Rapid Extraction of Plutonium from Urine by Pyrosulfate Fusion and PERALS Spectroscopy

R.L. Metzger, P.H. Pouquette, and G.W. Klingler

Radiation Safety Engineering, Inc.

Chandler, AZ

Abstract

To effectively treat accident victims exposed to airborne isotopes of Plutonium, chelation therapy must be started before the Plutonium is fixed in bone. Urine bioassay samples must be processed rapidly after an accident to identify those patients that should be treated. We introduce a method to rapidly analyze a urine bioassay sample within four hours of the receipt of the samples using a pyrosulfate fusion in platinum crucibles to rapidly destroy all organics and solubilize all salts in the sample. The Plutonium is separated by solvent extraction in centrifuge tubes using an extractive scintillator with P,P' - di(2-ethylhexyl)methanediphosphonic acid (DIPEX) as the extractant. The organic phase is counted on a PERALS spectrometer. For a 100 mL urine sample, recoveries of the isotopes of Plutonium are >85% and the recovery for each individual sample may be traced using a ^{236}Pu tracer solution. The lower limit of detection (LLD) for a two hour count is 0.04 Bq/L. For a person exposed to ICRP Class S airborne ^{239}Pu with an Activity Median Aerodynamic Diameter (AMAD) of approximately 5 microns two hours before the sample was taken, this LLD corresponds to an intake of 0.012 MBq, and a committed effective dose equivalent of 200 mSv.

Key Words: Dosimetry, Radiochemistry, Plutonium

Introduction

In the aftermath of an accident or the detonation of a radioactive dispersive device containing transuranic radionuclides, there will be a need to identify people in the plume of the device that will need

to be treated to reduce their body burden of the radionuclide (s). The most common treatment for airborne exposures to transuranic radionuclides is with chelating agents to chelate and excrete the heavy metals before they deposit and lodge in bone. Consequently, the identification of those that need to be treated must occur quickly after the accident for the treatment to be effective. Conceivably, a large number of people will have to be screened following an accident or detonation of an RDD to identify those that will need to be treated. Directly counting nasal smears is a good tool to identify recent inhalation of radionuclides, but the value of the test drops rapidly as the time since the exposure increases. Deposition of radionuclides on clothing will also help identify those who have been heavily exposed. For bioassay techniques, the fraction of an intake that appears in urine shortly after an acute exposure is quite low, particularly for insoluble forms of the transuranics, and fecal transit times are frequently too slow to allow analysis to be performed in time for effective treatment. Practically, a quick urine bioassay method with the sensitivity to identify the small fraction to urine that occurs after an acute exposure to a transuranic radionuclide is desirable. In this work we have developed a rapid method to screen urine for Plutonium isotopes that involves a minimum of complex chemistry and therefore can maximize throughput of samples. Plutonium was chosen for this work as it has a high inhalation dose coefficient and is commonly found in insoluble matrices, making it a difficult analytical challenge.

Method Development

A method was developed to allow batch screening of urine samples for isotopes of Plutonium using a pyrosulfate fusion [Sills 1994], extractive scintillators, and Photo-Electron Rejecting Alpha Liquid Scintillation (PERALS)[1] spectroscopy. Extractive scintillators contain an organophilic metal ion extractant that allows the phase transfer of a nuclide(s) into the scintillator from an aqueous solution [McDowell 1994]. The Actinex[2] extractive scintillator used in this work uses P,P' - di(2-

[1]ORDELA, Inc., 1009 Alvin Weinberg Dr., Oak Ridge, TN 37830

[2]ETRAC, Inc., 1009 Alvin Weinberg Dr., Oak Ridge, TN 37830

ethylhexyl)methanediphosphonic acid (DIPEX) as the extractant. This extractant has a high affinity for actinic radionuclides. The PERALS spectrometer uses pulse shape discrimination to isolate the longer pulses resulting from alpha interactions in the scintillator from those resulting from β - Υ emissions. A timing circuit and gate are then used to reject the β - Υ pulses and the alpha pulses are sent to a multichannel analyzer for display of the alpha energy spectrum. The counter typically has a background of 0.03 counts per minute under an alpha peak, and an alpha counting efficiency of >99 percent. Energy resolution is about 220 keV Full Width at Half Maximim (FWHM) at an alpha energy of 5 MeV. The lower limit of detection for a two hour count ranged from 0.002 to 0.003 Bq depending on the specific spectrometer used.

The method consists of reducing the volume of an aliquot of urine (typically 100 to 200 mL single void) in the presence of nitric acid and H_2O_2 until ~5 mL remain. This is quantitatively transferred to a platinum crucible where the remaining organics are charred to prevent bumping during the subsequent pyrosulfate fusion. Two grams of KF and 1.3 grams of KHF are then added to the crucible and it is heated over the full heat of a Fischer blast burner until a clear melt is obtained. The crucible is then set aside to cool briefly and 4 mL of concentrated H_2SO_4 are slowly added to the melt, and then 2 grams of anhydrous sodium sulfate are added after the cake has transposed. This mixture is then heated over a small flame from the blast burner until the evolution of H_2SO_4 has slowed and clear red pyrosulfate fusion is obtained. The crucible is then set aside to cool and the resulting cake is dissolved in 25 mL of boiling 0.5 *M* HCL. This clear solution is then transferred to a 50 mL centrifuge tube and 2 mL of the Actinex extractive scintillator is added. The tube is then equilibrated with the organic scintillator for 30 minutes and then centrifuged to speed the separation of the organic and aqueous phases. One mL of the extractive scintillator is drawn off of the organic phase on the top with a calibrated pipet and this aliquot is sparged with dry argon to remove oxygen (a quenching agent). The Actinex is then counted directly on the PERALS spectrometer for two hours. The recoveries of the Pu range from 70 to 92% and can be

calculated directly by adding a known activity of ^{236}Pu tracer to the urine sample at the start of the process. The total time required from the receipt of the sample to the end of the count is less than six hours.

Dosimetry

If we assume an acute exposure of ICRP Type S ^{239}Pu with an Activity Median Aerodynamic Diameter (AMAD) of 5 microns, the fraction that appears in urine (*f1*) in the first hours after the exposure is 3.2×10^{-7} of the intake activity [Eckerman 2005]. If we further assume that a 100 mL sample from a 200 mL void four hours after the exposure is analyzed, the resulting intake estimate at the LLD for the method is $0.002\text{Bq} / (3.2 \times 10^{-7} \times 2) = 0.013$ MBq estimated intake. The dose coefficient for Type S, 5 micron AMAD ^{239}Pu is 16 Sv/Bq [Eckerman 2005] so the resulting dose that can be detected is approximately 200 mSv.

Conclusion

A simple radiochemistry separations method has been developed for screening urine bioassay samples taken shortly after an incident resulting in airborne exposures to transuranic radionuclides. The method is fast enough to provide bioassay data to medical professionals in time to effectively treat affected patients with chelating agents, if required to reduce the projected dose equivalent.

References

American Chemical Society. Reagents, Chemicals, American Chemical Society Specifications. Washington D.C.

ASTM Method D 6239-98a. Standard test method for uranium in drinking water by high-resolution alpha liquid scintillation spectrometry. Annual Book of ASTM Standards. Vol 11.02.1999.

Eckerman KF. et.al.DCAL: User’s guide to the DCAL system. ORNL/TM. (in press).

McDowell WJ, McDowell BL. Liquid scintillation alpha spectrometry. Boca Raton, Florida: CRC Press Inc.; 1994.

Sill DS, Sill CW. Simultaneous determination of the actinides in small environmental samples. Radioactivity and Radiochemistry. Vol 5, No. 2, 1994.