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Comparison of sample preparation methods for reliable plutonium and neptunium urinalysis using automatic extraction chromatography

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ABSTRACT

This paper describes improvement and comparison of analytical methods for simultaneous determination of trace-level plutonium and neptunium in urine samples by inductively coupled plasma mass spectrometry (ICP-MS). Four sample pre-concentration techniques, including calcium phosphate, iron hydroxide and manganese dioxide co-precipitation and evaporation were compared and the applicability of different techniques was discussed in order to evaluate and establish the optimal method for in vivo radioassay program. The analytical results indicate that the various sample pre-concentration approaches afford dissimilar method performances and care should be taken for specific experimental parameters for improving chemical yields. The best analytical performances in terms of turnaround time (6 h) and chemical yields for plutonium (88.7 ± 11.6%) and neptunium (94.2 ± 2.0%) were achieved by manganese dioxide co-precipitation. The need of drying ashing (≥7 h) for calcium phosphate co-precipitation and long-term aging (5 d) for iron hydroxide co-precipitation, respectively, rendered time-consuming analytical protocols. Despite the fact that evaporation is also somewhat time-consuming (1.5 d), it endows urinalysis methods with better reliability and repeatability compared with co-precipitation techniques. In view of the applicability of different pre-concentration techniques proposed previously in the literature, the main challenge behind relevant method development is pointed to be the release of plutonium and neptunium associated with organic compounds in real urine assays. In this work, different protocols for decomposing organic matter in urine were investigated, of which potassium persulfate ($K_2S_2O_8$) treatment provided the highest chemical yield of neptunium in the iron hydroxide co-precipitation step, yet, the occurrence of sulfur compounds in the processed sample deteriorated the analytical performance of the ensuing extraction chromatographic separation with chemical yields of ≤50%.

1. Introduction

Due to the alpha emission with considerably long half-lives and readily enrichment in bones and livers, neptunium (namely, ^{237}Np ($t_{1/2}$=2.144 × 10^6 yr)) and plutonium isotopes (namely, ^{239}Pu ($t_{1/2}$=2.411 × 10^4 yr) and ^{240}Pu ($t_{1/2}$=6.561 × 10^3 yr)) are regarded as highly radiological and biological toxic radionuclides to human health [1]. Therefore, Np and Pu exposure assessment is imperative for radiation protection and medical intervention to workers or individuals who are exposed to Np and Pu in nuclear facilities or after a radiological/nuclear incident, respectively. Urinalysis for ^{237}Np and Pu isotopes is widely used to estimate the internal radiation dose of individuals. For this purpose, it is essential to develop reliable and effective methods for Np and Pu urine bioassays.

The International Commission on Radiological Protection (ICRP) has recommended an annual limit of dose equivalent to 1 mSv for the general public [2]. Due to the long retention time of Np and Pu in the human body and thus the very low excretion rates in urine, it is required to measure ultra-trace levels of Np and Pu to be able to meet the ICRP screen criteria of annual internal dose limit. To this point, large urine volumes (e.g., ≥1 L) are normally required to cope with the sensitivity demands even in the modern mass spectrometric detection techniques, e.g., accelerator mass spectrometry (AMS). Over the past few decades, a number of urine bioassay methods have been developed for actinides determination

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[3–24]; however, efforts devoted to determination of Np and Pu (especially Np) in large volume ($\geq$1 L) of urine samples are still limited to a few works [4,19,24–26].

In the case of ^{237}Np determination, the choice for tracer is very restricted. No suitable alpha-emitting Np tracer is available. Thus, the beta emitter ^{239}Np is commonly used instead, since it can be obtained from neutron irradiation of ^{238}U or by milking a sample of ^{243}Am with which it is in equilibrium as the alpha-decay daughter (^{243}Am$\rightarrow$^{239}Np+^{4}He). However, because of the short half-life of ^{239}Np (2.36 d), it needs a regular weekly preparation and standardization which is time consuming and expensive. Furthermore, ^{239}Np decays to ^{239}Pu, which increases the sample background for ^{239}Pu in cases where sequential analysis of Np and Pu is performed for the same sample. ^{235}Np can be used as a tracer because of its relatively long half-life ($t_{1/2}$=396.1 d) compared to other Np isotopic tracers, but it contains ^{237}Np as an impurity from the tracer preparation process. Another cyclotron produced isotope, ^{236}Np ($t_{1/2}=1.54\times10^{5}$ yr), could also be used as a tracer, but it is not easy to generate and still not available in a pure form to most researchers. A further option is to use a non-isotopic tracer like ^{242}Pu and to measure the mass concentrations of ^{242}Pu and ^{237}Np simultaneously by ICP-MS. ^{236}Pu can also be used as a tracer instead of ^{242}Pu since the latter tracer interferes with the ^{237}Np measurement when alpha spectrometry is employed. Several researchers have used ^{242}Pu as a tracer for Pu and ^{237}Np determination in environmental samples [27,28].

The matrix composition of urine is very complicated and unpredictable due to the large variation in diet from one individual to another and with time [29]. The changeable matrix effects pose inevitable challenges to the method development for Np and Pu urinalysis especially when handling large sample volumes. An important issue for urinalysis is the complete decomposition of organic matter or the liberation of endogenous radionuclides into free ions from organic matter associations. This is, to the best of our knowledge, still a bottleneck hampering the applicability of most developed radioassays for real urine samples, as the endogenous Np and Pu species in urine are always associated with different organic substances (e.g., nitrogenous compounds, vitamins, hormone, organic acids and miscellaneous organic compounds) to some extent [29]. This is because Pu and Np follow a tortuous metabolic system once entering the human body and react with a number of body fluids. Whenever the release of organically bound Pu and Np is not complete or the species of endogenous Pu and Np are not identical to the spiked chemical yield tracer, analytical results might lack reliability due to the isotopic disequilibrium between the intrinsic Pu/Np and the tracer. In addition, the high content of organic components in the urine could significantly deteriorate the analytical performance of further chemical purification protocols, especially for anion exchange or extraction chromatographic separations. Consequently, there is a quest for novel sample pre-concentration protocols enabling to release quantitatively the organically associated Pu and Np to ensure the accuracy of the urinalysis methods.

Evaporation and co-precipitation are the most often used pre-concentration methods for urinalysis of actinides. Phosphate co-precipitation methods, using calcium phosphate ($Ca_3(PO_4)_2$) [24], or bismuth phosphate ($BiPO_4$) [6] have been widely applied for urine bioassays of transuranics. In recently years, a co-precipitation based on titanium hydroxide (HTiO) [22,26] has been patented for pre-concentration of Pu from 1.4 L of urine, yet applied in few laboratories. Recently, manganese dioxide (MnO_2) and iron hydroxide ($Fe(OH)_3$) co-precipitation protocols have been exploited for urine Np and Pu assays [30,31]. Nevertheless, the analytical applicability of individual pre-concentration technique has not been systemically compared and little effort has been devoted to investigate the urine matrix effects on the analytical performance for actinides urinalysis.

This work aims to investigate and compare the analytical performances of different sample pre-concentration techniques and organic matter decomposition protocols for the determination of Pu and Np in urine in order to select the optimal procedure for in vivo radioassay program. Four sample pre-concentration techniques including evaporation, $Ca_3(PO_4)_2$, MnO_2 and $Fe(OH)_3$ co-precipitation for 1 L urine analysis were performed and the effects of the various parameters (e.g., valence adjustment reagents, organic matter decomposition protocol, urine matrix effect, and aging of urine) on the analytical performances with respects to the chemical yields of Pu and Np, the coherence of Np and Pu behavior and the turnaround time were evaluated. Challenges in liberating organically associated Pu and Np were also tackled by testing and comparing different approaches for the decomposition of organic matter.

2. Experimental

2.1. Reagents and samples

^{237}Np solution of 0.01175 Bq g^{-1} in 2 mol L^{-1} HNO_3 was prepared by dilution of a stock solution supplied by the Center for Nuclear Technologies, Technical University of Denmark (DTU-Nutech). ^{242}Pu standard solution (0.1037 Bq g^{-1} in 2 mol L^{-1} HNO_3) was prepared by dilution of NBL-CRM 130 (New Brunswick Laboratory, Argonne, IL). TEVA extraction chromatographic resin (100–150 μm particle size) was purchased from TRISKEM International (Bruz, France). All chemicals used in this work were analytical grade reagents, and all solutions were prepared with deionized water (18 MΩ cm). Human urine samples were collected individually or pooled together from Danish healthy residents and preserved in clean and sealed polyethylene barrels under 5 °C. Unless otherwise stated, 1 L aliquot of urine spiked with 0.5 mBq of ^{237}Np, 5 mBq of ^{239}Pu and 5 mBq of ^{242}Pu was used as a sample throughout this work. One seawater sample collected from Roskilde Fjord, Denmark (55°41′N, 12°5′E) in 2012 was used for investigating efficiency of the $Fe(OH)_3$ co-precipitation.

2.2. Sample pre-concentration

2.2.1. Co-precipitation techniques

For calcium phosphate co-precipitation, 1 mL (or 2 mL) of 1.3 mol L^{-1} $Ca(NO_3)_2$ and 2 mL (or 4 mL) of 0.65 mol L^{-1} KH_2PO_4 were added to the sample aliquot. In some cases, the sample was heated to 40–60 °C as indicated in Table 1. Conc. $NH_3\cdot H_2O$ was added until pH=9–10 to co-precipitate Pu and Np with $Ca_3(PO_4)_2$. For manganese dioxide co-precipitation, the sample pH was adjusted to 7–8 using conc. $NH_3\cdot H_2O$, and 5 mL of 0.2 mol L^{-1} $KMnO_4$ solution was slowly added while stirring. 1–2 mL of 25% $NH_3\cdot H_2O$ was then added to adjust the pH to 9–10 and the sample was stirred for 10 min to allow for the complete uptake of Pu and Np onto the formed MnO_2. For iron hydroxide co-precipitation, the sample aliquot was boiled on a hotplate at 200 °C for 2 h and then stored for 5 d. 1 mL of 3 mol L^{-1} $FeCl_3$ solution was added and conc. $NH_3\cdot H_2O$ was added to adjust the pH to 8–9.

After forming the desired precipitate, each sample was centrifuged at 4000 rpm for 10 min, the supernatant was discarded, and the precipitate was then dry ashed or wet digested to further decompose the organic matter contained. In the dry ashing approach, the precipitate was transferred to a beaker with water and heated on a hotplate to dryness and then ashed in a muffle oven at 550 °C overnight. Due to the difficulties in dissolving the MnO_2 residue after ashing, the dry ashing operation was not applied to the sample from MnO_2 co-precipitation.