is mentioned because instructions on water collection stated samples had to be drinking water commonly consumed by the participating persons. Water specimens were

sampled from personal well water, regional municipal tap water, bottled water, and water from drinking fountains found at Sandia.

A control factor on urine samples requiring specimen collection within a 24-hour time frame of the drinking water collection was not applied. However, it is useful to note that the majority of fluid samples returned were taken within a 24 hour to 48-hour period of each other. Also there was no control factor regulating the length of hair samples, nor was there any factor applied to washing hair that might contain cosmetic or hygienic residue. And finally, there was no factor to control differences among participants' gender, age, and ethnicity. Due to the limited scope of this study, the aforementioned control factors are considerations for follow up studies.

Sample Preparation and Analysis

Urine and water samples were acidified with 0.25 ml of 16 molar nitric acid before they could be prepared for analysis on the ICP-MS. The samples were then left out at room temperature for 12 hours. Acidification of these samples kept the uranium in solution and prevented the uranium from precipitating onto the walls of the plastic bottles.

Sample preparation for the drinking water was not needed. Twenty ml of water was transferred directly in test tubes and analyzed by ICP-MS. Urine is diluted before it can be analyzed to prevent clogging of sampling tubes and syringes. One ml of urine was mixed with 1 ml of 16 molar nitric acid and 18 ml of de-ionized water and placed in a test tube for analysis. For the hair samples, 0.1 g of hair was placed in a test tube along with 4 ml of 16 molar nitric acid and completely digested in a microwave oven. Samples were then brought up to a total volume of 50 ml with de-ionized water. In the case where a sample appeared to have

precipitated and/or colloids were in solution, they were placed on the centrifuge for 10 minutes at 2000 rpm. Finally, 20 ml were placed in a test tube and analyzed.

The ICP-MS instrument employed is manufactured by Perkin-Elmer, model number Elan-6100. A de-ionized water sample was used to establish the instrument background and four natural uranium standards with concentrations ranging from 0.5 to 5.0 μg/l of total uranium were used to calibrate the unit. It was determined that a combined calibration using the U-235 and U-238 intensities was highly linear and valid over the limited mass scan range of 230-242 amu. A 2 minute acidic water rinse was used between samples to clear out any residual contamination from previous samples. The detector was operated in the pulse counting mode. Another de-ionized water sample was used as a blank for the measurement, and all reported values are relative to this blank sample. The minimum detectable concentration (MDC) for each isotope was determined by measuring the variation in five blank counts. Finally, the blank and standard samples were re-analyzed at the end of the analysis run to check for contamination and/or calibration drifts. The typical sample preparation times ranged from less than an hour for water samples to a few hours for hair samples. The ICP-MS analysis time, including instrument setup, quality control checks, and calibration runs took about four hours.

Results and Discussion

The average concentration, minimum detectable concentration (MDC), and the observed range of U-238, U-235, U-236, and Th-232 content in drinking water, urine, and hair samples are presented in Tables 1 through 3, respectively.

The average concentration and the vast majority of individual of values for U-238 and U-235 were above the MDC in drinking water. The distribution for U-238 and U-235 follows a log

normal distribution with a few outliers with high values relative to the observed averages – see Figure 1 for U-238 distribution curve. The samples with uranium concentrations came from wells in the James Springs area known for large amounts of naturally occurring uranium in ground water. The very few negative values were from bottled water sources – meaning these samples had less uranium than the calibration blank. The observed concentration levels of U-236 and Th-232 were below their respective detection limits and were normally distributed about the blank value.

For urine samples the vast majority of observed values for U-238 are above its detection limit and follow a log normal distribution as shown in Figure 2. Observed U-235, U-236, and Th-232 values are below their respective detection limits. In particular, there was no detectable Th-232 in any of the urine samples.

Nearly all hair samples had detectable amounts of U-238, U-235, and Th-232 isotopes (i.e. the observed levels were above their respective detection limits). The distribution curves for these isotopes were log normal, and as a typical example, the distribution graph for U-238 is shown in Figure 3. There was no detectable U-236 in hair, and the distribution was normal about zero (after blank subtraction).

A correlation plot of U-238 for the three sample types did not reveal any clear relationships, except for a weak positive correlation between U-238 values for hair and water samples at very high drinking water concentrations. The correlation graph is shown in Figure 4. The apparent positive correlation is forced by the very high water concentrations from James Springs region. Without these points, the fitted line is relatively flat (no correlation). The main conclusion to be drawn from this graph is that for most samples, there is no relationship between the submitted water and hair samples, perhaps due to various drinking water sources at work and

home and competing pathways (e.g. food) for uranium intake. The few exceptions were for the areas with very high concentrations of uranium in drinking water, which also seems to have been reflected in high values for the hair samples from the same individuals.

The U-238 to U-235 mass ratios for individual data points for water samples were calculated and plotted in Figure 5. The mass ratio graph in drinking water shows significant statistical fluctuations where the U-235 concentration is close to the detection limit. The statistical fluctuations are reduced, and stay relatively constant, after the U-235 concentration reaches 2.6 ng/l which is about ten times the detection limit for U-235. The average mass ratio of 139.5 agrees with the expected value of 137.8 within the statistical uncertainties. The one sigma standard deviation of the observed mass ratio for data points above 2.6 ng/l is 1.8 or 1.3%.

The U-238 to U-235 mass ratios for individual data points for hair samples were calculated and plotted in Figure 6. The mass ratio graph of U-238 to U-235 in hair shows no significant statistical fluctuations for lower concentrations. This is due to the fact that all observed values are well above the detection limit. All samples had enough detectable uranium well above the detection limit to make a quantitative measurement of the mass ratio possible. The observed average mass ratio is 140.8, which again corresponds well with the expected value of 137.8 within the statistical variations. The one-sigma standard deviation for the mass ratio is 3.5 or 2.5% which is a bit higher than for water. The histogram of ratio values is shown in Figure 7 which approximates a Normal distribution. As a side note, a simple calculation predicts that an accumulation of about 80 ng/g of depleted uranium, 18 ng/g of typical reactor fuel (4% enrichment), and only 0.5 ng/g of weapons grade uranium, in an average hair sample (290 ng/g of natural uranium) will produce a U-238/U-235 mass ratio that is three sigma away from the

natural uranium ratio. This indicates that hair is a useful bioassay for monitoring exposure to enriched uranium.

The U-235 concentrations in the vast majority of the urine samples were too close to the detection limit to produce a reliable U-238 to U-235 mass ratio. The urine samples were diluted in the sample preparation process, resulting in U-235 concentrations at or below the detection limit, prohibiting an accurate measurement of the mass ratio. However, the employed sample preparation procedure did meet the Internal Dosimetry requirements (MDC of 0.1 μg/l for total uranium) and data was reliable enough to determine isotopic background levels.

Conclusions

Results show that hair retains enough detectable uranium to be a viable candidate for bioassay measurements. However, analytical methods need to be paired with a bio-kinetic model of uranium uptake and subsequent excretion through hair to determine dose levels that can be reliably obtained by this method. Background levels have been determined for U-235, U-236, U-238, and Th-232 isotopes in hair, urine, and drinking water. These levels are useful for setting action levels to determine possible exposure to anthropogenic sources of uranium.

The employed analytical methods produce high quality results that meet the stated requirements in a short time. The sample analysis process, from sample preparation to counting and reporting, takes less than a day as compared with, at best, many days for radiochemical separation and alpha spectrometry. The ICP-MS methods have superior detection limits and accuracy for most thorium and uranium isotopes. One notable exception is U-234 where some additional concentration is required to achieve a detection limit similar to alpha spectrometry.

The determination of exposure source is possible for water samples and hair by taking the mass ratio of U-238 to U-235 and comparing it to the expected natural ratio of uranium as long as the U-235 concentration is greater than ten times the detection limit. The vast majority of exposures are caused by depleted or enriched uranium and a separate study concluded that accumulation of a very small amount of depleted or enriched uranium in hair samples will result in a significant deviation of the mass ratio from the expected value for natural uranium. U-236 is another useful isotope for determining whether the uranium is man-made. The determination of exposure source in urine, however, could not be achieved in this study, due to the dilution of the urine samples. A procedure with improved detection limits is needed when such determination is necessary. For future studies, the analytical methods will be modified to improve the accuracy and precision of the mass ratio measurement.

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Table 1. Water Samples Summary Results

Isotope	Average (ng/l)	MDC (ng/l)	Range (ng/l)
U-238	3290	2.0	-5.9 to 35,760
U-235	23.6	0.4	-0.02 to 254
U-236	0.03	0.4	-0.03 to 0.09
Th-232	-2.32	1.0	-3.30 to 0.3

Table 2. Urine Samples Summary Results

Isotope	Average (ng/l)	MDC (ng/l)	Range (ng/l)
U-238	41.1	15	-5.83 to 390
U-235	0.47	7	-0.55 to 1.72
U-236	-0.6	7	-1.7 to 0.50
Th-232	-4.3	12	-7.6 to –0.57

Table 3. Hair Samples Summary Results

Isotope	Average (ng/g)	MDC (ng/g)	Range (ng/g)
U-238	290	0.3	20.1 to 1330
U-235	2.1	0.1	0.15 to 9.30
U-236	-0.0017	0.1	-0.011 to 0.009
Th-232	2.4	0.3	0.21 to 15.8

Figure 1. Observed Distribution of U-238 in Water Samples.

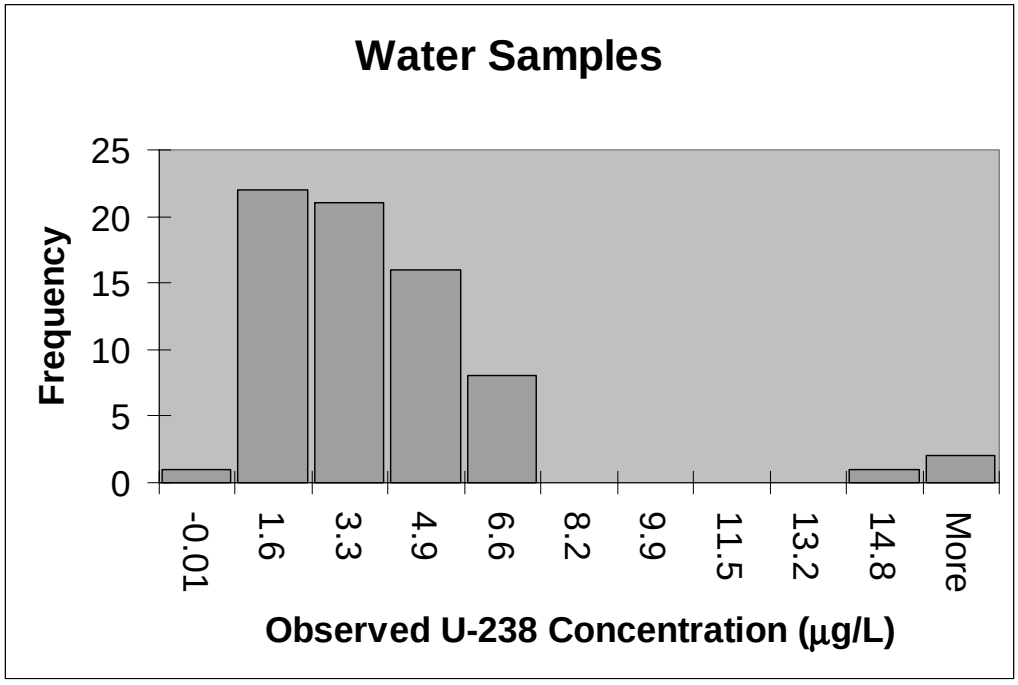

Figure 2. Observed Distribution of U-238 in Urine Samples.

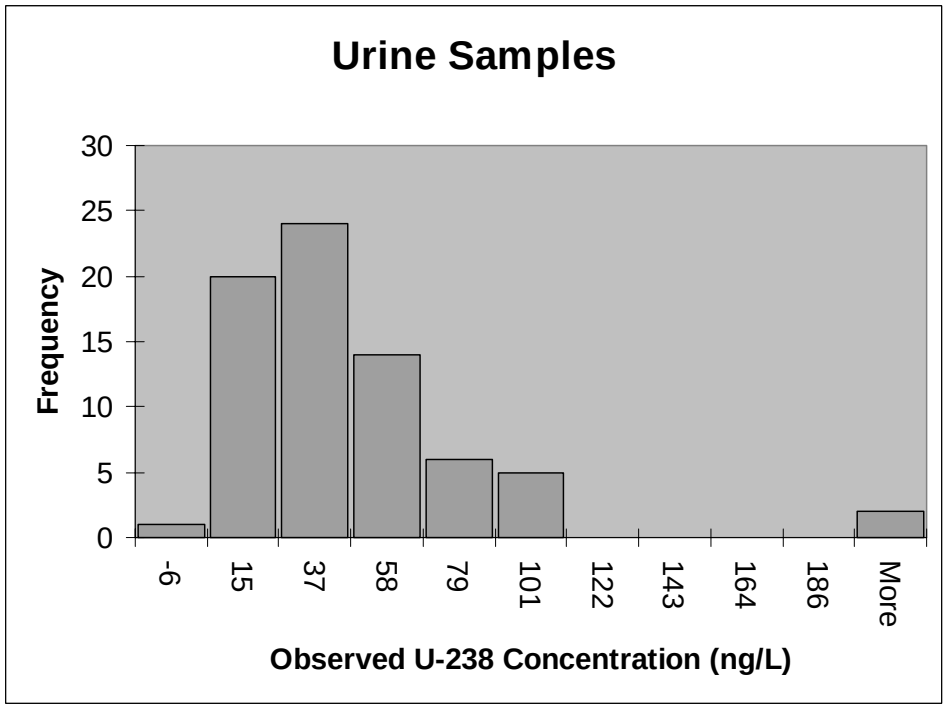

Figure 3. Observed Distribution of U-238 in Hair Samples.

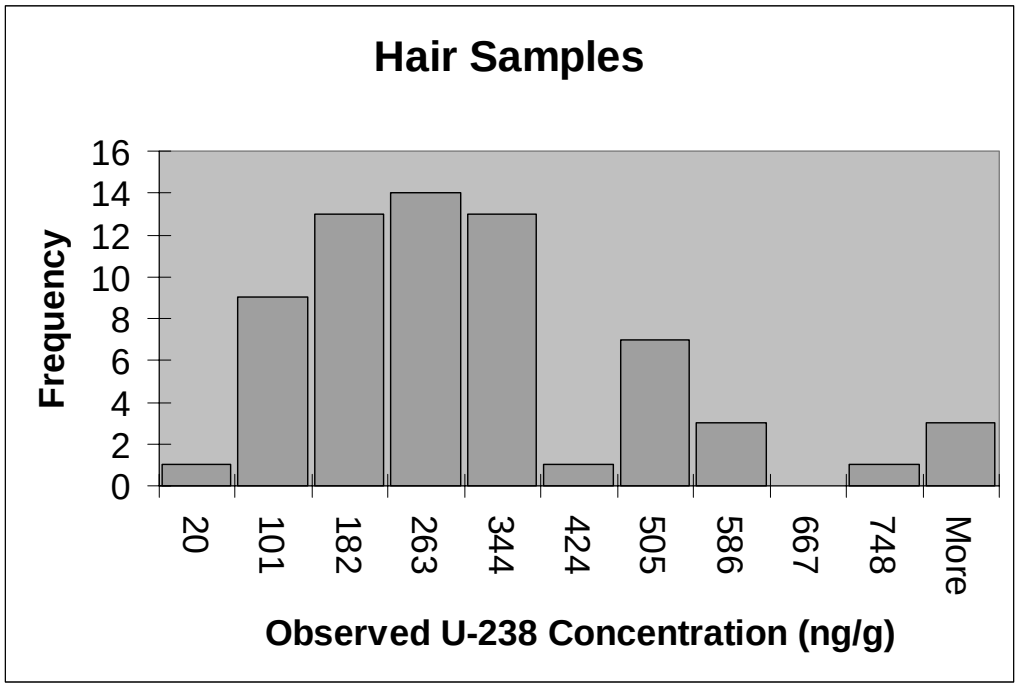

Figure 4. Correlation of Observed U-238 in Hair and Water Samples.

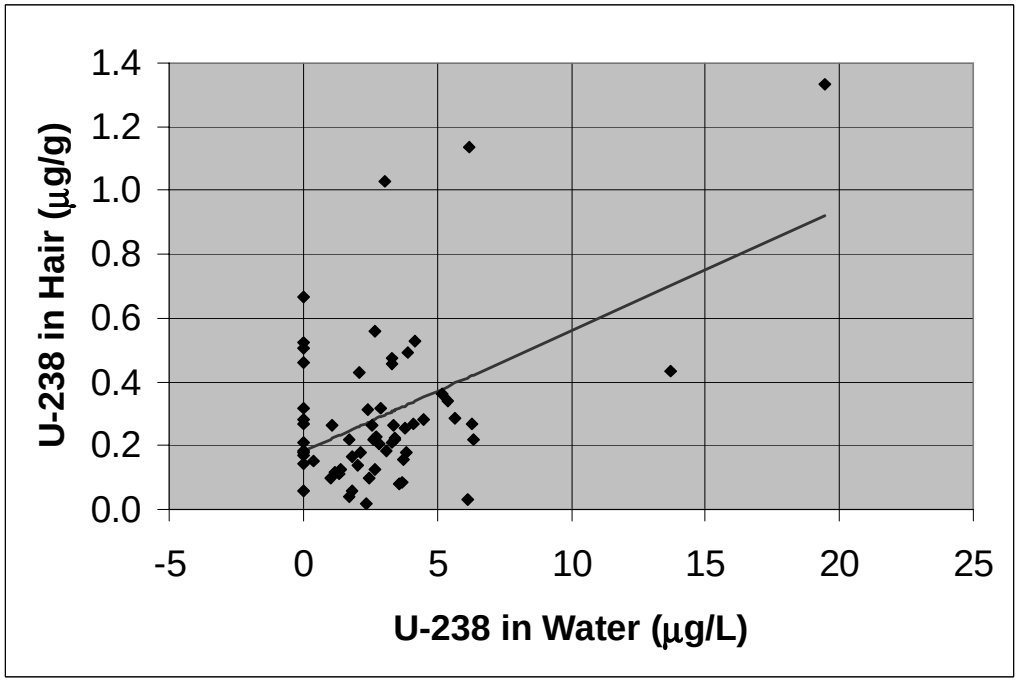

Figure 5. U-238 to U-235 Mass Ratio in Drinking Water (error bars at 2σ), the Staright Line is the Expected Natural Uranium Ratio.

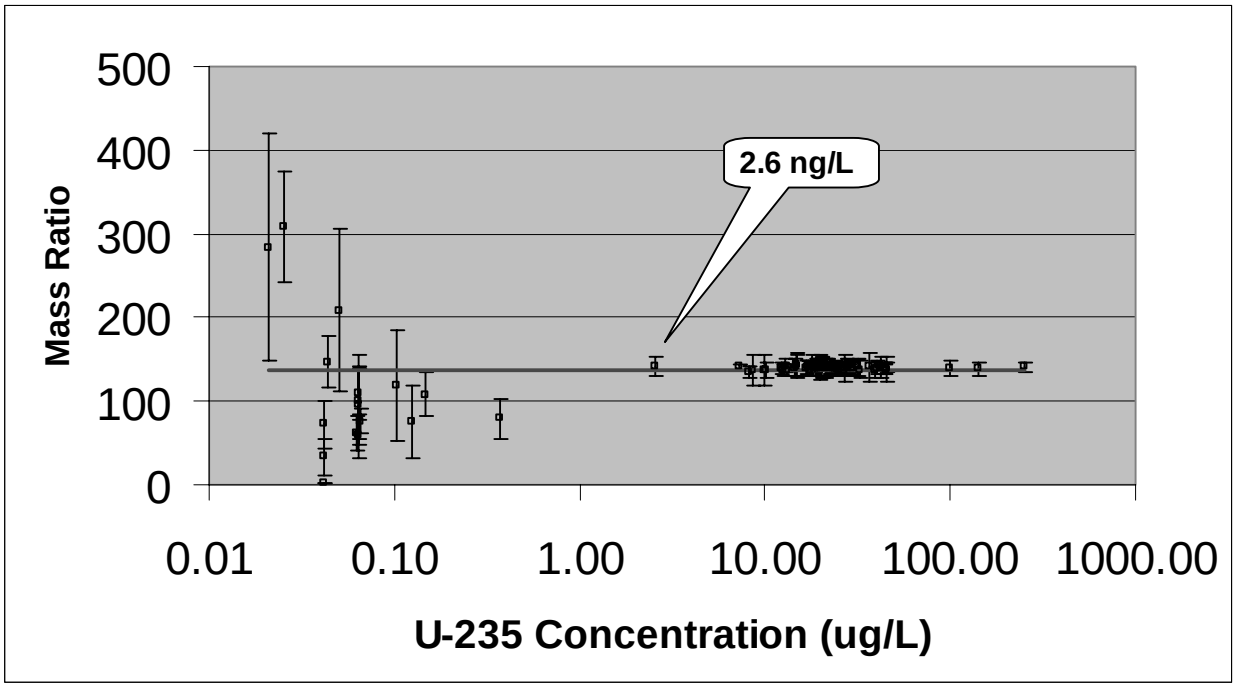

Figure 6. U-238 to U-235 Mass Ratio in Hair (error bars at 2σ)σ), the Straight Line is the Expected Natural Uranium Ratio. Plotted on the same scale as Figure 5.

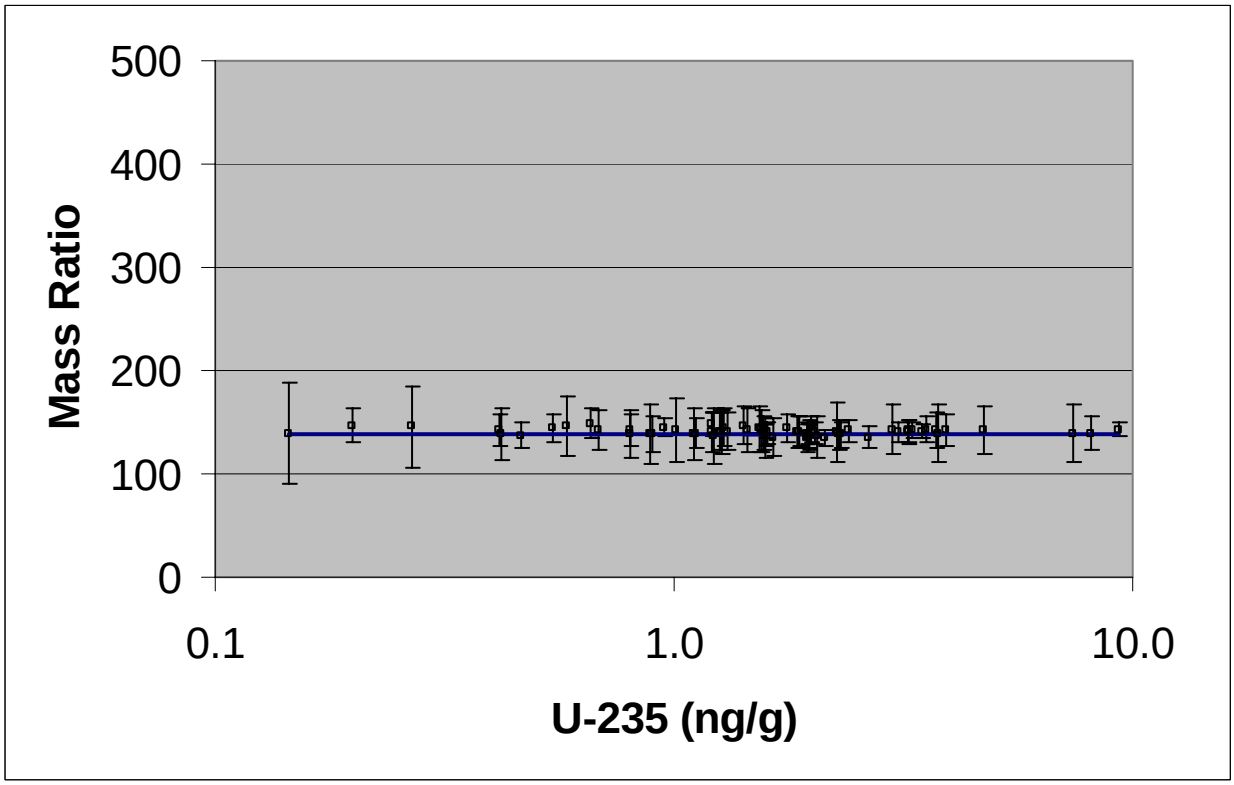

Figure 7. Histogram of U-238/U-235 Mass Ratios for Hair.