LA-UR-

12-01414

Approved for public release;
distribution is unlimited.

Title: Rusty Nails Adsorb Trace Plutonium from the Environment

Author(s): Warren J. Oldham, Jr.
Brent S. Matteson
Jeffrey L. Miller
Cody T. Lake
Moses Attrep, Jr.

Intended for: Slides to be presented at the Methods and Applications of
Radioanalytical Chemistry (MARC IX) Conference in Kona
Hawaii (March 25-30, 2012)

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Oldham, WJ; Matteson, BL; Miller, JL; Lake, CT; Attrep, M

Nuclear and Radiochemistry Group (C-NR), Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Rusty Nails Absorb Trace Plutonium from the Environment

Plutonium released into the environment displays a strong affinity for particulate and mineral surfaces such as iron oxides, manganese oxides, and aluminosilicates. Iron oxides are of particular interest because iron and iron-containing alloys are extensively used in contemporary society and may inadvertently function as high efficiency plutonium scavengers. Metals of this class, commonly covered with an oxide coating, could adsorb and sequester trace levels of plutonium encountered within their local environment. To test this intriguing idea we have collected discarded metal artifacts (rusty nails, bottle caps, etc) from remote environments around New Mexico and have analyzed their surfaces for adsorbed plutonium. The analytical method uses dilute hydrochloric acid to leach the oxide coating down to bare metal. The plutonium analyte contained within this solution is then purified using an anion-exchange procedure and then assayed using alpha spectrometry and ICP-MS. Plutonium present in these environments due to fallout during the era of atmospheric nuclear testing is easily measured using this technique. Given the observed variation in absolute plutonium concentration as a function of sample size, time of exposure, etc we have also measured natural uranium contained in the same samples for use as a concentration proxy to facilitate sample inter-comparison.

Rusty Nails Adsorb Trace Plutonium from the Environment

Oldham WJ, Matteson BS, Miller JL,
Lake CT, Attrep M

Plutonium Pourbaix Diagram

Experimental Design and Analytical Methods

1. Leach sample in 3M HCl
2. Filter and trace with ^{242}Pu
3. Pre-concentrate with a LaF_3 precipitation
4. Anion-exchange purification
5. Electroplate from $\text{NaHSO}_4/\text{Na}_2\text{SO}_4$ for alpha spectrometry
6. Strip planchette: ICPMS

ICP-Q-MS
Thermo-Fisher X-series II

Limits of Detection = $\sim 4 \times 10^7$ atoms

Plutonium Isotopic Standards (SRM 949f)
and standard reference materials
(SRM4353A) used to validate performance

CHEMISTRY
NSA

Sedgwick Mountain Summit, New Mexico

Collection Date: September 5, 2010

35° 10.470' N; 108° 5.712' W

$^{239+240}\text{Pu} = 0.714 (\pm 3.4\%) \text{ dpm}$
 $S\text{-value} = 0.038 (\pm 16\%)$
 $^{239}\text{Pu} = 7.86 \times 10^9 \text{ atoms}$
 $^{240}\text{Pu}/^{239}\text{Pu} = 0.174 \pm 0.005$

Operated by the Los Alamos National Security, LLC for the DOE/NNSA

Hill Top Mine, Colorado

Collection Date: August 2011

39° 12.912' N; 106° 10.438' W

Courtesy of Jake Turin

$^{239}\text{Pu} = 3.13 \pm 0.13 \times 10^9 \text{ atoms/sample}$
 $^{240}\text{Pu}/^{239}\text{Pu} = 0.205 \pm 0.016$

Operated by the Los Alamos National Security, LLC for the DOE/NNSA

Pagosa Springs, Colorado

Collection: Pagosa Springs, Colorado
 Coordinates: 37° 15.816' N; 107° 0.795' W
 Description: rusty cans and nails
 Collection Date: August 14, 2010

Los Alamos
 NATIONAL LABORATORY
 EST. 1943

Operated by the Los Alamos National Security, LLC for the DOE/NSA

$^{239+240}\text{Pu} = 1.24 (\pm 3\%) \text{ dpm}$
 $S\text{-value} = 0.046 (\pm 11\%)$
 $^{239}\text{Pu} = 1.38 \times 10^{10} \text{ atoms}$
 $^{240}\text{Pu}/^{239}\text{Pu} = 0.174 \pm 0.018$

CHEMISTRY
NSA

Plutonium ICP-MS Data Summary: Ten Samples from Five Sites

Median value = 2.82×10^9 atoms/sample

Average 240/239 = 0.176 ± 0.012

Maximum = 2.23×10^{10}

Minimum = 2.44×10^8

Los Alamos
 NATIONAL LABORATORY
 EST. 1943

Operated by the Los Alamos National Security, LLC for the DOE/NSA

CHEMISTRY
NSA

Normalize ^{239}Pu with co-adsorbed ^{238}U as a concentration proxy?

Operated by the Los Alamos National Security, LLC for the DOE/NSA

ICP-MS Measurements of Pu and U for Different Number of Nails from One Location

Samples	239 (atoms/sample)	$\pm$	238 (atoms/sample)	$\pm$	$^{239}/^{238}$ (ppm)	$\pm$
4 Nails	2.44E+08	1.40E+07	5.14E+14	1.26E+12	0.47	0.03
8 Nails	5.63E+08	8.58E+07	7.55E+14	1.91E+12	0.75	0.11
12 Nails	1.36E+09	1.39E+07	8.02E+14	1.89E+12	1.70	0.02
15 Nails	1.03E+09	2.83E+07	1.29E+15	3.00E+12	0.80	0.02
30 Nails	1.33E+09	4.54E+07	2.14E+15	7.10E+12	0.62	0.02

$[\text{PuO}_2]^+ \text{ ppq } (10^{-15})$

$[\text{UO}_2]^{+2} \text{ ppb } (10^{-9})$

$\text{Pu/U} \sim 0.7 \text{ ppm}$

Operated by the Los Alamos National Security, LLC for the DOE/NSA

Nails from Kerr Family Lease near Roswell, NM

Gallinas Peak, New Mexico

$^{239}\text{Pu} = 1.78 \pm 0.08 \times 10^9 \text{ atoms}$
 $^{240}\text{Pu}/^{239}\text{Pu} = 0.116 \pm 0.011$
 $^{238}\text{U} = 3.85 \times 10^{15} \text{ atoms } (\pm 0.2\%)$
 $^{239}\text{Pu}/^{238}\text{U} = 0.46 \pm 0.02 \text{ ppm}$

$^{239}\text{Pu} = 8.62 \pm 0.05 \times 10^{10} \text{ atoms}$
 $^{240}\text{Pu}/^{239}\text{Pu} = 0.069 \pm 0.002$
 $^{238}\text{U} = 3.09 \times 10^{16} \text{ atoms } (\pm 0.3\%)$
 $^{239}\text{Pu}/^{238}\text{U} = 2.79 \pm 0.02 \text{ ppm}$

Operated by the Los Alamos National Security, LLC for the DOE/NSA

Comparison of $^{240}\text{Pu}/^{239}\text{Pu}$ vs $^{238}\text{U}/^{239}\text{Pu}$ for Samples from Roswell and Gallinas Peak

T. Widner and S. Flack
Health Physics 2010, 98, 480-497.

Operated by the Los Alamos National Security, LLC for the DOE/NSA

Acknowledgment

We gratefully acknowledge the U.S. Department of Energy through the LANL/LDRD Program for financial support this work.

The project was funded as part of the Science of Signatures institutional initiative (Project Number: 20120459-ER).

Operated by the Los Alamos National Security, LLC for the DOE/NSA