LLNL-JRNL-411670

Separation of Uranium and Plutonium Isotopes for Measurement by Multi Collector Inductively Coupled Plasma Mass Spectroscopy

R. E. Martinelli, T. F. Hamilton, R. W. Williams, S. R. Kehl

April 2009

Journal of Radioanalytical Nuclear Chemistry

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Separation of Uranium and Plutonium Isotopes for Measurement by Multi Collector Inductively Coupled Plasma Mass Spectroscopy

R.E. Martinelli[1], T.F. Hamilton[1], R.W. Williams[2], S.R. Kehl[1]

[1]Center for Accelerator Mass Spectrometry; [2]Chemical Sciences Division, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94551-0808

Abstract

Uranium (U) and plutonium (Pu) isotopes in coral soils, contaminated by nuclear weapons testing in the northern Marshall Islands, were isolated by ion-exchange chromatography and analyzed by mass spectrometry. The soil samples were spiked with ^{233}U and ^{242}Pu tracers, dissolved in minerals acids, and U and Pu isotopes isolated and purified on commercially available ion-exchange columns. The ion-exchange technique employed a TEVA® column coupled to a UTEVA® column. U and Pu isotope fractions were then further isolated using separate elution schemes, and the purified fractions containing U and Pu isotopes analyzed sequentially using multi-collector inductively coupled plasma mass spectrometer (MCICP-MS). High precision measurements of ^{234}U/^{235}U, ^{238}U/^{235}U, ^{236}U/^{235}U, and ^{240}Pu/^{239}Pu in soil samples were attained using the described methodology and instrumentation, and provide a basis for conducting more detailed assessments of the behavior and transfer of uranium and plutonium in the environment.

INTRODUCTION

The U.S. nuclear testing program in the Marshall Islands (1946-58) produced significant close-in contamination of islands and the lagoon on Bikini and Enewetak Atolls.[1] The radioactive fallout debris contained significant quantities of unfissioned nuclear fuel [including plutonium-239 (^{239}Pu) and uranium-235 (^{235}U)] in addition to range of fission and activation

products. Historically, studies on the levels and distribution of Pu and U isotopes in the terrestrial and marine environment at test sites in the Marshall Islands have largely been based on gamma- and alpha-spectrometric measurements.[2,3,4,5,6,7] However, there has been a growing interest in developing more detailed assessments on the re-distribution of Pu and U isotopes through the atoll ecosystem with identification of specific source input-terms and biological transfers that may impact on human health.[8,9] This paper describes the methodology employed at the Center for Accelerator Mass Spectrometry (CAMS), Lawrence Livermore National Laboratory (LLNL), for analysis of U and Pu isotopes in carbonaceous soils using mass spectrometry. The radiochemical separation scheme has proven to be a convenient and reliable method for the isolation of U and Pu isotopes using a single digest scheme, especially in relation to analyzing coral soils (1-5 gram) of known heterogeneity. The general radiochemical separation procedure appears to be equally applicable to analysis of U and Pu isotopes in nuclear materials.[9]

EXPERIMENTAL

Preparation of reagents and supplies

The uranium and plutonium tracers employed in sample preparation, instrument calibrations, and quality control/quality assurance samples were all National Institute of Standards and Technology (NIST) traceable. They were purchased from either the New Brunswick Laboratory or the Eckert and Ziegler Isotope Products Laboratories.

Both ultra-pure and reagent grade chemicals were employed. The use of ultra-pure reagents was required for the uranium sample preparation. For plutonium isotopic separations and measurements reagent grade chemicals can be employed.

The 69-70% nitric acid (HNO_3), 37% hydrochloric acid (HCl), 95-98% sulfuric acid (H_2SO_4), and 47-52% hydrofluoric acid (HF) employed were ultra-pure reagents (SEASTAR™

Chemicals Inc. BASELINE®). The 30% hydrogen peroxide (H_2O_2), sodium nitrite ($NaNO_2$), aluminum nitrate ($Al(NO_3)_3$), boric acid (H_3BO_3), and n-octanol employed were reagent grade (Mallinckrodt Baker, Inc.).

Type I ultrapure water (resistivity of 18.2 MΩ.cm at 25 °C, and Total Organic Carbon levels below 10 parts per billion) was used for the preparations of all stock reagent solutions (produced from a Milli-Q® synthesis A10 water purification system).

TEVA® and UTEVA® columns were purchased from Eichrom Industries LLC., and AG®1-X8 columns were purchased from BioRad Laboratories. Prior to use, all labware coming into contact with samples was acid leached, rinsed with ultrapure water, and air dried in a laminar flow hood.

Sample Digestion

Soil samples were weighed into a homopolymer polypropylene digest vessel and dried at 80 °C for 48 hours. The samples were then re-weighed and spiked with the desired tracer (^{233}U and ^{242}Pu). A drop or two of n-octanol was added to each sample, and then an appropriate amount of HNO_3 added (normally between 25 and 50 mL). The digest vessels were then covered with a watch glass, and the samples digested at a temperature between 106 and 110 °C in a 25 Well HotBlock® Digest System (Environmental Express) for one to two days. H_2O_2 was added, as necessary, until the sample digests were rendered into clear and colorless solution. The samples were then taken to dryness. The samples were then treated with HF to ensure dissolution of any resistant materials. Saturated boric acid solution was then added, and the sample digest again evaporated to dryness.

The dried sample residues were rehydrated with 15 mL of 2.5 M HNO_3-1 M $Al(NO_3)_3$ and filtered through a 0.45 micron syringe filter (using a polyethersulfone membrane). Any

background uranium present in the $Al(NO_3)_3$ solution was removed by feeding the 2.5 M HNO_3-1 M $Al(NO_3)_3$ column solution through a large separate UTEVA® colum.

Sample Preparation

The Pu and U isotopes were isolated and purified using stacked or coupled, 50-100 micrometer mesh, TEVA® and UTEVA® columns. The TEVA® column was placed above UTEVA® column (both columns were outfitted with 20 mL funnels).

Prior to column chemistry, the oxidative state of Pu was adjusted to 4+ by adding 1 mL of 4 M $NaNO_2$ per 10 mL of sample, and allowing the sample to sit for several hours in a loosely capped vial. The stacked columns were conditioned with 6 mL of 3 M HNO_3. An additional mL of the 3 M HNO_3 was added to the lower UTEVA® column, while the 6 mL of 3 M HNO_3 was added to the upper column.

The sample was then loaded onto the upper TEVA® column, and allowed to drain through both columns. The upper TEVA® column was then rinsed with two 5 mL aliquots of 3 M HNO_3. At this stage the ion-exchange columns were decoupled, and processed separately.

The TEVA® column received two additional 5 mL aliquot rinses of 3 M HNO_3. The TEVA® column containing Pu isotopes was then washed with 3 mL of a 9 M HCl solution, followed by four 5 mL rinses of an 8 M HCl solution. The Pu was eluted off column using three 10 mL rinses of a 0.01 M HCl-0.05 M HF-0.1 M NH_4I solution into a 50 mL glass beaker. 3 mL of concentrated HNO_3 was added to the sample beaker, a watch glass placed on top of the beaker, and the sample evaporated to dryness.

The dried Pu eluent from the TEVA® column was processed through an additional AG®X1-8 (BioRad Laboratories) column. The residue was rehydrated with 10 mL of 8 M HNO3, and the Pu oxidative state adjusted with 4 M $NaNO_2$. The AG®X1-8 column was

preconditioned with 20 mL of 8 M HNO_3. The sample was loaded on column, and received four 5 mL rinses of an 8 M HNO_3 solution. The column then washed with four 5 mL aliquots of concentrated HCl and the Pu eluted off column using four 5 mL aliquots of a 12 M HCl-0.1 M NH4I solution. 3 mL of concentrated HNO_3 was added to the beaker, a watch glass was placed on top of the beaker, and the sample evaporated to dryness.

The UTEVA® column received two 5 mL rinses of a 3 M HNO_3 solution, and then washed with 5 mL rinses of a 5 M HCl-0.05 M oxalic acid solution. The uranium was eluted off column using four 5 mL aliquots of a 0.02M H_2SO_4 solution and collected in 30 mL Teflon® vials. 3 mL of concentrated HNO_3 was added to the vial, watch glass placed on top of the vial, and the sample evaporated to dryness.

The sample preparation for MCICP-MS analysis was the same for both purified uranium and plutonium fractions. The final sample was 3 mL of a 2% ultra pure nitric acid solution (0.45 micrometer syringe filtered).

Determination of Uranium by MCICP-MS

The Environmental Radiochemistry Group at LLNL utilizes an IsoProbe MCICP-MS (GV Instruments Inc.) for a wide range of isotopic measurements[7]. It is outfitted with a Cetac Aridus desolvating nebulizer. This magnetic sector mass spectrometry system allows for the simultaneous measurement of different ion mass beams. The collector block analyzer array contains 9 faraday and 8 pulse counting detectors. The pulse counters include 6 channeltrons which may be positioned for simultaneous multi-isotope ion collection, one fixed high-mass channeltron, and a Daly detector. Ions along the axial beam are filtered by a wide aperture retarding potential (WARP) filter and measured on the Daly detectors for high abundance sensitivity applications. All of the faraday cups may be positioned for simultaneous multi-

collection of higher ion currents. Simultaneous multi-collection allows isotope ratios to be measured with high precision because the fluctuations in ion beam intensity are seen by each detector at the same time.

Standard reference materials are used to determine instrumental mass bias or detector gain shifts.[7] Pu and U isotopic standards are analyzed using the same data acquisition methods as for the samples. Certified reference materials used for Pu and U isotope measurements include NBS SRM 960 (U-Nat), NBL CRM U010 (1% enriched), CRM 128 ($^{239}Pu/^{242}Pu \cong 0.9989$) and CRM138 ($^{240}Pu/^{239}Pu \cong 0.2409$). At least one of these QC check samples are analyzed for each batch of samples, and no more than eight unknown samples are analyzed between QC check analyses.

U and Pu Measurements

U isotope data acquisitions were made using simultaneous multi-collection techniques. Faraday cups are used to determine the intensities of beams from ^{233}U, ^{235}U, and ^{238}U while the pulse-counting Daly detector was used to measure the lower intensity beams from ^{234}U and ^{236}U.[7]

Pu isotope data acquisitions were also made using simultaneous multi-collection techniques. Three different data acquisition techniques are common. From lowest to highest intensity these are: (1) simultaneous pulse counting of all isotopes using channeltron detectors; (2) simultaneous Faraday/Pulse-counting, where only the major isotopes (^{239}Pu and ^{240}Pu) are collected with the Faraday detector; and (3) simultaneous Faraday multi-collection.[7]

RESULTS AND DISCUSSION

The results of quality control measurements for U isotope ratios in NBL CRM U010 (1% enriched) using MCICP-MS are shown in Table 1. The accuracy and precision of the measurement data is excellent. For the example data shown, the measurement bias for $^{234}U/^{238}U$,

$^{235}U/^{238}U$ and $^{236}U/^{238}U$ relative to the new NBL reference values for 5 replicate measurements averaged −0.04%, +0.01% and +0.06%, respectively. The measurement bias was well within 1 SD of the 5 replicate measurements and implies that MCICP-MS is a very powerful tool for U detection and isotope ratio determination.

Quality assurance data for measurement of $^{239}Pu/^{240}Pu$ atom ratios in CRM-138 ($^{240}Pu/^{239}Pu$ = 0.0861 ± 0.0001) based on MCICP-MS are shown Figure 1. The average combined measurement precision and accuracy of CRM-138 quality control measurements for $^{240}Pu/^{239}Pu$ between November 2004 and June 2006 were 0.8% and <0.1%, respectively.

Some preliminary data on the U and Pu isotopic composition of surface soils from Enewetak Atoll are shown in Table 2. Natural background uranium contains 99.2745 atom % ^{238}U, 0.72% atom % ^{235}U, 0.0055 atom % ^{234}U and < 10^{-10} atom % ^{236}U with a $^{238}U/^{235}U$ isotopic ratio of around 137.88. A review of historical environmental data from the Marshall Islands indicate that there is no statistical difference in the total U content of soil and sediments between southern and northern atolls that can be directly attributable to the nuclear test program on Bikini and Enewetak.[12] However, high precision MCICP-MS analyses of soil samples from the Marshall Islands provide definitive evidence of an anthropogenic source of uranium based on anomalies in the $^{238}U/^{235}U$ and $^{236}U/^{235}U$ isotopic ratios (Table 2).[13] For example, the $^{238}U/^{235}U$ atom ratio in soils based on this small subset of data ranged from 107.13 up to natural abundance levels. Variations in the $^{236}U/^{235}U$ content of these soils above natural background are even more pronounced, and ranged from 0.00004 to 0.00425 compared with a lower limit of detection for $^{236}U/^{235}U$ of around 1×10^{-5}.

The total Pu content of soil samples collected from northern islands on northern Enewetak was significantly elevated over background levels expected from world-wide fallout

deposition, and ranged from 0.01 to 0.87 ng g^{-1} (Table 2). Additionally, the wide ranging $^{240}Pu/^{239}Pu$ atom ratios observed in surface soils (0.1 to 0.31) relative to that contained in global fallout (0.176 ± 0.014)[14] could potentially be used to identify and study the impacts of specific test events on the levels and distribution of plutonium in the atoll environment. Moreover, we were able to identify that our internal quality control soil (8207; Table 2) contained a typical isotopic signature from the Bravo test. A large quantity of this material was offered to the IAEA during the 1990s as an intercomparison sample. The material was subsequently listed as Pacific Sediment (IAEA-367) from Enewetak Atoll but, based on the isotopic data and upon further investigation, we were able to confirm that this particular sample was actually collected from the terrestrial environment on Bikini Atoll.

CONCLUSIONS

The ion-exchange chromatographic methodology described here provides a convenient method for the separation of U and Pu isotopes for measurement by high-precision MCICP-MS. Coupled Eichrom column methodologies have been employed to measure U and Pu isotopes in nuclear and environmental materials from a single aqueous digest. Sequential analysis of U and Pu isotopes on the same sample aliquot has the added advantage of reducing the effects of sample heterogeneity on isotopic ratio determination. In general, the MCICP-MS instrumentation used at LLNL offers excellent precision and accuracy for measurement of U and Pu isotopes in nuclear and environmental samples. The column methodology and MCICP-MS analysis were successfully applied to a small subset of soil samples collected from the Marshall Islands. These preliminary analyses show that isotopic data based on MCICP-MS (or AMS) may useful in developing more detailed assessments of source-terms and/or identifying material-specific transfers through the atoll environment.

ACKNOWLEDGEMENTS

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

REFERENCES

1. T.F. HAMILTON, Linking legacies of the cold war to arrival of anthropogenic radionuclides in the oceans through the 20th century, H.D. Livingston (editor), Marine Radioactivity, Vol. 6, Elsevier Science, Amsterdam, 2004, 30–87.
2. W.R. SCHELL, F.G. LOWMAN, R.P. MARSHALL, Geochemistry of Transuranic Elements at Bikini Atoll, In: Transuranic Elements in the Environment, W.C. Hanson (Ed.), DOE/TIC-22800, 1980, pp. 541–577.
3. V.E. NOSHKIN, Transuranium radionuclides in components of the benthic environment of Enewetak Atoll, In: Transuranic Elements in the Environment, W.C. Hanson (Ed.), DOE/TIC-22800, 1980, pp. 578–601.
4. K.M. WONG, T. JOKELA, V.E. NOSHKIN, Report UCRL-ID-116497, Lawrence Livermore National Laboratory, 1994, 27 pp.
5. W.L. ROBISON, V.E. NOSHKIN, Sci. Total Environ., 237/238 (1997), 311.
6. V.E. NOSHKIN, W.L. ROBISON, K.M. WONG, T.A. JOKELA, H.E. JONES, Health Phys., 73 (1997), 234.
7. V.E. NOSHKIN, W.L. ROBISON, K.M. WONG, R.J. EAGLE, J. Radioanal. Nucl. Chem., 234 (1998), 84.
8. T.F. HAMILTON, R.E. MARTINELLI, S.R. KEHL, J.E. MCANINCH, J. Environ. Monit., 10 (2008) 1134.

9. T. HAMILTON, J. JERNSTRÖEM, S. KEHL, R. MARTINELLI, M. ERIKSSON, M. BIELEWSKI, A. RIVERS, R. WILLIAMS, M. BETTI, J. Radioanal. Nucl. Chem. (this issue).
10. R.E. MARTINELLI, T.F. HAMILTON, T.A. BROWN, A.A. MARCHETTI, R.W. WILLIAMS, S.J. TUMEY, Report UCRL-TR-232228, Lawrence Livermore National Laboratory, 2006, 11 pp.
11. R.W. WILLIAMS, Report UCRL-TR-210128, Lawrence Livermore National Laboratory, 2005, 11 pp
12. W.L. ROBISON, V.E. NOSHKIN, T.F. HAMILTON, C.L. CONRADO, K.T. BOGEN, Report UCRL-LR-143980, Lawrence Livermore National Laboratory, 2001, 21 pp.
13. T.H. HAMILTON, W.L. ROBISON, Report UCRL-MI-204441, Lawrence Livermore National Laboratory, 2004, 4 pp.
14. P.W. KREY, E.P. HARDY, C. PACHUCKI, F. ROURKE, J. COLUZZA, W.K. BENSON, Mass isotopic composition of global fallout plutonium in soil, In: Proceedings of Transuranium Nuclides in the Environment, International Atomic Energy Agency (IAEA), Vienna, 1976, 671-678.

Table 1.

Quality Control Sample	Multi Collector Inductively Coupled Plasma Mass Spectrometry					
	$^{234}U/^{238}U$		$^{235}U/^{238}U$		$^{236}U/^{238}U$	
U010-1	0.00005441	± 0.00000005	0.010129	± 0.000007	0.00006935	± 0.00000008
U010-2	0.00005446	± 0.00000006	0.010136	± 0.000007	0.00006928	± 0.00000006
U010-3	0.00005452	± 0.00000005	0.010142	± 0.000002	0.00006922	± 0.00000006
U010-4	0.00005444	± 0.00000006	0.010144	± 0.000006	0.00006940	± 0.00000007
U010-5	0.00005437	± 0.00000005	0.010145	± 0.0000045	0.00006943	± 0.00000006
Mean & standard deviation (N=5)	0.00005444	± 0.00000006	0.010142	± 0.000007	0.00006933	± 0.00000009
Certified value (U010)	0.00005466	± 0.00000056	0.010140	± 0.000010	0.0000688	± 0.00000078
(New NBL value)	0.00005442	± 0.00000007	0.010140	± 0.000010	0.00006929	± 0.00000012
Measurement Bias (NBL value)	-0.04%		0.01%		0.06%	

Individual measurement uncertainty = ± 2σ level.

Table 2

Sample ID	$^{238}U/^{235}U$ atom ratio		$^{236}U/^{235}U$ atom ratio		$^{234}U/^{235}U$ atom ratio		Total U $\mu g\ g^{-1}$		$^{240}Pu/^{239}Pu$ atom ratio		Total Pu $ng\ g^{-1}$	
RFB-722	136.20	± 0.11	0.00057	± 0.00001	0.00860	± 0.00004	1.94	± 0.03	0.274	± 0.001	0.194	±0.008
RFB-727	137.46	± 0.07	0.000040	± 0.000005	0.00860	± 0.00003	1.70	± 0.02	0.129	± 0.002	0.0122	± 0.0005
RFB-740	136.38	± 0.32	0.00079	± 0.00001	0.00882	± 0.00004	1.67	± 0.02	0.2645	± 0.0003	0.187	± 0.008
RFB-745	119.95	± 0.28	0.00297	± 0.00002	0.00937	± 0.00004	1.74	± 0.02	0.3028	± 0.0004	0.40	± 0.02
RFB-761	137.09	± 0.08	0.00057	± 0.00001	0.00869	± 0.00005	1.81	± 0.02	0.1752	± 0.0003	0.40	± 0.016
RFB-762	137.69	± 0.08	0.00024	± 0.00001	0.00862	± 0.00005	1.68	± 0.02	0.0999	± 0.0001	0.87	± 0.03
RFB-769	127.42	± 0.11	0.00142	± 0.00001	0.00906	± 0.00004	1.93	± 0.03	0.236	± 0.002	0.165	± 0.007
RFB-774	137.26	± 0.09	0.00062	± 0.00001	0.00886	± 0.00004	1.80	± 0.02	0.329	± 0.004	0.110	± 0.005
RFB-779	107.13	± 0.09	0.00425	± 0.00003	0.00976	± 0.00005	1.72	± 0.02	0.2406	± 0.0001	0.60	± 0.02
RFB-780	136.83	± 0.12	0.00048	± 0.00001	0.00875	± 0.00004	2.21	±0.03	0.135	± 0.003	0.161	± 0.007
Internal Reference Sample (IAEA-367 Pacific Sediment)												
8207	137.88	± 0.12	0.000042	± 0.000006	0.00863	± 0.00004	1.77	± 0.02	0.290	± 0.006	0.0145	± 0.0007
8207	137.67	± 0.09	0.000072	± 0.000005	0.00857	± 0.00004	1.80	± 0.02	0.302	± 0.002	0.0120	± 0.0005
8207	137.83	± 0.09	0.000042	± 0.000004	0.00863	± 0.00004	1.83	± 0.02	0.306	± 0.006	0.0125	± 0.0006

Measurement uncertainties = ± 2σ

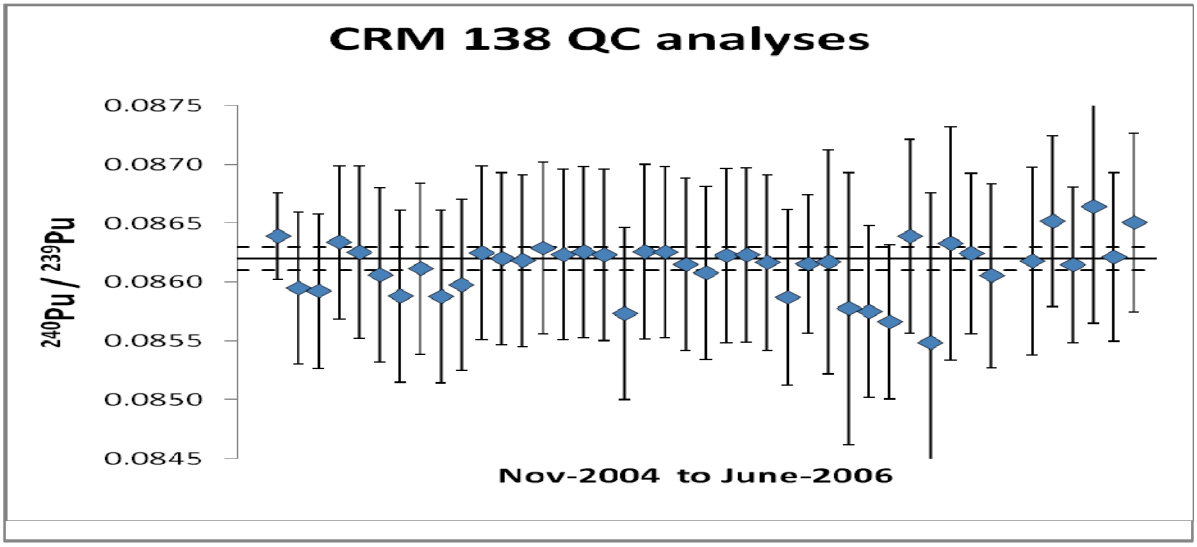
List of Tables and Figures

Table 1. Quality control measurements of U isotope ratios in NBL CRM U010 (1% enriched).

Table 2. Measurements of U and Pu, and U and Pu isotope ratios in selected surface soils samples collected from northern islands on Enewetak Atoll.

Figure 1. Quality control measurements for Pu isotope ratios in CRM-138 ($^{240}Pu/^{239}Pu = 0.0861 \pm 0.0001$) (November 2004–June 2006).

Figure 1


CRM 138 QC analyses
0.0875
0.0870
0.0865
0.0860
0.0855
0.0850
0.0845
240Pu / 239Pu
Nov-2004 to June-2006