Feasibility of Determining Pu-239 Environmental and Occupational Levels in Urinary Excretion by Fission Track Analysis

by
Melinda P. Krahenbuhl
Christy M. Seiger-Webster
Cynthia L. Henderson
Rian B. Smith
Dong-ok Choe
David M. Slaughter

DOE/NV/10865--T2

Introduction

A. Significance of Research

The results of bioassay programs for detecting human exposure to plutonium are currently playing a role that they were never intended or prepared to fulfill. With little resistance or support from the scientific community, the regulatory community established exposure limits for plutonium burdens based largely on imprecise inference of causes and effects; thus, to an extent, incomplete data and analysis formed the basis for most existing bioassay programs. At the time these early programs were developed, they were used only to determine the occupational exposure to radiation workers and populations unintentionally exposed to occupational levels during open air testing (i.e. Castle Bravo, 1954.) The results from these programs are now used in litigation to determine cause, negligence and responsibility for health problems associated with the populations surrounding facilities that store, handle and process nuclear materials. As this role is beyond the scope of most bioassay programs' designs, concern for the use of existing bioassay programs in this manner is rising. It is imperative that defendable, scientifically-based, more sensitive techniques be researched and developed to measure the presence of Plutonium (Pu), which in turn can be used to establish and predict the health effects of a minimal Pu exposure. Currently, estimates to predict systemic deposition using urinalysis data are several times greater than the exposure levels measured by autopsy. The scientific research conducted in this study can serve to narrow this discrepancy and provide the regulatory community with a more reliable basis for establishing regulatory exposure limits and accurately predicting systemic deposition.[1] Furthermore, this research and the continued development of more sophisticated detection techniques can serve to dispel general public concern over the possibility of radiation exposure from ongoing site remediation and closure efforts.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

B. Basic Description of FTA

In 1958 and 1959, two independent teams at Harwell laboratories observed microscopic tracks in the surfaces of lithium fluoride and mica. These tracks were determined to be caused by fission fragments and heavy charged particles. Since these discoveries, fission track analysis (FTA) and solid state nuclear track detectors (SSNTDS) applications have expanded to include geochronology, cosmic ray physics, nuclear physics, meteoritic and lunar science, chemical analysis, autoradiography, and dosimetry. In the early 80's, FTA was utilized to determine Pu burdens in tissue samples and was later extended to include urine samples. These early bioassay programs have since been improved through lower detection limits, proper selection of detectors, optimization of track elucidation, increased selectivity of chemical preparations, improved track counting techniques, and better data reduction methodology. Currently, the detection limit is approximately 70 aCi/L with statistically significant results at 140 aCi/L for an ideal sample matrix.

C. Research Objectives

The overall objective of this project is to develop a non-intrusive process that accurately determines the Pu burden of environmentally exposed individuals. The technique should retain the flexibility to determine occupational exposures as well. In the present study, we have engineered an experimental bioassay technique described by Wrenn, et.al.[2] in order to meet this objective. This technique quantifies the presence of Pu in urine using Fission Track Analysis (FTA). An outline of the FTA process protocol is shown in Figure 1. We established the baseline deficiencies of existing FTA technology: limited yield, lack of appropriate reagent additions to account for volume and matrix dependency of the chemical processing, insufficient mathematical interpretation, and inaccurate quantification of fissile contaminants. Once the deficiencies were identified, the contributing factors were analytically and experimentally evaluated. The FTA protocol was revised according to this evaluation and includes the following improvements. We updated the procedures to include a chemical tracer, Pu-236. The introduction of a tracer into the process required us to modify the mathematical model used to quantify the Pu burden inherent in the sample matrix. In addition, we added flexibility to the procedures to accommodate variations in sample volume and established a more aggressive quality control program. We tested the revised protocol by using it to determine the plutonium burden in twenty samples. The results of this testing are presented in this report. Furthermore, we compared the methodology of the new protocol with the FTA procedures established at Brookhaven National Laboratory.[3] A brief discussion of this comparison is also included with this report.

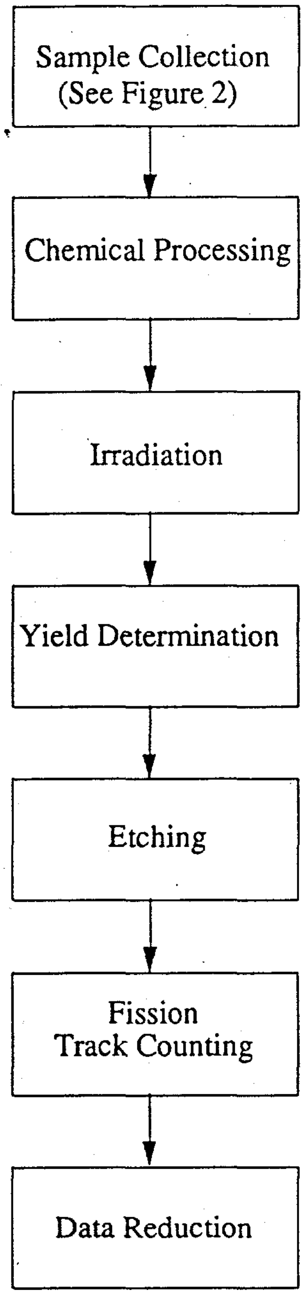


Figure 1. Process Protocol for Fission Track Analysis of Plutonium in Urine

D. Experimental Facilities

Experimental facilities located at the CENTER were utilized for this program and include: radiochemistry laboratories equipped with multiple centrifuges, muffle furnaces, fumehoods, and Class 100 clean work areas; a 100kW TRIGA research reactor; a full complement of radiation measurement equipment and dosimetry (i.e. Liquid Scintillation, alpha and gamma spectroscopy, and radon emanation and scintillation, etc.); and a full complement of Sun Sparc stations, multiple PC's, Macintoshes, and parallel processing computers. The CENTER also has a microscopy laboratory equipped with optical microscopes, and automated and semi-automated stages used for FTA. In the future, the microscope systems can be interfaced with data acquisition systems and state of the art optical imaging software. Facilities external to the CENTER were also utilized. In order to achieve the target fluence, 10^{17} n/cm^2, Lexan slides containing deposited samples were shipped to the Reactor Laboratory at the Massachusetts Institute of Technology for irradiation in their 5 MW research nuclear reactor.

Process Methodology

A. Chemical Separation

The first objective of the process is to effect the radiochemical separation of Pu-239 from the urine sample. This is accomplished through a chemically induced precipitation followed by anion exchange chromatography. Figure 2 outlines the protocol necessary to isolate and determine Pu-239 from human urine. Various steps that serve to eliminate interfering chemicals or convert the Pu-239 to a more reactive species are incorporated into the procedures for this process. These procedures are briefly discussed in this section.

The plutonium is co-precipitated with a calculated amount of rhodizonic acid to form salts. Previous investigators introduced rhodizonic acid according to a linear dependence determined by sample volume. In order to establish a clear, well-documented, scientific basis for this linear formula, a series of experiments were conducted to examine the plutonium content of all discard streams and the product stream prior to the ion exchange. (A detailed schematic of the method used for measuring the plutonium content is outlined in Figure 3.) Eight samples of various volumes of synthetic urine, from 250 ml to 2 liters, were spiked with approximately 100 pCi of Pu-238. Four of these samples were processed using a linear extension of 2 grams of rhodizonic acid per liter of solution. The other four samples were precipitated with rhodizonic acid added in amounts determined by an exponential dependency on volume. The discard streams (supernate, precipitate, and organic) and the process stream (recovery) were analyzed for Pu-238. The results

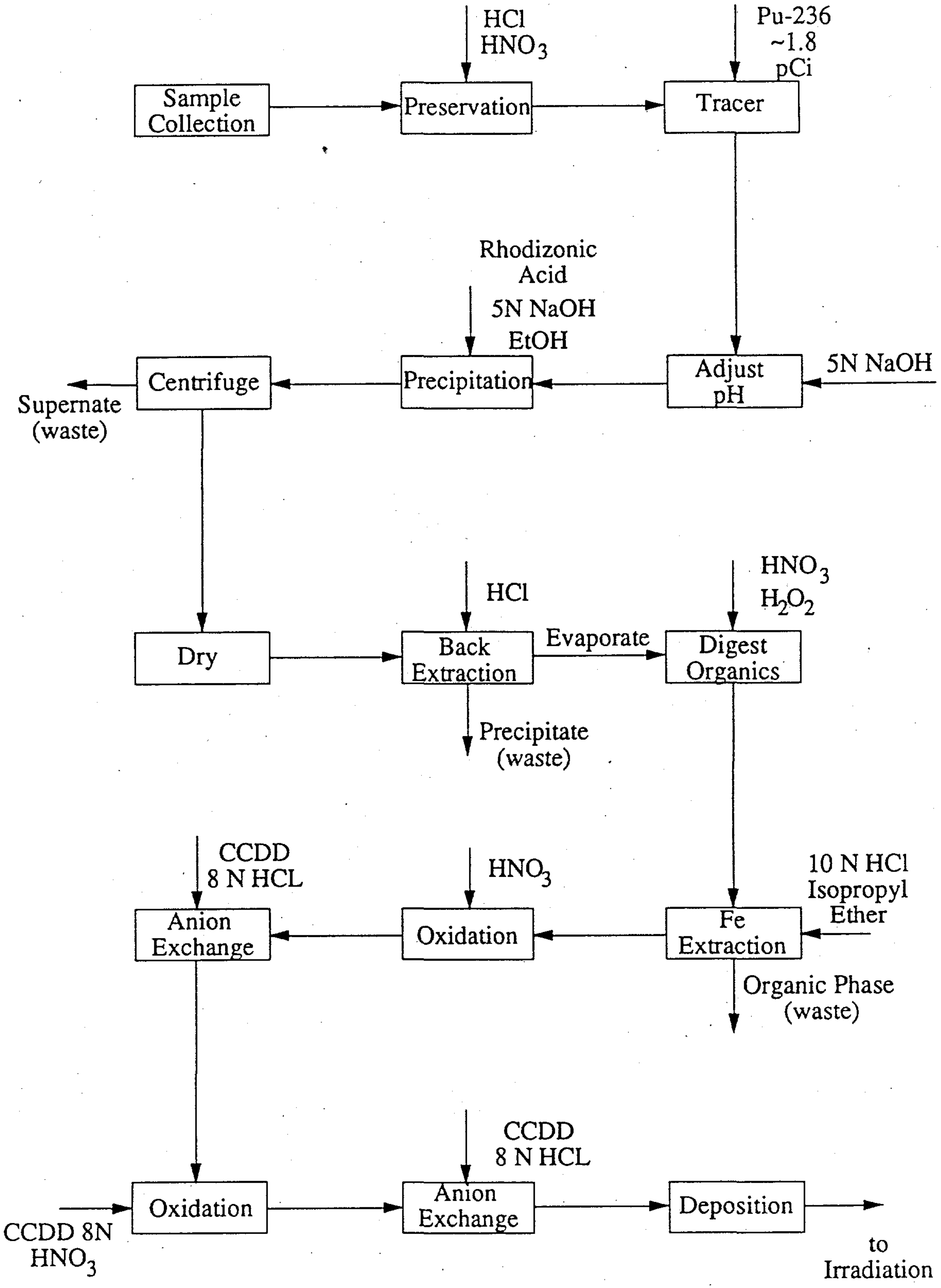


Figure 2. Chemical Process to Concentrate Pu from Urine Samples

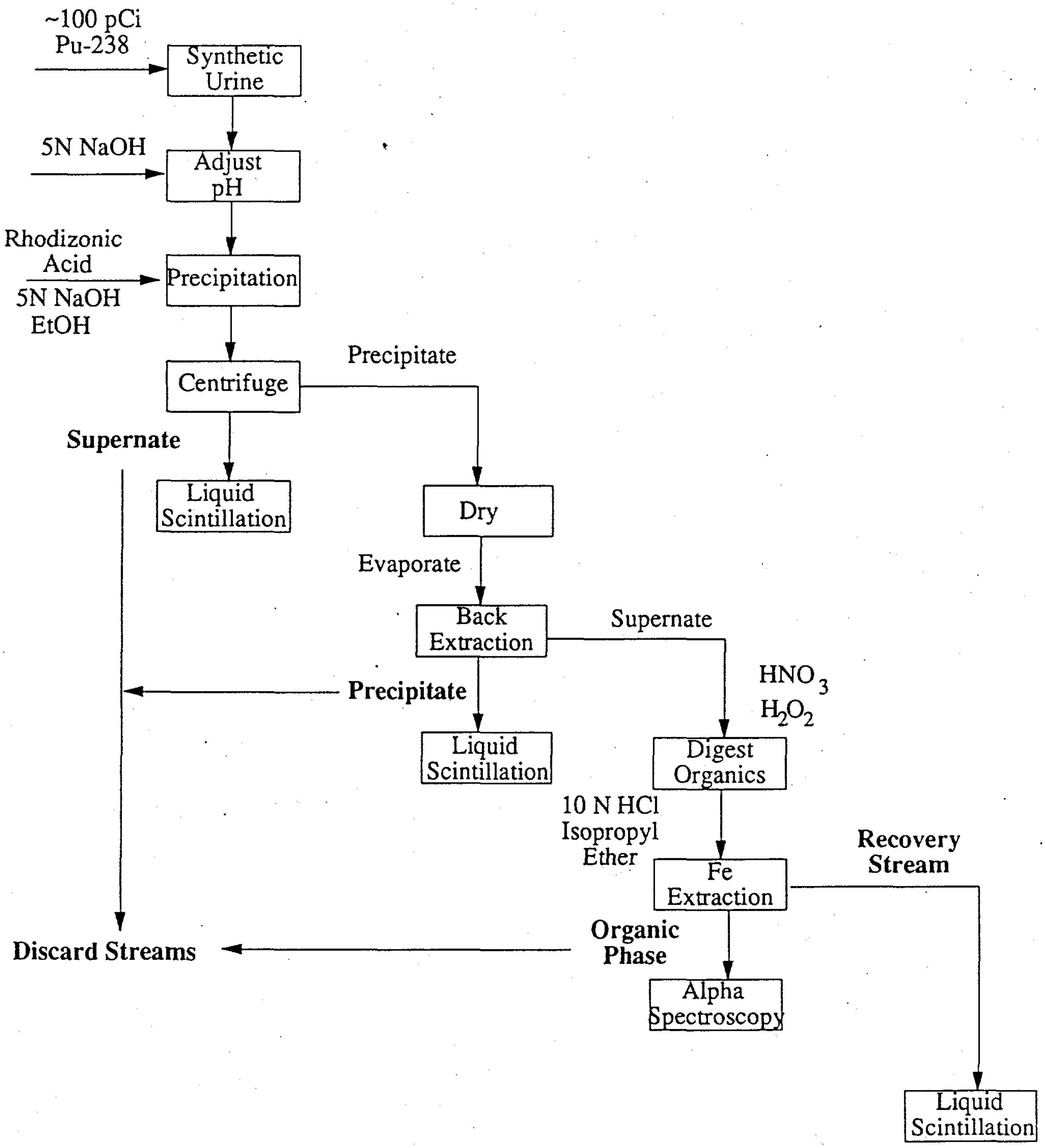


Figure 3. Chemical Process to Determine Pu Retention and Loss

are presented in Table 1. The process stream reflects the effective recovery of Pu. The Pu recoveries associated with the main process stream ranged between 40 percent to 100 percent. In general, the data indicate that the linear addition of rhodizonic acid is insufficient as the volume increases. This conclusion is supported by measuring significant amounts of plutonium in discard streams. Introducing rhodizonic aoid according to an exponential dependency significantly increased the recovery of Pu. The following equation calculates the quantity of rhodizonic acid needed to extract plutonium and was derived from the experimentation described above.

$$x = 400^{\left(\frac{\ln V}{5.298}\right)} \qquad 1.32$$

where:

X is rhodizonic acid in milligrams
V is sample volume in ml.

The major loss of Pu remains in the initial precipitation of salts from the stabilized bulk urine samples. Many undesirable salts, transition elements and actinides are precipitated along with the Pu from the bulk urine samples because the rhodizonic acid precipitation is not selective. However, we found that most undesirable precipitants are selectively eliminated during back extraction with 8 N HCl. Additionally, the samples are wet ashed with HNO_3 to digest any remaining organics, and the Fe ions are selectively removed using liquid/liquid extraction with isopropyl ether. Reducing the amount of Fe ions improves the selectivity of the anion exchange columns. The results of the experimentation also indicate little plutonium is lost in the two steps taken to concentrate the Pu: back extraction, and the liquid/liquid extraction of iron ions.

The sample is oxidized with an excess of HNO_3 to ensure the Pu is in the correct valence state before it is passed through the column (see Fig. 2.) Next, the sample is dried and redissolved in 10% 8N HCl + Cl_2 and 8N HCl. The solution is then passed through the column. The plutonium is eluted from the columns with a solution of 1 percent by volume HI in 8 N HCl. Sample collection begins when the HI solution contacts the resin bed. Sample collection continues until at least five bed volumes of the HI solution have passed through the column. The second column procedure simply duplicates the operation of the first column with two notable exceptions: the bed volume is significantly smaller, and the chromatography is performed in a class 100 cleanroom. The clean room minimizes particulates containing uranium which could contaminate the Pu-burdened elutant deposited on the lexan slide. In addition, air drying and packing of the lexan slides are performed in the clean room to ensure minimal contamination of the slides from dust. Both columns are packed with multi sized Bio-Rad AG1 ion exchange resin pre-cleaned and equilibrated with 8 N HCL. The flow rate for the first column (0.8 ml/min to 1.0 ml/min) is

			Discard Streams			
Sample ID	Volume (ml)	Rhodizonic acid (g)	Supernate %	Precipitate %	Organic Phase	Recovery Stream
1	250	0.50	4.4 ± 0.5	0.17± 0.10	ND	81.9± 9.3
2	500	1.00	1.3± 0.1	0.25± 0.03	ND	99.7± 9.5
3 E	500	1.10	3.0± 0.3	0.63± 0.08	ND	96.9± 9.2
4 E	1000	2.45	17.2± 2.0	ND	ND	86.4± 8.6
5	1000	2.00	20.6± 2.5	0.17± 0.03	ND	109.± 13.0 ?
6	1000	2.00	12.8± 1.9	0.99± 0.14	ND	43.2± 4.8
7	2000	4.00	70.6± 6.3	0.06± 0.04	ND	41.7± 4.8
8	2000	4.00	4.5± 0.5	0.24± 0.06	ND	98.7± 10.4
9 E	2000	5.40	30.9± 4.9	1.60± 0.20	ND	96.9± 9.7

ND - None detected
E - Exponential model

Table 1. Percent Recovery of Pu-238 from Rhodizonic Acid Precipitation
(Linear and Exponential Increases)

controlled using a multi-channel peristaltic pump. The bed volume used for a 2000 ml urine sample is 3.58 cm^3. The second column flow rate is varied between .0011 ml/min and .00021 ml/min and is controlled using a syringe pump. The bed volume for the second column is significantly smaller at 0.078 cm^3.

Another set of experiments was conducted to evaluate the efficiency of the columns. This experimentation analyzed the effluent streams of selectively prepared test samples run through the columns. If the column is performing as expected, the effluent stream will contain no Pu or U. Fourteen test samples that were designed to emulate the chemical constituents of a urine sample after the Fe extraction phase of the chemical process were loaded onto the columns. These test samples consisted of 8 N HCl spiked with a multi-nuclide tracer of thorium-229, uranium-232 or uranium-233, and plutonium-238. Each of these nuclides has an equilibrium distribution of oxidation states. Of the fourteen test samples, four were loaded onto the columns without any preparation and nine were wet ashed with an excess of HNO_3 to achieve an oxidation state of Pu+4. The test samples were then subjected to all HCL washes and the HI elution of the FTA process protocol for urine samples. Collection of 10 ml aliquots began with sample loading and continued throughout the experiment. The collected 10 ml aliquots were wet ashed with HNO_3 to minimize attenuating salts. The aliquots were redissolved, deposited on slides and analyzed with alpha spectroscopy. Each of the fractions were counted for 6 hours. Results from this set of experiments are shown in Table 2. The test samples that were not properly oxidized to force the desired ionic state (1-4) resulted in sporadic U, Pu and Th content in the elutant. For the properly conditioned samples (5-13), the subsequent HCL washes cleared the thorium contaminant while not removing any of the selected actinides. When 1 percent by volume HI solution was introduced, it selectively removed the Pu while leaving the U fixed to the resin. To verify further the selective removal of Pu, a uranium elution was performed using 0.1N HCL. The effects of the uranium elution were observed by analyzing the effluent derived from this experiment. The results are recorded on the bottom of Table 2. Only uranium was detected in our analysis, which confirms that thorium and Pu have been previously removed. Sample 14 was a reagent blank. Therefore, it is not surprising that plutonium was undetected; and, thorium and uranium, as a result of their ubiquitous nature, were found. Sample 14 results suggest that the HCl washes did not elevate actinide levels.

These experimental results strongly suggest that the selected resin will separate the Pu from uranium and thorium if the samples are properly wet ashed and the resin is eluted with the proper reagents.

		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10	Sample 11	Sample 12	Sample 13	Sample 14
Sample Loading	Pu	40	898	79	67	0	0	0	0	0	0	0	0	0	0
	U	86	3033	657	87	0	0	0	0	0	0	0	0	0	0
	Th	15	134	32	38	5309	160	4548	46	20	5329	4234	9356	1941	15
8N HCl + Cl_2 Wash	Pu	5	16	1	15	0	0	0	0	0	0	0	0	0	0
	U	8	14	6	6	0	0	0	0	0	0	0	0	0	0
	Th	2	7	0	9	1191	6	810	11	4	614	458	256	223	3
8N HCl Wash	Pu	5	22	2181	462	0	0	0	0	0	0	0	0	0	0
	U	5	20	416	786	0	0	0	0	0	0	0	0	0	0
	Th	4	4	51	62	39	25	25	96	10	58	34	9	272	10
Pu Elution 8N HCl + 1% HI	Pu	3048	939	1216	2084	278	778	492	16	629	34	401	1162	383	10
	U	3050	741	376	857	0	0	0	0	0	0	0	0	0	0
	Th	411	154	39	72	0	0	0	0	0	0	0	0	0	0
8N HCl Wash	Pu	77	42	14	32	0	0	0	0	0	0	0	0	0	0
	U	61	54	10	6	1356	12	6	6	9	2	5	11	8	2
	Th	8	15	10	10	0	0	0	0	0	0	0	0	0	0
U Elution 0.1N HCl	Pu	17	16	0	4	0	0	0	0	0	0	0	0	0	0
	U	20	50	0	25	753	1393	21	1450	20	111	1549	3813	774	13
	Th	2	3	0	5	0	0	0	0	0	0	0	0	0	0

Table 2. Selectivity Of The Ion Exchange Columns

B. Irradiation and Alpha Counting

The elutant containing the Pu is deposited on a lexan slide, dried and irradiated to a fluence of approximately 10^{17} nt/cm^2 in a well thermalized (0.025 eV) neutron stream. The lexan slides are exposed to a neutron field that contains an average cadmium ratio of 90. Fissionable material that may be present in the urine or reagents and their respective thermal and fast fission cross-sections are listed in Table 3. Pu-239 and U-235 are the dominant contributors to the fission process. Only the chemical elimination of U-235 allows for the determination of Pu-239 by this FTA technique. The Pu yield is determined by comparing the amount of the Pu-236 tracer remaining in the spiked sample after processing to the known amount of Pu-236 initially deposited in the sample. Amounts of Pu-236 are determined by counting the slides for 24 hours in a calibrated alpha spectroscopy system. Samples with yields less than 10% are rejected. A duplicate sample may be requested and analyzed to determine the cause of process failure. Pu-236 was chosen as the chemical tracer for two reasons: a short enough half life to count with alpha spectroscopy and a significantly small fission cross-section to minimize the formation of fission tracks due to Pu-236.

Although Pu-236 and its daughter product, U-232, have thermal fission cross-sections and resultant fission tracks, the accuracy of the technique is not compromised because the amount of fission tracks resulting from these materials can be accurately quantified and accounted for in the calculation of Pu-239. The quantity of tracer added is 1 pCi, and the maximum concentration of the daughter is < 0.25 pCi. The probability that the tracer addition will fission versus the Pu-239 is calculated by the following equation, which is a function of isotope abundance:

$$\text{probability}_i = \frac{\sigma_i}{\sum_{0}^{j=n} \sigma_j} \qquad 2.$$

The alpha counting also provides information on the concentration of naturally occurring uranium isotopes remaining in the samples. A typical urine sample contains nanograms (10^{-9}) of natural uranium. Twenty alpha counts above background is sufficient to determine the presence of 2.5 femtograms of U-238 and 0.3 femtograms of U-235, the major constituents of natural uranium, using current counting conditions. Including the presence of naturally occurring uranium into the probability equation and graphing it as a function of Pu-239 abundance results in a quantification of contaminants.

Isotope	Half-life (years)	Thermal Fission Cross-section (barns)	Fast Fission Cross-section (barns)
Pu-236	2.87	16	~2
Pu-239	2.410E4	750	1.85
U-232	70.0	75	~2
U-235	7.04E8	585	1.4
U-238	4.47E9	5E-6	.095

Table 3. Relevant Fissionable Isotopes

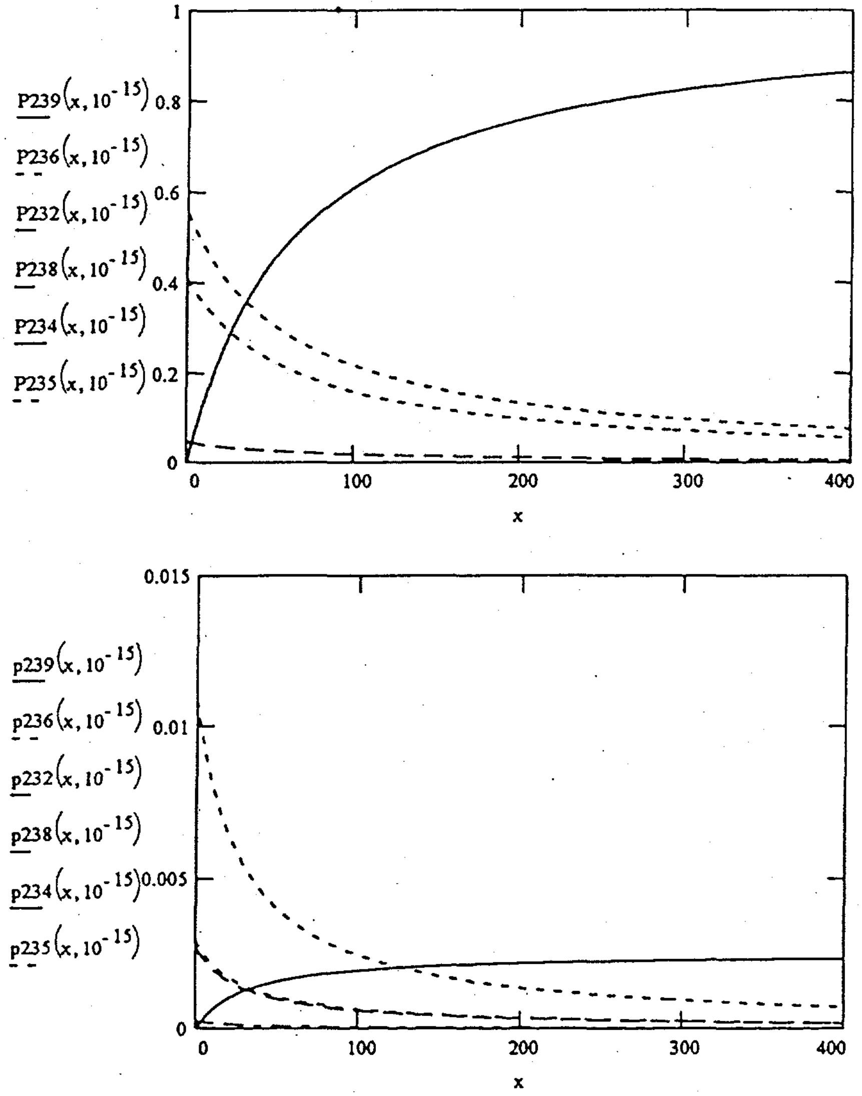
Figure 4 shows the significance of the fissionable contaminants to Pu-239 for thermal fission (Fig.4a) and for fast fission (Fig. 4b). Normalizing the probability function by mass provides a means to evaluate the relative contributions from different fissionable isotopes. Due to the high cadmium ratio associated with our irradiation, thermal fission dominate. When Pu-239 is present at concentrations greater than 100 aCi, it dominates the fission process although it is orders of magnitude lower in concentration than uranium. It is interesting to note that the amount of contaminants is significant below the FTA detection limit of 70 aCi/L. For a fast fission spectrum (Fig. 4b), the fissionable contaminants remain significant to 170 aCi and could account for over half the fission events recorded in the LEXAN.

C. Etching and Track Counting

The fission tracks created on the lexan are enhanced by etching with a caustic solution. The duration for etching is dependent upon temperature and etchant concentration. For lexan slides, fission track elicitation is optimal with 6.5 N KOH for eleven minutes at a constant temperature of 70° C. Fission tracks are counted using a Boeckeler automated stage in conjunction with a Nikon microscope (200X magnification). Fission tracks are identified by their characteristic carrot shaped aperture and can be distinguished from scratches and other surface defects by evaluating the track for depth. Due to the possibility of human error, each slide is counted at least twice. If the two counts do not agree within at least 25%, a third count is performed.

D. Data Reduction

The Pu activity of the submitted urine sample is determined by subtracting the amount of activity derived from other possible sources of fission tracks. It is assumed that U is removed during the chemical separation process and the Pu is selectively concentrated and deposited on lexan slides. The fission background resulting from the addition of Pu-236 to the sample is accounted for by direct depositing the same amount of Pu-236 in the reagent blanks. Lexan slides containing processed human or synthetic urine, reagent blanks, lexan blanks (slides with no deposited material), Pu-239 flux monitors, and chemical yield monitors (direct deposits of known amounts of Pu-236) serve as detectors of fissionable material. Derived from a simple mass balance, the following equation relates the fission track data obtained from each detector to calculate the Pu activity (aCi/l) associated with each submitted urine sample.



Graph A

Graph B

Figure 4. Potential Fissionable Contaminants Associated with FTA of Urine

$$A = \frac{1}{\varepsilon V}\left\{\frac{N_{U+R+L} - N_L}{Y_S} - \frac{N_{R+L} - N_L}{Y_R}\right\} \qquad 3.$$

where:

N_{U+R+L} = gross fission tracks in sample
N_{R+L} = gross fission tracks in Reagent Blanks+Lexan Blank
N_L = gross fission tracks in Lexan Blank Only
V = volume of sample analyzed(liters)
e = track registration efficiency (from Pu-239 flux monitors)
Y_S = chemical yield of Pu^{236} tracer for the Spiked Sample
Y_R = chemical yield of Pu^{236} tracer for the Reagent Blank

The gross number of tracks (N) for a sample is given by the following equation:

$$N = \sum_{i=0}^{i=n} (\#\text{ of tracks in drop i}) \qquad 4.$$

The efficiency of track registration was determined experimentally by directly depositing known activities of Pu-239 on the lexan slides and measuring the resultant fission tracks. The activity deposited was correlated with the amount of resultant fission tracks, thus creating a linear relationship with the y intercept through zero and the slope, ~ 2.26 tracks/ aCi. This conversion factor varies slightly due to small discrepancies in irradiation times and cadmium ratio associated with neutron exposure in the nuclear reactor. In order to accurately assess the variations, each irradiation container (referred to as a "rabbit") contains a flux monitor (i.e. direct deposit of known amounts of Pu-239 on a lexan slide) along with the detectors for processed urine samples.

Comparison of Fission Track Analysis Procedures

To establish a baseline, seventeen urine samples were processed by the CENTER using the Fission Track Analysis (FTA) technique as described by Wrenn, et.al.[2] but with the inclusion of the Pu-236 tracer. The results of this processing revealed Pu yields significantly lower than expected. The activity conversion factor was found to be 2.26 tracks/ aCi. Using this value as ε and setting it equal to Wrenns' rounded mean and registration efficiency (1.6 tracks aCi^{-1})[2], the yield should be approximately 70%. Our results indicate the average chemical yield to be approximately 15%.

Actual yields were determined using the Pu-236 tracer. In addition, the chemical yields demonstrated a correlation with volume; the larger the volume of urine processed, the lower the Pu yield. Our findings, while contrary to that reported by Wrenn et.al.[2], are consistent with current knowledge of most chemical kinetic and mixing processes.

Once the new protocol was established, nine samples were processed for plutonium burden determination. The changes to the process resulted in an increase of the chemical yield to an average of 47%.

Additionally, the data reduction methodology was evaluated for applicability. The methodology established by the CENTER for calculating Pu content in the urine differs from that presented in the previous work by other investigators. As reported by Wrenn et al., their evaluation was based on a simplified formulation which was the best scientifically supported approach at the time of publication. The more comprehensive CENTER approach presented in this paper includes measuring the plutonium loss by monitoring a Pu-236 tracer, adding reagents to the sample volume according to an exponential dependency, and compensating for tracks from that reagent addition.

In contrast to Brookhaven National Laboratory's procedures[3], the revised CENTER procedures include a number of specific preparatory steps designed to remove interfering ions before anion exchange. The preparatory steps consist of rhodizonic acid precipitation, back extraction and liquid/liquid extraction. We achieve an overall yield of 47% through the use of these steps. Brookhaven reports an overall yield of no greater than 35% .

Our procedure specifies the use of a lexan detector. Brookhaven uses a silica glass detector. The benefits of using lexan, which include simplicity of preparation and ease of counting (identification and storage), outweigh the benefit of using a fused silica glass detector to reduce background (4.5 tracks/cm^2 tracks for lexan vs. 4 tracks/cm2 for fused silica glass.) The characteristic carrot shaped fission track aperture created in the lexan is easier to distinguish from artifacts in contrast to the fission tracks created in the fused silica, which closely resemble scratches and other artifacts. Additionally, the lexan is more sensitive to low energy particles (.55 MeV protons and 1 MeV alphas for lexan vs. 100 MeV for Ar-40 atoms in fused silica glass.) [4,5]

As previously mentioned, the major constituent of natural uranium is U-238 and U-235. Unfortunately, these isotopes have comparable fast fission cross sections to Pu-239. The CENTER utilizes a highly thermalized port (average Cd ratio of 96); therefore, the contribution of fast fission can be disregarded. In contrast, Brookhaven utilizes a High Flux Beam reactor or a Medical Research Reactor. They have not quantified the fast fission component, though it is impossible to assume that its contribution is not significant.

This process differs from previous ultra-sensitive techniques by including a chemical tracer in each sample and reagent blank. Previously, Pu recoveries were estimated using experimental data generated from spiked samples of various concentrations. Brookhaven used 10 pCi and estimated a recovery of 35%. Wrenn used 100-600 aCi and estimated a recovery of 60%. Both may be accurate, but they contain a fundamental flaw. The primary mechanism for separation and concentration of Pu in the FTA process is the use of anion exchange columns. The controlling mechanism of ion-exchange columns is diffusion, which is a strong function of concentration. The use of an experimental matrix with an isotope tracer concentration several orders of magnitude greater than the amount of Pu-239 expected in the sample favorably biases the diffusion-limited mass transfer process occurring in the anion exchange columns to a higher recovery. Therefore, at low concentrations, aCi level, the recovery would be inflated. Another flaw exists in that it is questionable to use an experimental technique (ultra-sensitive FTA) to confirm itself. Both of these issues are addressed in the revised CENTER procedures by including a tracer at a lower concentration in each sample and reagent blank.

Quality Assurance Program

Cleaning of the reagents entails two passes through an ion exchange column followed by two sub-boiling distillations[6]. Control charts monitor the cleaning process and add to the overall understanding of the plutonium versus fissionable material balance. Although the reagents are cleaned (with the exception of the ETOH), direct deposits of reagents on lexan slides are included with each rabbit, irradiated, and the resulting fission tracks are counted to quantify the fissionable material present. These "reagent " slides determine the amount of tracks present due to the chemical reagents introduced in the process. The tracks resulting from added reagents are referred to as fission background. Data derived from fission track analysis of cleaned De-ionized water is reproducible and presented in Figure 5. These results are representative of the statistical variations in our quality control processes.

Reagent Blanks, reagent monitors, a lexan monitor and direct deposit of Pu-236 are used to evaluate the fission background as well as characterize the quality of the chemical separation

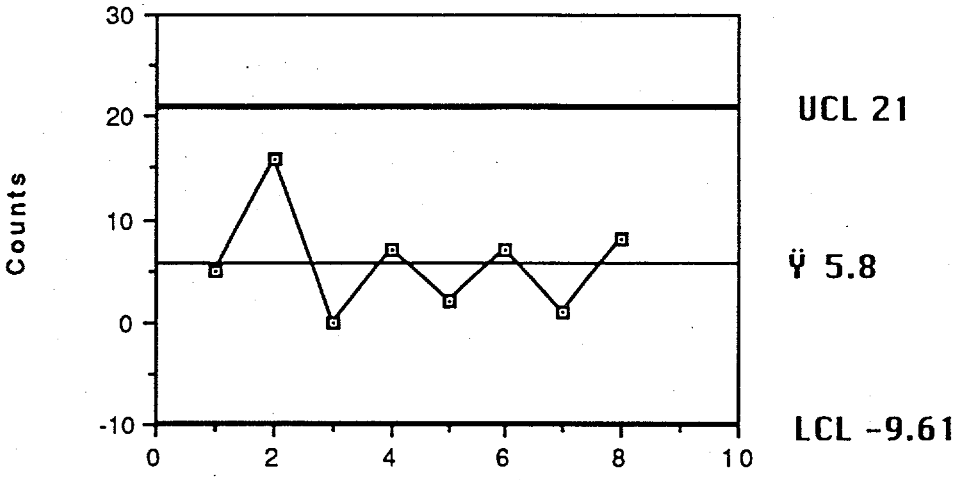


Figure 5. Statistical Variation in Fissionable Background for "BBDD" Water

process. Reagent blanks,"samples" which contain no urine, are designed to account for fissionable material added with the reagents during the processing. Specifically, reagent blanks start with a solution of cleaned deionized water, HNO_3 and HCl. HNO_3 and HCl are used to dissolve and rinse solids that may remain in the sample containers after transferring the solution to erlenmeyer flasks. This mixture is then processed following the same protocols and procedures as if urine was present, including the addition of the Pu-236 tracer and other processing reagents. As shown in Figure 6a, both the yield and number of fission tracks registered for the reagent blanks are volume dependent. The track counts from reagent blanks are indicative of the overall effectiveness of the FTA process. When insufficient reagents are added, the process produces a random pattern of fission tracks and chemical yield as a function of volume. For example, Figure 6b shows the results of 7 reagent blanks which had an insufficient amount of rhodizonic acid added for the volume processed. Plotting the data resulted in no readily apparent correlation.
As with all chemical processes, the chemical separation of Pu-239 is not 100% efficient. Some uranium remains, and some plutonium is lost. In order to account for and quantify these inefficiencies, two quality control procedures are employed: the use of a Pu-236 tracer to determine Pu yield and the measurement of fission tracks contributed by the chemical reagents added in the separation process. A Pu-236 radioactive tracer of known quantity is added before chemical processing begins and reagents are introduced. At the conclusion of the chemical separation and neutron irradiation, the alpha emitting Pu-236 is quantitatively measured by an alpha spectrometer. Since the reactivity of the Pu-239 and Pu-236 isotopes is similar, the ratio of Pu-236 measured after sample processing and irradiation to the known amount initially introduced can be assumed to represent the Pu-239 yield for that specific processed sample.

The elutant from the second column is direct deposited onto four circles scribed into the lexan. Approximately 100 ul are deposited into each circle. This step serves two quality assurance purposes. First, the fission tracks are more evenly dispersed by dividing the sample, thus errors associated with the counting process are reduced. Secondly, it provides the ability to compare elution patterns. The results from the fission track counts and alpha spectroscopy counts of the four circles form an elution pattern. Since both methods are measuring Pu content, the patterns derived from the fission track analysis and the alpha spectroscopy analysis should be similar. If the patterns obtained from the counts of the four circles do not match, it is likely that the processing of the sample failed, the sample was contaminated, or uranium was not eliminated by the process.

An acceptable fission track elution pattern will contain trends clearly similar to the pattern derived from alpha spectroscopy analysis. (See Figure 7a, which shows a progressive reduction of Pu-236 from the previous circle.) Small variations are acceptable and are due, in part, to

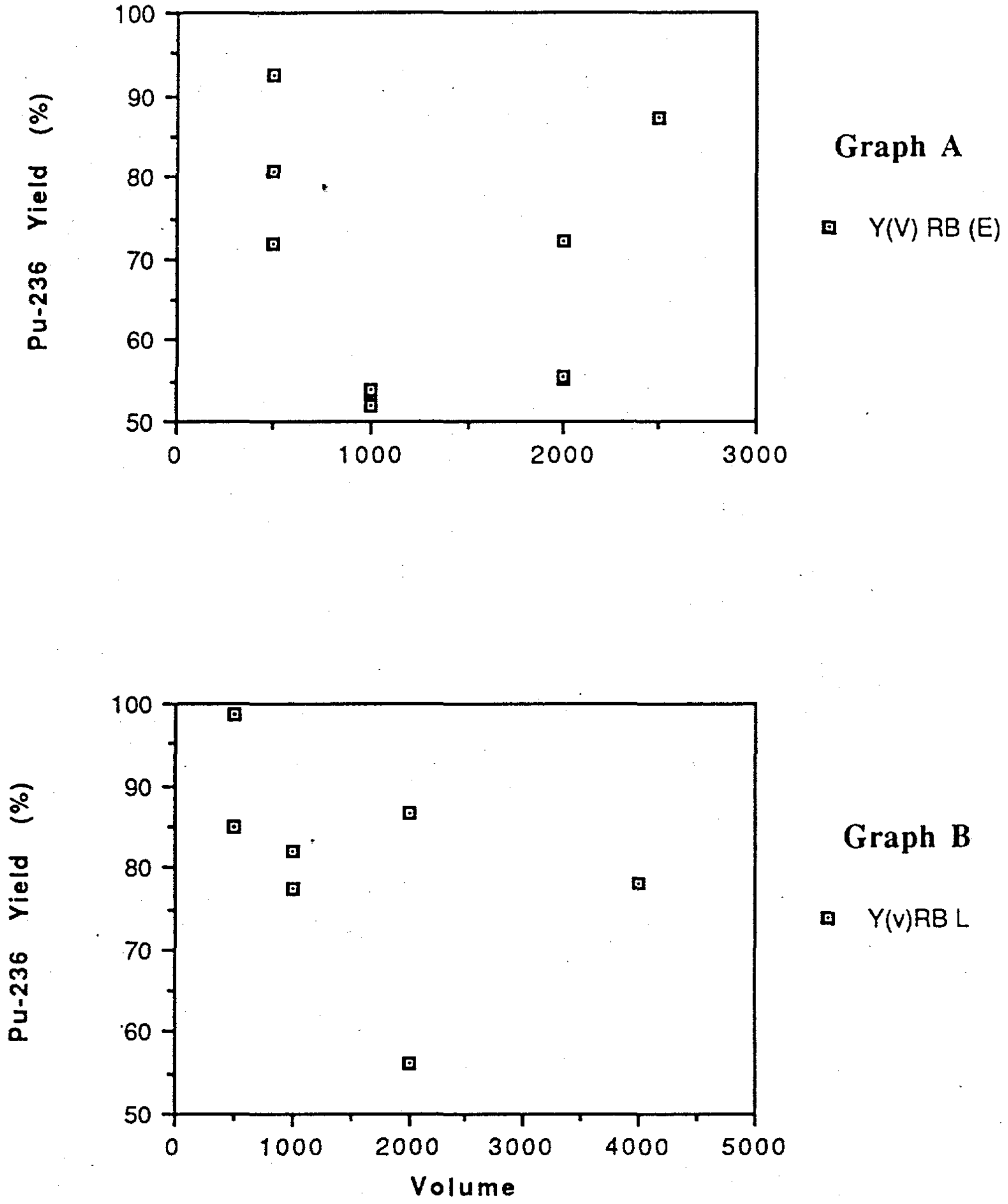


Figure 6. Pu Yield and Fission Tracks Obtained from Reagent Additions

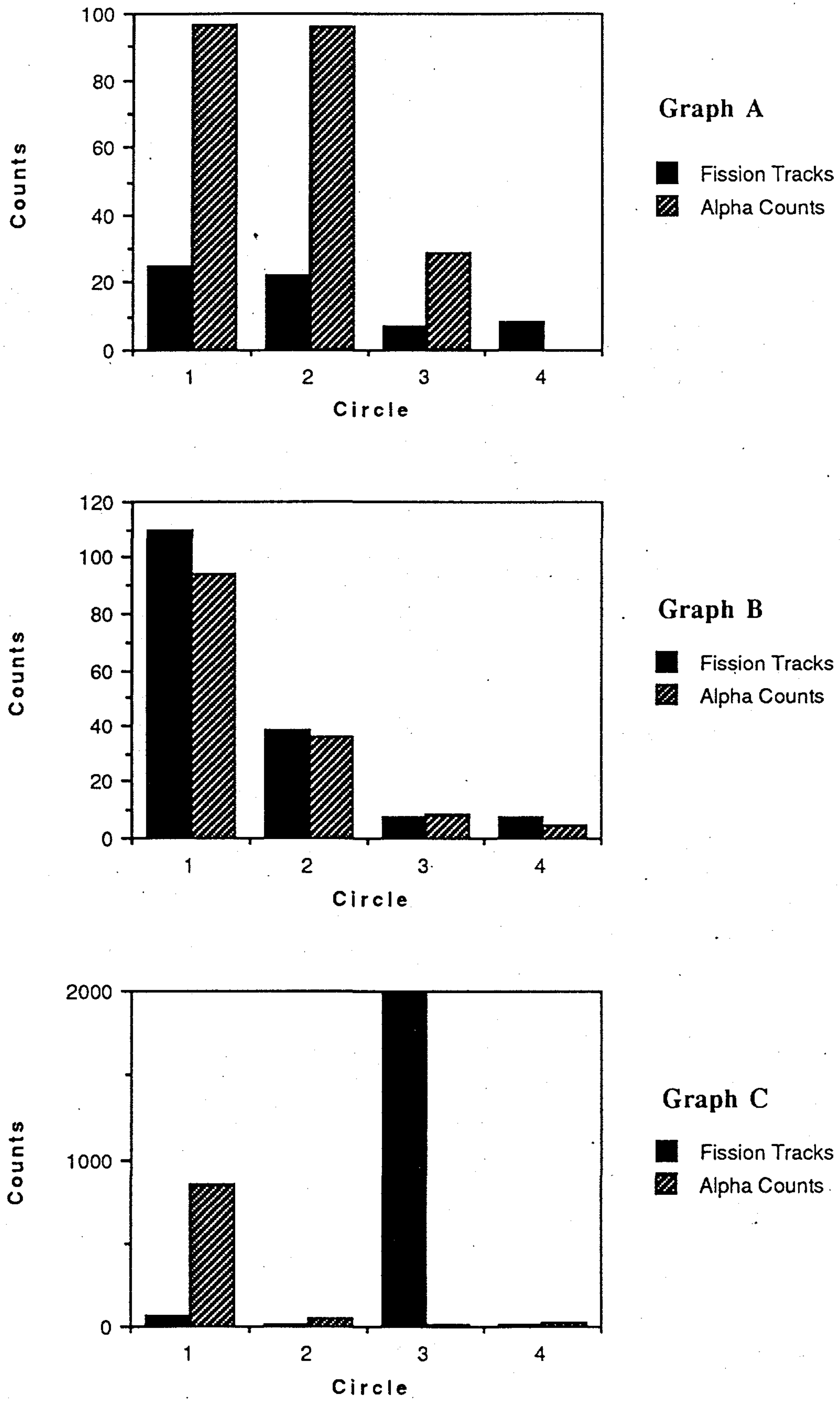


Figure 7. Elution Patterns for Pu-236 (Alpha Counts) and Pu-239 (Fission Tracks)

characteristics of elutant deposition (i.e., column packing and drop size where drop size is impacted by temperature, humidity, and shape of column end.) However, there must be a distinct correlation between the two measures. Figure 7b shows a pattern of fission track counts that correlates reasonably well with the Pu-236 alpha counts, thus indicating a valid result. The first two drops contain relatively more counts and tracks than the next two circles. Figure 7c shows differing measured patterns. In this case, the tracks caused by fissile material do not follow the pattern established from the alpha spectroscopy count of Pu-236. This suggests that fissile material other than Pu is present. Therefore, uranium and other fissile materials have not been effectively eliminated by the chemical.separation process. The results from this sample would be disallowed and a second specimen would be requested for retesting.

Field Trial

Using the newly developed procedure, sixteen urine samples and 4 synthetic urine control samples were processed to determine the Pu burden. The samples were collected from two geographical areas, and only minimal histories were provided. The results of the field trial are presented in Table 4. They indicate that the process is strongly dependent on the ability to accurately count fission tracks. Counting accuracy is impacted by the surface of the detector and the efficiency of the etching. These sample data reported are from two geographical areas and provided to CENTER with minimal histories. Furthermore, Of the sixteen samples, 6 were duplicates and 2 were occupationally exposed. Three of the samples processed indicate a plutonium burden below the detection limit for the specific volume processed. Two samples' yields were out of bounds. The cause for the low yield was determined in each case. Sample 1095 had a matrix interference, which was confirmed by processing a duplicate sample. The synthetic urine sample developed channeling in the first column, a processing error which results in a low yield. Six of the samples contain quantities lower than 2 times background and are indicative of an environmentally exposed individual. Sample 1135 is a confirmed occupationally exposed individual. The remaining three samples are from radiation workers, and the results indicate elevated levels of Pu-239. Of course, the small number of samples collected and processed is insufficient for drawing general conclusions on the individual plutonium burden of each specific geographical population.

The chemical yields of the revised CENTER process are compared to the chemical yields of the previous method in Figure 8. As shown in the figure, the yields have increased significantly from the previous method and are now reproducible. Although the Pu yield is still reduced as the sample volume increases, this reduction is markedly smaller than previously measured. The

Sample ID	Volume (ml)	Yield (%)	Gross Tracks	Net Activity (aCi)	Net Concentration (aCi/L)
1109	1869	42.3	177.5	92.3±9.5 [1]	49.34
1091	1883	67.3	59.5	BDL[1,2]	-
1095	1796	5.1[3]	-	-	-
1095 (A)	1402	6.5[3]	-	-	-
1135 (O)	205.4	94.2	69291	30788±2680[1]	149858
1135 (O)	13.73	87.1	4011	1887±151[1]	137368
1092	2113.8	21.15	89	39.3±13.2	18.6
1106	2245.2	63.39	51	BDL[4]	44.8
1110	2299	48.56	97.3	BDL[5]	-
1117	2267.5	52.38	200	25.25±14.2	11.13
1120	2477.5	34.64	46.5	BDL[6]	-
1125	2128	38.85	209	116.96±8.5	55.0
2201	1862.1	65.79	1331.5	960.05±65.4	515.6
2201(A)	1862.1	61.55	1213.5	930.6±62.0	499.7
2202	1753.7	57.48	2174.5	1934±145	1102.7
2208	1829.8	63.58	1040	748.5±48.1	409.1
syn urine1[7]	1000	67.06	186	58.0±12.0[1]	57.96
syn urine 2[7]	1000	29.02	140.5	134.8±7.8[1]	134.78
syn urine 3[7,8]	2000	6.96	-	-	-
syn urine 4[7]	2000	46.38	101.82	60.7±11.8[1]	30.34

BDL- Gross number of fission tracks from the sample did not exceed number of fission tracks produced in reagent blank.
A - Sample Duplicate
O - Occupationally Exposed
Batch $\varepsilon = 0.55$ aCi/track except where otherwise noted.

1 - Batch $\varepsilon = 0.4190$ aCi/track
2 - Detection Limit 71.9 ±11.1 aCi
3 - Sample yield out of acceptable limit. Sample duplicates confirmed matrix interference.
4 - Detection Limit 170.5 ±7.1 aCi
5 - Detection Limit 174.4 ±7.1 aCi
6 - Detection Limit 187.8 ±7.2 aCi
7 - Sample spiked with ~160 aCi of Pu- 239
8 - 1st anion exchange column developed channeling. Sample yield out of acceptable limit.

Table 4. Plutonium Activity in Urine

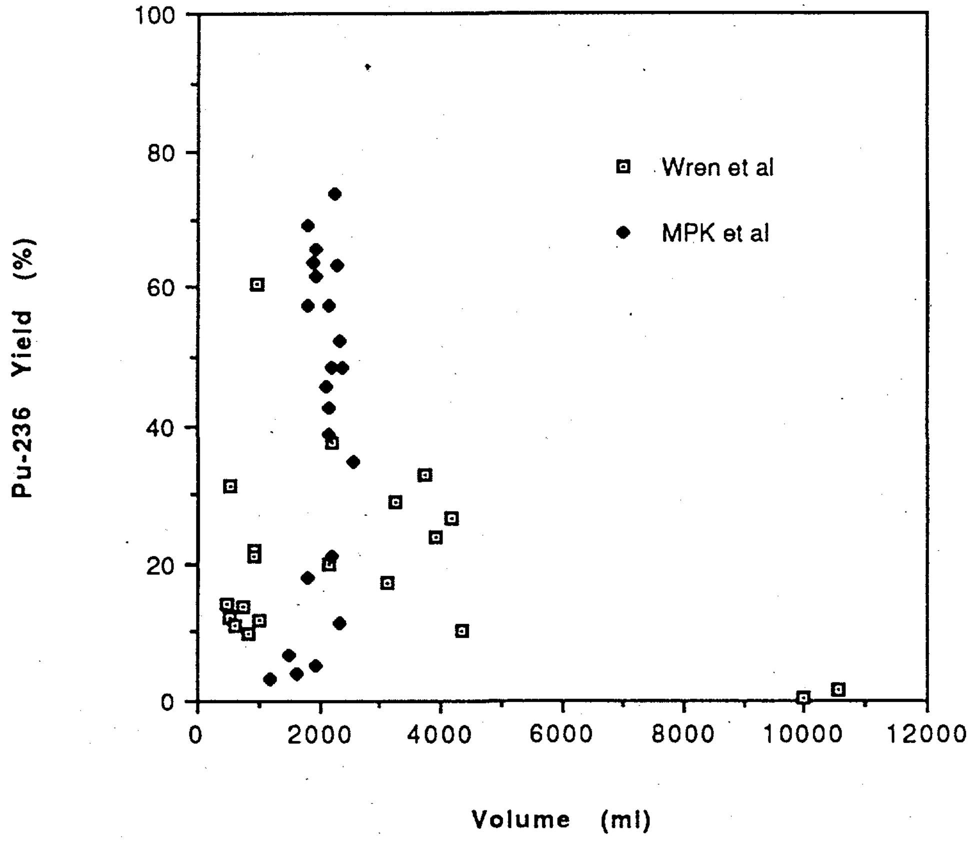


Figure 8. Comparison of Pu-236 Yield for Two FTA Techniques

significant variability associated with the process was determined to be associated with the chemical constituents found in the urine. For a given urine composition, Pu yield and fission tracks present were reproducible with a measured variation of less than 5 percent. However, the chemical yield for different chemical compositions (holding all process parameters constant) may vary from 40 to 80 percent. This suggests that better knowledge of the specific chemical composition of an individual urine sample can greatly assist in improving the yield and track registries.

Conclusions

The current FTA technique is capable of determining Pu-239 concentrations at the aCi level. This detection level is sufficient to determine environmental levels of plutonium excreted in urine. Early results from CENTER field tests to examine Pu in urine can distinguish non-occupationally exposed subjects, occupationally exposed and radiation workers. Additionally, we established the presence of a strong correlation of chemical yield and fission track background with sample volume. The chemical yield decreases with an increase in sample volume, and the amount of fission track background increases with an increase in sample volume. However, an increase in sample volume does not result in higher accuracy or lower detection limits due to competing process efficiencies. We recommend that subsequent samples should be limited to approximately 2 liters. The detection limit for a 2 liter sample is 76 aCi/L.

The methodologies used to separate and concentrate the Pu do not make adjustments for variation in urine composition, and there is no existing data that correlates the effects of the urine matrix to FTA efficiency and sensitivity. These areas form a number of directions for future FTA research.

Acknowledgments

The authors gratefully acknowledge the DOE (DE-FCO8-89NV10865), and the University of Utah for providing financial support. Additionally, the authors thank Colorado State University and the Nevada Test Site for supplying the CENTER with urine samples from occupationally and environmentally exposed subjects. Lastly, the authors sincerely appreciate the contributions of the following graduate and undergraduates at the CENTER: Henry F. Moeller, Stephannie D. Mecham, Brenda Newton, Byron P. Lawrence, Adam Z. Rogers, Justin L. Wilde, and Thomas M. Cantrell.

References

1. Kathren R.L., K.R.Heid, M.J. Swint, "Comparison of Estimates of Systemic Pu from Urinary Excretion with Estimates from Post-Mortem Tissue Analysis," Health Physics, Vol. 53, pp. 487-493, November, 1987.

2. Wrenn M.E., N.P. Singh, and Y.H. Xue, "Urinary Excretion of ^{239}Pu by the General Population: Measurement Technique and Results," Radiation Protection Dosimetry, Vol. 53, Nos. 1-4, pp. 81-84, 1994.

3. Moorthy, A.R., C.J. Schopfer, S. Banerjee, "Plutonium from Atmospheric Weapons Testing: Fission Track Analysis of Urine Samples," Analytical Chemistry, Vol. 60, No. 14, July, 1988.

4. Fleischer, R.L.,P.B. Price, R.M. Walker, "Nuclear Tracks in Solids: Principles and Applications," University of California Press: Berkeley, CA, 1975.

5. Hepburn C., A.H. Windle, "Review Solid State Nuclear Track Detectors," Journal of Material Science, 15, pp. 279-301, 1980.

6. Kuehner, E.C., R. Alvarez, P.J. Paulsen and T.J. Murphy, "Production and Analysis of Special High-Purity Acids Purified by Sub-Boiling Distillation," Analytical Chemistry, Vol. 44, No. 12, October, 1972.

7. Somogyi G., K. Grabisch, R. Scherzer, W. Enge,"Revision of the Concept of Registration Thresholds in Plastic Track Detectors," Nuclear Instruments and Methods, 134, pp. 129-141, 1976.

8. Bruenger F.W., J.M. Smith, "Quantitative Assay for Plutonium and Uranium in Tissue Using Fission Track Detection," Nuclear Tracks and Radiation Measurement, Vol. 8, No. 1-4, pp. 511-514, 1984.