

**<sup>239</sup>Pu in urine by ICP-MS and FTA methods and their application to occupational exposure measurements.**

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**Abstract**

Measurement of <sup>239</sup>Pu in urine by Fission Track Analysis (FTA) was first reported by Brookhaven National Laboratory (BNL) in 1988. Several enhancements of this method have taken place since then and it has been used primarily for assessing environmental exposures from atmospheric nuclear bomb tests. Advances in the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) <sup>239</sup>Pu in urine method at BNL have resulted in a detection limit that is competitive with the detection limit for the FTA method. Part 1 of the paper describes the details of the sample treatment and analysis by the ICP-MS and FTA methods. The ICP-MS and FTA methods were recently used to measure <sup>239</sup>Pu in urine of a few workers who had been exposed to mixtures of fission and activation products including actinides at a nuclear power plant. Part 2 of the paper describe the results, their dosimetric interpretation and the implications for monitoring occupational intakes of <sup>239</sup>Pu.

**Part 1: The Fission Track Analysis and ICP-MS Methods for Measurement of <sup>239</sup>Pu in Urine**

**Fission Track Analyses**

Fission Track Analysis (FTA) has been used to monitor <sup>239</sup>Pu in the urine of Marshall Islanders in a program funded by the Department of Energy, Office of International Health Programs (EH 63). The technique was developed to provide assurances that the radiation dose to residents would not exceed recognized international standards or recommendations. The uptake of <sup>239</sup>Pu can be estimated from the excretion of <sup>239</sup>Pu in the urine of an individual. The analytical technique must have sufficient sensitivity to quantify <sup>239</sup>Pu below a level equivalent to 1 mSv per year with known statistical confidence that considers internal dose assessment uncertainties.

The FTA method was developed at Brookhaven National Laboratory (BNL) to detect and measure <sup>239</sup>Pu in 24-h urine samples at a sensitivity of about 100 aCi [Moorthy et al, 1988]. Plutonium-239 atoms are bombarded with thermal neutrons, causing the plutonium to fission. The total plutonium activity in the sample can be interpreted from the number of fission events that occur in the sample. Each fission event produces two fission fragments, one of which causes a visible track on a quartz slide. The number of tracks observed on the slide can be directly related to the total plutonium activity using a calibration curve. The current minimum detection level (MDL) for the FTA system <sup>239</sup>Pu is about 50-80 aCi. This represents the most sensitive detection method available for <sup>239</sup>Pu. A 100 aCi detection sensitivity is adequate for determining a committed effective dose equivalent (CEDE) of 44 mSv (e.g., approximately 1 mrem y<sup>-1</sup>) obtained from a single 24-h urine sample due to a single acute uptake of plutonium for Marshallese [Sun, 1992; 1993; 1994; 1995].

The FTA method requires three major processing steps: 1) chemical separation, including digestion and <sup>235</sup>U elimination in sample preparation; 2) neutron induced fission in a nuclear reactor, and 3) counting fission track images (in 3 dimensions). Each of the three steps requires about one week to complete: including paperwork and QA analysis, it takes a total of four weeks to complete one FTA measurement. This long sample analysis time and concomitant high cost per analysis, the analysis of only a single isotope of plutonium, and interference from <sup>235</sup>U, offset the ultra-low detection sensitivity advantage of this method.

## ICP-MS

Although FTA is very sensitive, it is also expensive and requires long turnaround times. An emerging technology, Inductively Coupled Plasma Mass Spectrometry (ICP-MS), offered great potential as a rapid alternative ultra-sensitive measurement method that is easy to operate and only requires a minimum amount of sample preparation. The attraction of faster, less expensive analyses of very low levels of plutonium in urine at comparable sensitivity motivated the Department of Energy to fund BNL to demonstrate the ability of ICP-MS to determine  $^{239}\text{Pu}$  activities in urine bioassays at a detection level comparable with FTA.

ICP-MS can be used for analyzing low-levels of Pu and other transuranic isotopes because these isotopes have a low specific activity ( $\text{Bq g}^{-1}$ ).  $^{239}\text{Pu}$ , as an example, has a specific activity of  $2.3 \text{ GBq g}^{-1}$ . It translates that 1 Bq has about 1012 atoms. On the other hand, only one million (10<sup>6</sup>) atoms are required to obtain a reliable result using an ICP-MS method. Therefore, it is easy, in theory, to obtain an MDL at 2-3 Bq levels of  $^{239}\text{Pu}$ . Other benefits for using a ICP-MS method are: 1) obtaining isotopic compositions; 2) speeding analytical processes; and 3) reducing costs (i.e., compared to the FTA method), and 4) allowing an assessment of the radiological impacts due not only to  $^{239}\text{Pu}$ , but also for  $^{238}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$ , etc.

An ICP-MS sorts out isotopes according to their ratios of mass to charge ( $m/e$ ). Like the FTA method,  $^{239}\text{Pu}$  activity is determined based on the number of atoms in the sample, not the radioactivity. The ICP-MS method uses plasma gas, produced when electrons from an external source are introduced into a neutral gas passing through a quadrupole electromagnetic field to sort  $m/e$  ratios in the gas.

The ICP is formed in a quartz torch which usually consists of three tubes. The plasma gas is passed through these tubes at different flow rates. The sample is introduced into one of the tubes via a gaseous nebulizer, and is transported to the plasma in the form of an aerosol. Once combined, the ions travel through a cooled sampling cone in which the gas expands, and then passes into a skimmer cone. Lenses are used to focus the ions into a quadrupole mass analyzer where they are sorted based upon their  $m/e$  ratios. The ions are then detected using an electron multiplier [Vela, 1993].

The ICP-MS method can simultaneously analyze low-level amounts of long-lived radionuclides like  $^{237}\text{Np}$ ,  $^{238}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{240}\text{Pu}$ . Wyse [1994] indicated that the major benefits of the ICP-MS method are an increase in the rate of sample processing and the ability to introduce an aqueous sample. Generally, ICP-MS has been used for determination of rare earth elements and actinides, including plutonium, in nuclear materials, soils, an infrequently, biota. An ICP-MS equipped with an ultrasonic nebulizer has been used to determine trace elements in ground waters at the  $\text{ng L}^{-1}$  (ppt) level [Stetzenbach, 1994]. Actinide determinations with sensitivities commonly at single figure ppg ( $\text{pg L}^{-1}$ ) have been reported by Liezers [1994], who also predict sub-ppg ( $\text{fg L}^{-1}$ ; 1.63 fg is approximately 100 aCi) in the near future. ICP-MS has been reported for use in the determination of uranium in urine [Gladney, 1989], with a detection limit of 25  $\text{pg L}^{-1}$  for  $^{238}\text{U}$ .

ICP-MS has been reported for determination of plutonium in urine for bioassay purposes. A comparison of FTA with ICP-MS was made using urine from Japanese workers [Kim, 1989], who were working at the pCi level. Determination of plutonium at femtogram levels as reported to be feasible by Hall [1990]; Wade [1992] developed a similar method for neptunium. Using a conventional pneumatic nebulizer (see below), Pickford [1994] reported detection limits of the order 4  $\text{fg L}^{-1}$  (about 650 aCi  $\text{L}^{-1}$ ), as well as chemical matrix interferences from sodium, calcium, and other anions. Wyse [1994] reports a detection sensitivity for  $^{239}\text{Pu}$  in urine 50-100 fg (4-8 fCi) using two different methods for sample introduction: electrothermal vaporization (ETV) and an ultrasonic nebulizer.

It is important to note that ICP-MS is matrix sensitive, and thus the measurement of radionuclides at typical concentrations in raw urine is not possible at this time. Sample preparation begins with FTA

procedures to pre-concentrate and separate plutonium from the urine matrix (e.g., co-precipitation, anion chromatography, extraction chromatography). For the ICP-MS method, we will make small modifications to the separation chemistry which will permit the simultaneous analysis of  $^{235}\text{U}$ ,  $^{237}\text{Np}$ ,  $^{238}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{240}\text{Pu}$ . Later, more efficient sample preparation procedures will be developed such that raw urine could be introduced with minimal pre-processing.

### **Reported results from ICP-MS**

During 1997-1998 the D.O.E. Office of International Health Programs contracted with the National Institute of Standards and Technology (NIST) to evaluate the state of the art (accuracy, precision and sensitivity) for  $^{239}\text{Pu}$  in synthetic urine measurements by inductively coupled plasma mass spectrometry, thermal ionization mass spectrometry, and fission track analysis in the concentration range of 3-56  $\mu\text{Bq}$  for 200g samples of synthetic urine. The major portion of the preparation tasks was performed by the Yankee Atomic Environmental Laboratory (YAEL), in terms of establishing the stability of  $^{99\text{m}}\text{Tc}$  tracer for  $^{239}\text{Pu}$  in the synthetic urine, executing the dilutions, conducting confirmational measurements, documenting the preparation work and distributing the samples to participating laboratories. NIST oversaw the development of the work plan and YAEL's preparation of the test materials, as well as certifying the test materials and evaluating the resulting data.

NIST reported the following in its findings:

Analytical Bias - Generally, biases approaching five percent were observed for the higher concentration test samples. "It is likely that the accuracy of the chemical yield monitors (tracers) is a considerable portion of this bias. In addition, FTA was handicapped with bias limitations when track density was high, and when batch chemical yield corrections were used."

BNL ICP-MS had the best set of bias values. "BNL ICP-MS results make an unambiguous statement of its terrific measurement capabilities for  $^{239}\text{Pu}$  at the  $\mu\text{Bq}$  level with its excellent accuracy and measurement precision. The excellent agreement with the NIST values lends support to the presumption that the test samples were stable and accessible during this exercise. The BNL ICP-MS value for the blank samples was extremely low, and was probably responsible for the good performance."

High Variable Blank - In contrast to its competition, BNL ICP-MS results had very low and consistent blanks. "Presumably, BNL has developed extreme sensitivity to sample and reagent contamination, and have developed extraordinary cleanroom techniques and ultra-pure reagents for analysis. The results of this study indicate that BNL's successes may be linked to their ability to control and minimize any blank contributions."

Low Chemical Yield - "... chemical yields for natural urine samples are typically in the 70-80 percent range."

Precision - "Superb analytical blank control by BNL played a key role in their excellent performance for measurement precision."

Minimum Detection Level "Routine alpha spectroscopy's MDA is about  $3 \times 10^6$  nBq. BNL's ICP-MS MDA is about 3000 times lower than for alpha spectroscopy. This is in contrast to the study by Lee et al (1995) and Hutchinson et al (1993) where they found ICP-MS only had comparable measurement capabilities to alpha spectroscopy for  $^{237}\text{Np}$  in synthetic urine. FTA's MDA is comparable to that expected from ICP and thermal ionization mass spectrometry, but is a factor of 10-100 times less certain."

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## **Part 2: Application of the ICP-MS and FTA Techniques to Detect and Monitor Occupational Exposures of <sup>239</sup>Pu at a Nuclear Power Plant**

### **The need for improved detection capability for <sup>239</sup>Pu in urine**

The traditional method for analysis of <sup>239</sup>Pu in urine involves radiochemical separation and alpha spectroscopy. It has a detection limit of  $\approx 1$  mBq/L. To achieve such a detection limit long count times are required in addition to the time needed for radiochemical separation and sample preparation for counting. It may be suitable for detection and follow-up of intakes near or above the ALI (Annual Limit of Intake). Under the ICRP 26 and 30 methodology the Stochastic Annual Limit of Intake (SALI) for <sup>239</sup>Pu is 600 Bq for a Class Y, 1  $\mu$ m AMAD particulate aerosol. The comparable value under the ICRP 60 and 68 methodology for a Type S 1  $\mu$ m AMAD particulate aerosol is 3300 Bq. The investigation level is typically 0.1 SALI. Intakes of <sup>239</sup>Pu in the 60-300 Bq range would not be detectable with this technique (see Figure 1). An improved capability with a detection limit of  $\approx 1$   $\mu$ Bq/L would alleviate the difficulty of dealing with "less than" results and enhance the interpretation of urine bioassay data. Such a capability would improve (a) the implementation of a routine monitoring program and (b) investigations where an intake is to be followed over a long time period.

### **Background**

Prior to October 1993 there were no recorded incidents of exposure to radionuclide mixtures containing actinides that were investigated with specific urine or fecal actinide bioassay methods at Ontario Hydro's CANDU power reactors. During the period October 1993 to May 1995 a few incidents occurred that required investigation and dose assessment for actinides. These assessments were based on fecal sampling and analysis. The significant incidents of this nature were associated with maintenance work on boiler tubes that accumulated crud contaminated with mixed fission and activation products including actinides. During investigations of these incidents some urine samples were collected for non-destructive gamma spectroscopic analysis of soluble fission and activation products. These urine samples were frozen and stored for analysis of actinides in the future using techniques such as FTA and ICP-MS for <sup>239</sup>Pu.

In 1997 a project, funded by the Candu Owners Group, was undertaken in cooperation with BNL to analyze 11 urine samples from 5 workers. Three additional samples from individuals not associated with nuclear power plant work were included as controls for a total of 14 urine submitted to BNL for analysis.

## Results and Discussion

Four (4) out of the 11 urine samples from workers showed  $^{239}\text{Pu}$  in urine values greater than the detection limit of 2  $\mu\text{Bq}$  for the ICP-MS method. These 4 samples were associated with two workers (#1 and #2) whose fecal samples showed  $^{239+240}\text{Pu}$  values above the detection limit of 7 mBq (see Table 1). Samples associated with the remaining workers gave values below the detection limit. Two urine samples from individuals not associated with work at power reactors were below the detection limit. The urine samples from worker #5 and the third individual not associated with work at power reactors encountered analytical difficulties and were not reported by BNL.

**Table 1. Fecal Sample Data**

Worker ID	Time (d)	$^{239+240}\text{Pu}$ (Bq)
	Post Intake	Measured in feces
1	12	3.45E-02
1	55	9.90E-03
1	56	7.70E-03
2	2	1.3
3	3	**
4	5	**
5	3	**

\*\* Fecal sample did not show presence of  $^{144}\text{Ce}$  and therefore not subjected to radiochemical analysis for transuranics

An analysis of the fecal sample data for workers #1 and #2 using different models predicts intakes of  $^{239+240}\text{Pu}$  in the 10-100 Bq range or, using a  $^{239}\text{Pu}:$  $^{240}\text{Pu}$  ratio of 1.4,  $^{239}\text{Pu}$  intakes in the range 5-60 Bq. The corresponding  $^{239}\text{Pu}$  in urine predicted values for daily excretion, based on ICRP 30 lung model and ICRP 30 plutonium biokinetic model, are within a factor of 2 of the measured values (see Table 2). The  $^{239}\text{Pu}$  in urine predicted values for daily excretion based on ICRP 66 lung model (default parameters) and ICRP 67 plutonium biokinetic model are lower than the measured values by as much as an order of magnitude. This is because the ICRP 66 lung model contains a key default parameter,  $s_t$  for Type S materials, and its use yields much lower predicted urinary excretion. When the value of  $s_t$  is increased from its default value of  $0.0001 \text{ d}^{-1}$  (half time of 7000 days) to  $0.001 \text{ d}^{-1}$  (half time of 700 days) the predicted urine excretion values are in much better agreement with the measured values. Considering the likely uncertainty in completeness of 24 hour fecal and urine collection in this limited data set, further refinements to the model predictions are not warranted. However, the data and predictions shown in Table 2 show promise for monitoring intakes of occupational  $^{239}\text{Pu}$  as low as 5 Bq provided a rigorous urine sample collection regime is followed.

**Table 2: Comparison of Measured  $^{239}\text{Pu}$  in Urine Values with Predicted Values using Calculated Intakes Based on Fecal Sample Data, particle size of 1  $\mu\text{m}$  AMAD and a  $^{239}\text{Pu}$ : $^{240}\text{Pu}$  Ratio of 1.4**

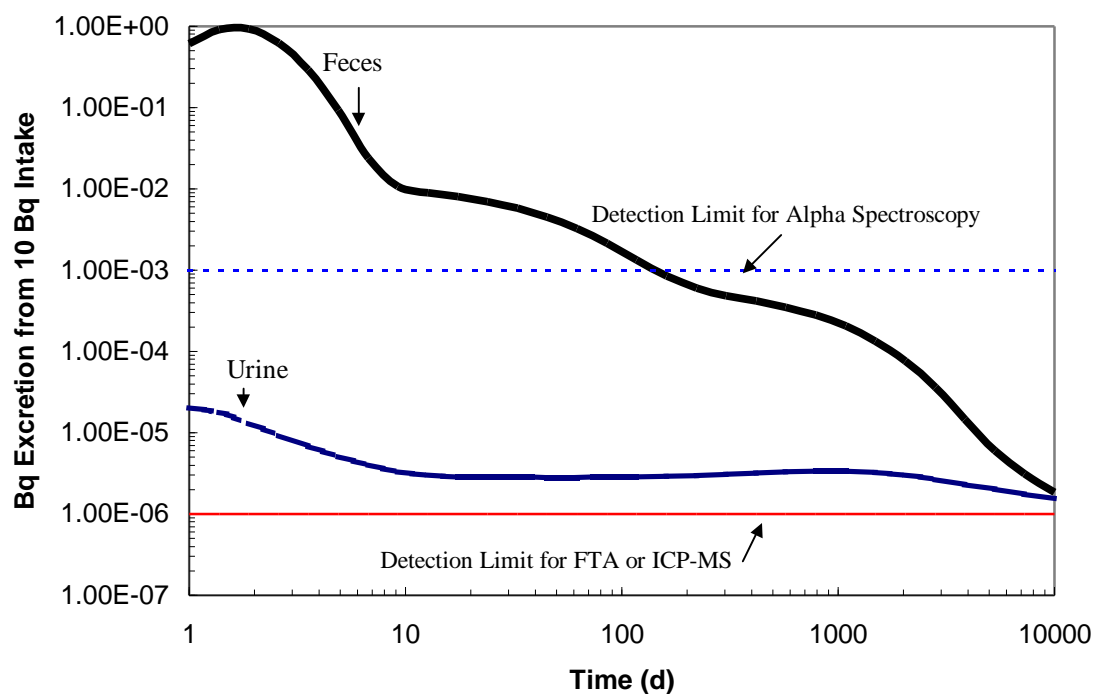
Worker ID	Time Post Intake d	Sample Volume Litres	Measured by ICP-MS at BNL $\mu\text{Bq}$	Predicted ICRP 30 Class Y Default $\mu\text{Bq/d}$	Predicted ICRP 66/67 Type S Default $\mu\text{Bq/d}$	Predicted ICRP 66/67 Type S Modified $\mu\text{Bq/d}$
1	52	0.995	37	51	5	38
1	82	1.563	58	52	5	40
1	85	0.531	20	52	5	40
2	2	0.561	21	15	10	20

### Conclusions

- Analysis of  $^{239}\text{Pu}$  in urine by the ICP-MS method provided independent confirmation of the exposure of two workers to actinides which had previously been positively identified by fecal bioassay.
- Provided information on  $^{238}\text{Pu}$  and  $^{240}\text{Pu}$  activities relative to  $^{239}\text{Pu}$  is available from a workplace sample or an early fecal sample, it may be possible to use the  $^{239}\text{Pu}$  in urine ICP-MS or FTA method for monitoring intakes of these three key plutonium radionuclides in the actinide mixture.
- Intakes of plutonium by the  $^{239}\text{Pu}$  in urine ICP-MS or FTA method could be monitored well beyond 100 days following exposure at which time fecal sample analysis may not be practical due to detection limit restrictions of the traditional alpha spectroscopy method.

**Figure 1.**

**Urinary and Fecal Excretion Resulting from an Intake of 10 Bq of Type S  $^{239}\text{Pu}$ , as Predicted by the Default ICRP 66 Lung Model Parameters and ICRP 67 Biokinetic Parameters for a 1  $\mu\text{m}$  AMAD aerosol.**



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