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Measurement of U and Pu isotope ratios in hair and nail samples using extraction chromatography and multi-collector inductively coupled plasma mass spectrometry

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ABSTRACT

A bioassay capable of monitoring occupational or environmental exposure to special nuclear materials would be a useful tool for nuclear nonproliferation programs. Hair and nail are potential biomonitors of exposure to U and Pu. A method is described to measure isotope ratios of ultra-trace concentrations of U and Pu in hair and nail samples. The method uses multiple extraction chromatography resins to separate U and Pu fractions from the sample matrix. The U recovery was quantitative while the Pu recovery ranged from 81% to 109%, with a U decontamination factor of 5×10^4. Following the separation $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{240}Pu/^{239}Pu$ were measured in human hair and hair and nail samples using multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). The human hair and nail samples had elevated ratios of $^{234}U/^{238}U$ which could reflect exposure to naturally fractionated U.

1. Introduction

The international Atomic Energy Agency (IAEA) maintains an Incident and Trafficking database which reported 16 incidents involving unauthorized possession of Pu or high enriched U since 1995. It is clear that demand exists for illicit nuclear materials. Pursuant to nuclear non-proliferation goals, monitoring programs have been developed to test terrestrial, marine and air samples for the presence of isotopes that are indicative of weapons production, testing and fuel reprocessing [5]. A convenient bioassay that is responsive to contact with U or Pu over the course of weeks or months could have utility for monitoring occupational exposure, monitoring health impacts from nuclear accidents such as Fukushima in large public health studies, and in qualitatively monitoring exposure to special nuclear materials used in clandestine nuclear activities. Samples may be collected weeks to months after an accident or exposure and tracked over time to monitor past and present exposure to U and Pu. The objective of this work was to develop a method to measure the isotopic ratios of ultra-trace levels of U and Pu in the toenail/fingernail/hair matrix. The analytical method will be used to investigate the toenail/fingernail/hair matrix as an indicator of exposure to special nuclear materials in future work.

The International Commision on Radiological Protection (ICRP) has published biokinetic and dosimeteric models that allow calculation of internal dose based on U measured in urine and fecal samples ([1]). In 2005 Wei Bo Li et al. [2] built on the ICRP model and published a U biokinetic model that calculates urinary and fecal excretion rates following acute and chronic injection and ingestion for six age groups [22]. The compartment model calculates that the maximum urinary excretion rate of U occurs 4 h after acute ingestion and falls to 1.5% of the maximum excretion rate within 48 h. The excretion rate of U in feces peaks within 24 h and falls to 1% of the maximum rate within 72 h. The whole body burden of U following acute exposure peaks at 7 h and falls to 70% of the peak body burden within 48 h and 68% of the peak body burden within 72 h. In USA, the average person is exposed to 0.9 $\mu g\ d^{-1}$ of U in the United States [6]. An average person that is acutely exposed to U may have an increased body burden of U but only a relatively small increase in urinary or fecal U levels a few days after the event. According to Li, if urine or feces are to be

Abbreviations: MC-ICPMS, multi collector inductively coupled plasma mass spectrometry; TEVA, trialkyl, methylammonium nitrate; UTEVA, dipentyl, pentalphosphonate; DGA, N,N,N′,N′-tetra-n-octyldiglycoamide

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used to calculate dose following an accident the samples must be collected within days of exposure or the internal dosimetery calculations may be misleading [11]. The analysis is further complicated if U isotope ratios are of interest since U in urine reflects both rapid turn over from the GI tract as well as intermediate and slow turnover from liver, kidney, and bone. An acute exposure to enriched U will result in a characteristic $^{235}U/^{238}U$ ratio measured in urine within a few days. However, several days after exposure the enriched U measured in urine will be diluted with natural U from diet and intermediate and slow turnover pools of whole body U.

A long term, integrative monitor of U exposure would have practical use in public health studies, monitoring occupational exposure, and monitoring clandestine nuclear activities. In 2009 Wei Bo Li published a U biokinetic model containing compartments for U excreted in hair and nail [11]. This compartment model could be used to calculate internal dose based on hair/nail levels of U following chronic and acute U ingestion. In the model, U is excreted into the hair/nail compartment from blood plasma and an intermediate turnover pool. In the case of chronic exposure, the U in a hair/nail sample reflects U exposure integrated over the growth time of the hair ornail sample. Hair grows at a rate of approximately 1.1 cm per month while nails grow distally from the nail base at 2 mm per month for finger nails and 0.5 mm per month for toenails. A 2 cm length of hair represents approximately two months of exposure. A 0.5 mm sample of fingernail or toenail represents approximately 1.5 months of integrated internal exposure 6–12 months prior to collection ([3,12,13]). In the case of an acute or intermitent exposure, the hair or nail may be subsampled to build a calendar of exposure. Hair and nail samples may contain a fraction of U and Pu from external contamination in addition to the levels that are internally deposited. Because toenails are relatively protected and hair has a much higher surface area than fingernails the expected order of externally deposited U is hair > fingernail > toenail (most to least). For the purposes of monitoring clandestine nuclear activities external contamination and internal exposure could provide useful information. In public health studies or to monitor occupational exposure, internal exposure may be desirable in which case toenails may be the most appropriate monitor since they are expected to have less external contamination.

Hair and nail have previously been used in several studies to monitor U in small population studies. Valkovic reported that the mean level of U in hair in 222 individuals from Iraq was 220 ng g^{-1} and in Tokyo the U concentration in hair was 56 ng g^{-1} and 85 ng g^{-1} for men and women, respectively [21]. The U concentration measured in the hair of volunteers from Sandia National laboratory was 290 ng g^{-1} [16]. In Israel the mean U concentration in the hair of in 99 volunteers was 62 ng g^{-1} [7]. The U in hair, nail, and urine samples was measured in a Finnish population exposed to 0.03–2775 μg d^{-1} of U from well water [10]. In this population the concentration of U in hair ranged from 6.5 to 250,000 ng g^{-1} and 1 to 34,200 ng g^{-1} in nails. The concentration of U in urine, toenails, and hair were highly correlated, and the concentration of uranium in hair and nails was 10–100 times greater than in urine. The high correlation between hair, nail, and urine demonstrates that hair and nail can monitor the internal body burden of U.

To our knowledge, there is not a biokinetic model available with a comparment for excretion of Pu into hair and nail. However, Toohey et al. reported the concentration of plutonium in hair following an injection of 4.8 μg (11 kBq) of ^{239}Pu into a human [19]. The hair plutonium concentration was followed as a function of time by segmenting the hair into 2 cm sections. The peak concentration was 9.5 ng kg^{-1} (22 Bq kg^{-1}) at 18 days post injection. At 500 days post injection the Pu concentration was 1.25 ng kg^{-1} (2.9 Bq kg^{-1}). Although levels of Pu in hair and nail cannot at this time be used to calculate internal dose the work by Toohey et al. demonstrates that Pu is excreted into hair samples. Pu measured in hair and nail should be considered a qualitative monitor of Pu exposure, and may have application in public health studies following a nuclear accident or in monitoring clandestine nuclear activities.

The objective of this work is to develop an analytical method capable of measuring U and Pu in hair and nail samples at low concentrations. The isotope ratios $^{235}U/^{238}U$, $^{234}U/^{238}U$, and $^{239}Pu/^{240}Pu$ will allow investigators the ability to distinguish between natural and enriched U and different sources of Pu. In this paper we present a method to separate U and Pu with near quantitative recovery and with emphasis on achieving a high decontamination factor (DF) between U and Pu. The isotope ratios are measured using multi collector inductively coupled plasma mass spectrometry (MC-ICPMS). Separation of U and Pu prior to MC-ICPMS analysis reduces potential isobaric interferences, including $^{238}U^{1}H$ which interferes with detection of ^{239}Pu and $^{232}Th^{2}H$ which interferes with detection of ^{234}U. A detailed list of isobaric interferences has been compiled by Truscott et al. [20]. In this work isotope ratios were measured using a Nu-Plasma II (MC-ICPMS) equipped with a DSN-100 desolvating nebulizer (DSN).

2. Experimental

2.1. Reagents

Pre-packed chromatography resins (2 mL, 50–100 μm bead size) were purchased from Eichrom (Lisle, IL). The resins used were TEVA (trialkyl, methylammonium nitrate), UTEVA (Dipentyl, pentalphosphonate), and DGA (N,N,N′,N′-tetra-n-octyldiglycoamide). The resins were used in conjunction with a vacuum extraction system (Eichrom). Trace metal grade nitric acid, hydrochloric acid, hydrogen peroxide, and hydrofluoric acid were purchased from Fisher Scientific. High purity water was obtained using a Millipore Milli-Q water treatment system. All chemicals were ACS grade and were used as received unless stated otherwise. All chemical reagents were prepared daily. A certified standard solution containing ^{239}Pu and ^{240}Pu was purchased from Eckert and Zeigler. A Certified standard solution of ^{242}Pu was purchase from NIST (SRM 4334I). Certified U_3O_8 materials (U010 and U630) were purchased from DOE New Brunswick Laboratory. The U_3O_8 was dissolved in nitric acid and diluted to make a 10 ng g^{-1} standard solution. Hair reference material samples were prepared from the Chinese CRM DC73347. Nail samples were collected from the central Missouri area under University of Missouri Health Science IRB 1202836. The hair and nail samples were not cleaned prior to analysis.

2.2. Digestion

Each sample was weighed into a digestion vessel with 3.1 mL of nitric acid and 1 mL of 30% high purity hydrogen peroxide. Two digestion blanks were included to check the analytical blank. The vessels were heated to 140 °C at 400 W for 10 min, and then ramped to 190 °C at 600 W for 25 min using a Milestone Ethos Plus microwave digestion system. After removing the vessels from the microwave, samples were cooled and transferred to acid leached 50 mL polypropylene vials and diluted to 8 mL with high purity water. Following digestion the solutions were clear indicating complete oxidation of organic material. To each digested sample, 8 mL of 2 M $Al(NO_3)_3$ and a 50 pg spike of ^{242}Pu was added to measure Pu recovery from the separation were then added to each sample. One sample from each set was split prior to

Table 1
Analysis of U quality control materials. The natural uranium standard is not isotope certified. The values are reported with expanded uncertainty ($k=2$).

Quality control	*N*	$^{235}U/^{238}U$	Uncertainty	$^{234}U/^{238}U$	Uncertainty
In-House Natural U Standard	1	0.00727	0.00019	0.0000533	0.0000050
Natural uranium		0.007257		0.0000544	
U630 standard	3	1.81	0.10	0.0175	0.0014
Certified U630		1.8067	0.0016	0.017651	0.000019

separation and spiked with 2.5 ng of U from a solution prepared from U010 to measure the recovery of U from the separation.

2.3. U and Pu separation

The separation was based on a procedure published by Maxwell et al. to rapidly determine ^{237}Np and Pu in urine samples [14,15]. We have modified the procedure to enable separation of U and Pu using the extraction resins TEVA, UTEVA and DGA. The oxidation state of Pu is adjusted before the samples are loaded onto the columns. To each sample vial, 0.5 mL of 1.5 M sulfamic acid and 1.25 mL of 1.5 M ascorbic acid are added to reduce all Pu to Pu(III). After 3 min, 1 mL of 3.5 M sodium nitrite is added, which oxidizes Pu(III) to Pu(IV). After 10 min, the sample is loaded onto the column for separation.

The first stage of the separation used a stacked TEVA and UTEVA column sitting on a vacuum box. The columns were rinsed with 10 mL of 3 M HNO_3 immediately prior to use and the sample solutions were added drop-wise at approximately 1 mL per minute. Each sample container was rinsed with 3 mL of 3 M HNO_3 and the rinse was loaded onto the columns. Pu(IV) and Th (IV) are retained on the TEVA column and U(VI) is retained on the UTEVA column under these conditions. The columns were rinsed with 30 mL of 3 M HNO_3 to minimize U retention on the TEVA column and remove the matrix and $Al(NO_3)_3$. The two columns were then separated.

Following Maxwell's procedure, the TEVA column containing the Pu fraction is transferred to a DGA column using 15 mL of 3 M HNO_3–0.1 M ascorbic acid–0.02 M ferrous nitrate to reduce Pu (IV) on the TEVA column to Pu(III). The Pu(III) is retained on the DGA column in 3 M HNO_3. The TEVA column is removed and the Pu on the DGA column is oxidized to Pu(IV) with 5 mL of 8 M HNO_3. Remaining trace U(VI) is removed by rinsing the DGA column with 30 mL of 0.1 M HNO_3. The Pu is eluted by on column reduction to Pu(III) with 11 mL of 0.02 M HCl–0.005 M HF–0.0001 M $TiCl_3$. The final solution is weighed and concentration measurements are reported by mass.

The loaded UTEVA column is rinsed with 30 mL of 3 M HNO_3 to remove remaining matrix. The U is eluted from the UTEVA column using 5 mL 0.02 M HNO_3–0.005 M HF acid. The collected solution is ready for U analysis by MC-ICPMS. The final solution is weighed and concentration measurements are reported by mass.

2.4. Isotope ratio analysis

The isotopic analysis was performed with a Nu-Plasma II MC-ICPMS equipped with a Nu-Plasma DSN-100 sample introduction system. The faraday gain calibration and signal optimization were performed daily. The ion counter gain correction and mass bias correction were made using a 20 ng g^{-1} U standard solution prepared from CRM U010. Each sample was bracketed with an acid matched instrument blank. Mass bias calibration and ion counter gain standards were analyzed at the beginning, midpoint, and end of each run. The 20 ng g^{-1} U standard solution produced an average ^{238}U signal of 9.5 V on a faraday cup. To minimize dead time, the ion count rate on the ion counters was limited to 2×10^6 cps. The mass bias correction was made using the exponential model ([24]). The $^{235}U/^{238}U$ mass bias measured over the course of the run was 1.019, 1.025 and 1.021. We applied an average mass bias factor to the samples. Using the method given by Hiess et al., the ^{238}U tail intensity was measured with a 10 ng g^{-1} U010 standard [8]. The intensity of the ^{238}U peak tail onto ^{234}U, ^{235}U, and ^{236}U were 0.01%, 0.0001%, and 0.02% respectively. This interference is less than instrument error and was omitted in the data reduction. A 0.05 μg/kg natural U solution prepared from a commercial standard, a 0.05 μg kg^{-1} solution prepared from NBL U630 and a 0.05 μg kg^{-1} sample prepared from the Eckert and Zeigler Pu standard were prepared and analyzed for quality control. The results from the U analysis are presented in Table 1. The average $^{240}Pu/^{239}Pu$ ratio with expanded uncertainty ($k=2$) measured in three samples of the Eckert and Zeigler standard was 2.032 $(21)\times10^{-2}$ and the certificate atom percent ratio is 2.1×10^{-2}.

The U isotope ratios in hair and nail samples were measured by placing ^{238}U and ^{235}U ion beams on faraday cups and the ^{234}U ion beam on an ion counter. Because the ^{235}U signal in all of the samples was less than 5 mV, the solutions were re-analyzed with the ^{238}U ion beam on a faraday cup and the ^{235}U ion beam on an ion counter. The Pu isotope ratios were measured on a different analysis day to minimize the instrumental U background. During the Pu analysis ^{239}Pu, ^{240}Pu and ^{242}Pu were measured on ion counters. We observed in our analysis that long wash out times of 15 or more minutes were required to adequately reduce Pu backgrounds in the instrument following the Pu standards. The U and Pu concentration in the sample were measured using an external calibration curve constructed from the U010 standard. An external precision of 0.5% and 1.2% was measured from repeated analysis of the U010 standard over the course of a day for $^{235}U/^{238}U$ and $^{234}U/^{238}U$ ratio, respectively.

3. Results and discussion

Table 2 shows the measured concentration and isotope ratio of U and Pu in hair and nail samples. The expanded uncertainty of the natural U standard was calculated using the method outlined by Williams and is reported in Table 1 [23]. The measured U recovery in the samples spiked with U010 was 104% and 105% respectively. The U decontamination factor was measured by adding 10 μg of natural U standard to a digested sample. After separation and analysis, 0.19 ng of U was measured in the Pu fraction which corresponds to a decontamination factor of 50,000. The ^{242}Pu recovery from the TEVA and DGA separation ranged from 82% to 109%. Plutonium was not detected in the hair and nail samples. The sample limit of detection for ^{239}Pu in this study was 0.1 ng kg^{-1} and the sample limit of detection for ^{240}Pu was 0.02 ng kg^{-1}. The sample limit of detection includes a dilution factor of 100.

In 1981 Bolotov et al. reported ^{239}Pu and ^{241}Am concentrations in human hair samples collected from environmentally exposed people living in the Semipalatinsk test region in Kazakhstan [4]. The hair concentration of ^{239}Pu ranged from 0.8 to 1.3 ng kg^{-1} in

Table 2
Measured U and Pu data in hair and nail samples. The isotope ratios are reported with combined standard uncertainty.

Sample	Mass, (g)	U, ($\mu g\ kg^{-1}$)	$^{235}U/^{238}U$	$^{234}U/^{238}U$	^{242}Pu recovery (%)	Pu, ($ng\ kg^{-1}$)
Subject 1 nail	0.0435	11	0.00737 (0.00019)	0.0002248 (0.0000056)	87	< LOD
Subject 1 nail	0.0365	9.4	0.00720 (0.00013)	0.0003041 (0.0000068)	91	< LOD
Subject 2 nail	0.0379	7.4	0.00718 (0.00010)	0.0002524 (0.0000058)	109	< LOD
DC73347 hair 1	0.0435	54	0.007293 (0.000075)	0.0001178 (0.0000028)	86	< LOD
DC73347 hair 2	0.0365	60	0.007313 (0.000072)	0.0001181 (0.0000022)	88	< LOD
DC73347 hair 3	0.0379	58	0.007264 (0.000071)	0.0001181 (0.0000024)	82	< LOD

6 samples collected near the Kazakhstan test sight and $0.3 \pm 0.08\ ng\ kg^{-1}$ from control samples collected in Dubna Russia. In 2005 Ryabikin et al. reported the ^{239}Pu concentration in hair samples of residents of east Kazakhstan to be $0.8 \pm 0.2\ ng\ kg^{-1}$ [18]. The detection limits achieved by this method are at the limit of being able to measure Pu in these environmentally exposed populations in the former Soviet Union. If necessary, the Pu detection limits could be reduced by evaporating the eluted sample from the DGA column from 11 mL to 3 mL.

It was expected that the U measured in the nail samples of the reported control samples would reflect exposure to natural sources of U. The nail samples were collected from two individuals. The first individual gave two samples about two months apart. The U concentration in the Chinese CRM DC73347 was not certified and it was expected that the hair would also reflect natural sources of U. The dilution factor in the hair samples ranged from 115 to 160. The U concentrations in hair and nail are reported in Table 2. The measured $^{235}U/^{238}U$ ratios in the hair and nail samples are within error of the natural ratio of 7.257×10^{-3}. The measured $^{234}U/^{238}U$ ratios in hair and nail deviate significantly from the natural ratio of 5.46×10^{-5}.

Potential isobaric interferences that would increase the signal at m/z 234 and cause an artificially high $^{234}U/^{238}U$ ratio were investigated. Potential mass interferences for ^{234}U include polyatomic combinations of the isotopes of Hg, Pt, Au, and Tl with isotopes of Cl, Ar, P, and S. In order to interfere with ^{234}U these elements would have to be present in the sample at relatively high levels following the chemical separation. To determine the presence of these elements, the U fraction of a hair sample was analyzed for Hg, Pt, Au, and Tl using a Perkin Elmer NexION quadrupole operated in standard mode. The measured concentration of Hg and Au in the diluted sample was 0.03 and 0.05 $ng\ g^{-1}$, respectively. The concentration of Tl and Pt were below the instrumental detection limit of 0.01 $ng\ g^{-1}$. A hair sample was then spiked with a solution containing 0.5 ng each of Hg, Pt, Au, and Tl. This is 2 times more Au, 3 times more Hg and 50 times more Tl or Pt than what was present in the original sample. The measured $^{234}U/^{238}U$ ratio in the original sample was $1.161\ (29) \times 10^{-4}$ and the ratio in the spiked sample was $1.175\ (20) \times 10^{-4}$ demonstrating that polyatomic interferences from Hg. Pt, Au and Tl at m/z 234 are not responsible for the elevated $^{234}U/^{238}U$ ratios measured in the hair and nail samples in this sample.

The disequilibrium of ^{234}U in minerals has been used to study geochemical and hydrological phenomena. The disequilibrium occurs when ^{238}U decays to ^{234}U in the $4n+2$ decay series by emission of an alpha particle and two beta particles. The resulting ^{234}U atom (or parent ^{234}Th) is dislodged from its lattice position in the mineral by alpha emission recoil. Uranium in ground waters that pass over U bearing minerals are enriched in ^{234}U and the minerals are depleted in ^{234}U. [17] In 1982 Banner et al. reported $^{234}U/^{238}U$ ratios in ground waters in central Missouri ranged from 1.1×10^{-5} to 8.8×10^{-4} [1]. In this study we measured the $^{234}U/^{238}U$ ratio in nail samples from individuals in mid Missouri to range from 2.2×10^{-4} to 3.0×10^{-4} while the $^{234}U/^{238}U$ ratio the Chinese hair CRM was 1.18×10^{-4}. These results suggest that hair and nail could reflect regional sources of U. This work supports a study published by Karpas in 2005 that reported on $^{234}U/^{238}U$ concentrations in hair, nails and urine [9]. Karpas demonstrated a significant correlation between the $^{234}U/^{238}U$ measured in drinking water and the $^{234}U/^{238}U$ measured in biological monitors of exposure urine, hair, and nail. It is intriguing that the $^{234}U/^{238}U$ ratio in biologic monitors such as hair and nail could be sensitive to regional U sources. Since the hair and nail samples are an integrated monitor of past exposure, a subdivided sample with a changing $^{234}U/^{238}U$ ratio might indicate that a major source of U exposure has changed. Differences in the $^{234}U/^{238}U$ ratio in hair or nail between the individual and the local population could indicate that the individual has recently moved to the area or has been in contact with a different source of U in the past.

4. Conclusion

This work demonstrates a method to analyze hair and nail samples for U and Pu using extraction chromatography and MC-ICPMS. The separation method had a high decontamination factor to remove U from the Pu fraction, limiting the isobaric interference of $^{238}U^{1}H$ on ^{239}Pu measurement. The recovery of U was quantitative and the recovery for Pu was greater than 80%. The MC-ICPMS method had a demonstrated sample limit of detection that was capable of measuring the Pu concentration observed in individuals who were exposed to fallout from nuclear weapons testing. The $^{234}U/^{238}U$ and $^{235}U/^{238}U$ isotope ratios were measured in nail samples collected from mid Missouri and a Chinese hair CRM. The $^{234}U/^{238}U$ ratio is elevated relative to the accepted ratio and the ^{234}U signal was demonstrated to be free of polyatomic interferences.

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