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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



J.N.W. Brown IV^a, J.D. Robertson^{a,b}, J.D. Brockman^{b,*}

^a Department of Chemistry, University of Missouri, Columbia, MO 65211, United States

^b Research Reactor, University of Missouri, Columbia, MO 65211, United States

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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 $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$ and $^{240}\text{Pu}/^{239}\text{Pu}$ 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 $^{234}\text{U}/^{238}\text{U}$ which could reflect exposure to naturally fractionated U.

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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 Commission on Radiological Protection (ICRP) has published biokinetic and dosimetric 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 $0.9 \mu\text{g d}^{-1}$ 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

* Correspondence to: 1513 Research Park Drive, Columbia, MO 65203, USA. Tel.: +1 573 884 809.

E-mail address: brockmanjd@missouri.edu (J.D. Brockman).

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used to calculate dose following an accident the samples must be collected within days of exposure or the internal dosimetry 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 $^{235}\text{U}/^{238}\text{U}$ 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 or nail 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 intermittent 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 99 volunteers was 62 ng g^{-1} [7]. The U in hair, nail, and urine samples was measured in a Finnish population exposed to $0.03\text{--}2775 \mu\text{g d}^{-1}$ of U from well water [10]. In this population the concentration of U in hair ranged from 6.5 to $250,000 \text{ ng g}^{-1}$ and 1 to $34,200 \text{ ng g}^{-1}$ 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 compartment for excretion of Pu into hair and nail. However, Toohey et al. reported the concentration of plutonium in hair following an injection of $4.8 \mu\text{g}$ (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 $^{235}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, and $^{239}\text{Pu}/^{240}\text{Pu}$ 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 $^{238}\text{U}^1\text{H}$ which interferes with detection of ^{239}Pu and $^{232}\text{Th}^2\text{H}$ 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 purchased 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 $140 \text{ }^\circ\text{C}$ at 400 W for 10 min, and then ramped to $190 \text{ }^\circ\text{C}$ 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 $\text{Al}(\text{NO}_3)_3$ 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

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