Spectrochimica Acta Part B 108 (2015) 28–34

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

On the distribution of uranium in hair: Non-destructive analysis using synchrotron radiation induced X-ray fluorescence microprobe techniques

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ARTICLE INFO

Article history:
Received 8 October 2014
Accepted 31 March 2015
Available online 11 April 2015

Keywords:
μ-XRF
Hair
Confocal
Uranium
Internal dosimetry

ABSTRACT

In the present study the distribution of uranium in single human hair shafts has been evaluated using two synchrotron radiation (SR) based micro X-ray fluorescence techniques; SR μ-XRF and confocal SR μ-XRF. The hair shafts originated from persons that have been exposed to elevated uranium concentrations. Two different groups have been studied, i) workers at a nuclear fuel fabrication factory, exposed mainly by inhalation and ii) owners of drilled bedrock wells exposed by ingestion of water. The measurements were carried out on the FLUO beamline at the synchrotron radiation facility ANKA, Karlsruhe. The experiment was optimized to detect U with a beam size of 6.8 μm × 3 μm beam focus allowing detection down to ppb levels of U in 10 s (SR μ-XRF setup) and 70 s (SR confocal μ-XRF setup) measurements. It was found that the uranium was present in a 10–15 μm peripheral layer of the hair shafts for both groups studied. Furthermore, potential external hair contamination was studied by scanning of unwashed hair shafts from the workers. Sites of very high uranium signal were identified as particles containing uranium. Such particles, were also seen in complementary analyses using variable pressure electron microscope coupled with energy dispersive X-ray analyzer (ESEM–EDX). However, the particles were not visible in washed hair shafts.
These findings can further increase the understanding of uranium excretion in hair and its potential use as a biomonitor.

1. Introduction

Screening for elevated levels of uranium is needed to prevent risks of health effects. By analyzing the uranium concentration in urine, it is possible to make assessments of the intake. Lately, excretion of uranium in hair has been studied in order to evaluate its use as a complementing biomonitor for uranium intake. Chronic intake studies show that hair has an advantage over urine because the excreted uranium is accumulated and stored in the hair. The potential of hair as a biomonitor relies on how well it reflects the amount of uranium retained in the body.

Intake of uranium via ingestion occurs naturally as trace amounts of uranium are present in foodstuffs and drinking water. Elevated levels of uranium exist in areas where the bedrock contains uranium rich minerals. Drilled bedrock wells in such areas may contain up to 5 orders of magnitude higher uranium concentrations in water than the world average value of 1 mBq/kg [1]. Intake of uranium via inhalation occurs in the nuclear industry (uranium mining, fuel enrichment and fabrication) and may also take place in military operations where ammunitions containing depleted uranium are used. The particle size and physiochemical form of the airborne uranium particles will determine the deposition and retention in the lung tissue, i.e. before being cleared to blood, showing retention half-lives of days for soluble uranium compounds (e.g. UF_6) to years for slowly soluble compounds (e.g. UO_2).

The principal health concerns from uranium intake are cancer induction in the respiratory tract (inhalation) and nephrotoxicity in the kidneys (ingestion and inhalation) [2,3]. Inhalation of high amounts of uranium can also cause deterministic effects such as pneumonia and lung fibrosis, but it is not the determining factor for dose limitations. Other organs and body parts, such as bone can also be affected [4] but to a lesser degree.

Monitoring of airborne uranium by personal air samplers (PAS) or area monitors are standard procedures in order to assure compliance with annual dose limits based on DAC-limits (Derived Air Concentration). However, dose determinations following inhalation intakes are difficult to perform and often associated with large uncertainties [3,5]. They are often based on uranium body burden derived from urine analyses. Hair analysis may complement urine analysis as biomonitor of uranium [6–16]. The uranium content in hair can be determined by different methods, e.g. ICP-MS and alpha spectrometry.

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http://dx.doi.org/10.1016/j.sab.2015.04.001
0584-8547/

However, a very sensitive method that also provides high spatial resolution and is non-destructive is synchrotron based micro x-ray fluorescence (SR μ-XRF). The size of the monochromatic beam determines the spatial resolution, while the uranium concentration in the hair shaft and the beam photon flux and detector setup determines the uranium detection limits. Scanning single hair shafts with SR μ-XRF opens the possibility to map the existence of uranium down to micrometer resolution. The technique has previously been used to determine the uranium distribution within particles of the same size as the hair shafts [17–19]. However, in those studies the concentration of uranium has been much higher (six orders of magnitude). This technique can not only yield longitudinal hair shaft profiles, but also latitudinal, i.e. it can tell if the uranium is evenly distributed, located in the core of the shafts or in the periphery. It may also reveal any existence of exogenous uranium, i.e. deposited on the shafts from the environment.

The aim of the present study is to analyze single scalp hair shafts of individuals exposed to uranium in order to evaluate the possibility of using hair as a biomonitor of uranium intake.

2. Materials and methods

2.1. Sample preparation

Hair samples were collected from two groups exposed to uranium; users of drilled bedrock well water living in the Östergötland County, Sweden (in the present work referred to as 'BP') and workers at a nuclear fuel fabrication factory in Sweden (referred to as 'WH'). Hair samples were also collected from a person with no known exposure to uranium (referred to as 'unexposed'). The BP group participated in a recent study of uranium in drinking water, hair and urine [16] and the WH group is currently participating in a study of uranium in urine and hair following inhalation. From each group, hair samples from the two persons with the highest exposure and with hair longer than 2 cm were selected. The hair shafts were cut from the scalp and stored in a refrigerator until preparation. Both unwashed and washed hair was studied, the latter prepared using an optimized washing procedure; bulk samples of 0.2 g hair were each placed in a 100 ml syringe filled with detergent (Triton-X of 1% concentration) for 12 h, followed by ultrasonic cleaning for 30 min using 55 °C water as wave transport medium. The detergent was then removed from the syringe through a filter to retain the hair inside the syringe. The sample was rinsed with two flushes of demineralized water. For the WH hairs this ultrasonic cleaning, clearance and rinse was repeated twice. Finally, the samples were rinsed with acetone and dried at room temperature. Just a few hair shafts from each sample were used for the μ-XRF measurements.

2.2. X-ray fluorescence microprobe (μ-XRF)

The μ-XRF and the confocal XRF measurements were carried out at the FLUO beamline in the ANKA synchrotron facility (Karlsruhe, Germany) [20]. A mono-chromatic beam with photon energy 18.1 ± 0.5 keV and a photon flux of ~10^{12} ph s^{-1} mm^{-2} was focused by a compound refractive X-ray lens (CRL) [21] down to a beam size of a few micrometers. The photon energy was selected in order to obtain ideal focus conditions of the lens and to optimize the conditions to excite the uranium L_3 electrons.

After the alignment of the beam, the focus dimensions were measured by knife edge scanning of a 5 μm thin Ni/Fe structure (IRMM 301 standard). The beam size was measured to 3.0 (±0.1) × 6.8 (±0.1) $μm^2$. The resulting microbeam had an intensity of about $4 \cdot 10^9$ ph s^{-1} in the focal spot.

The XRF measurements in confocal mode were performed with a Si(Li) detector (133 eV FWHM at 5.9 keV). On top of the Si(Li)-detector, a ploy capillary half lens was attached and lined to form a voxel with the incoming beam resulting in a voxel with the dimensions of; dx′ = 18.4 μm; dy′ = 6.8 μm; dz = 3.0 μm.

The U was determined from the corrected (detector dead-time and beam intensity) U L_α X-ray line. Elemental maps were produced with a step size of 3–5 μm, in the y- and z-direction and with a data accumulation time of 80–100 s per data point.

The X-ray spectra were de-convoluted with a software program called AXIL [22,23] using non-linear square fitting.

2.3. Scanning electron microscope (SEM)

Hair shafts were analyzed in a Carl Zeiss SEM (EVO LS15) equipped with energy dispersive analyzer (EDX) and with the possibility to analyze the specimens in variable pressure. The image was acquired using 20 kV accelerating voltage in a variable pressure-(VP) and in backscattered-mode. The hair shafts did not need coating, as is normally required in high vacuum SEM for making a conductive surface, since the VP mode was used here.

Particles on the hair shafts were identified, and by adjusting the contrast in the backscattered image only the particles containing high atomic number elements were selected (shown as bright spots on the BS image) for further analysis. These particles were analyzed by the EDX analyzer and the Aztec software (Oxford instruments). The EDX spectra were acquired in the energy range 0–20 keV by a 50 mm^2 electrically cooled silicon drift detector (X-Max, Oxford instruments). The X-Max detector used has an energy resolution (FWHM) of 127 eV at 5.9 keV. For the EDX analysis the accelerating voltage was increased to 30 kV in order to excite the U L_3 electrons but using lower current in order to prevent heat damage of the hair.

The washing effect on the hair shafts where studied by comparing unwashed and washed hair from the same person.

2.4. Experimental setup

The shafts were mounted on a holder, see Fig. 1, or placed on an adhesive carbon tape, and the setups were slightly modified between different experiments. A schematic overview of the general setup is shown in Fig. 2. The detector was placed in a 90° angle with the incoming beamline in the x/y plane to minimize scattered photons while the hair shaft was aligned with the z axis.

The experimental line scans were performed by moving the hair shafts either in the y direction or in the z direction, i.e. across the shaft or along the shaft. These are hereafter referred to as latitudinal and longitudinal scans, respectively. In the μ-XRF experiments, scattered radiation from the whole irradiated section is detected (illustrated as dotted lines in Fig. 2). In the experiments with the confocal lens applied on the detector, only parts of the irradiated section are detected (solid lines in Fig. 2).

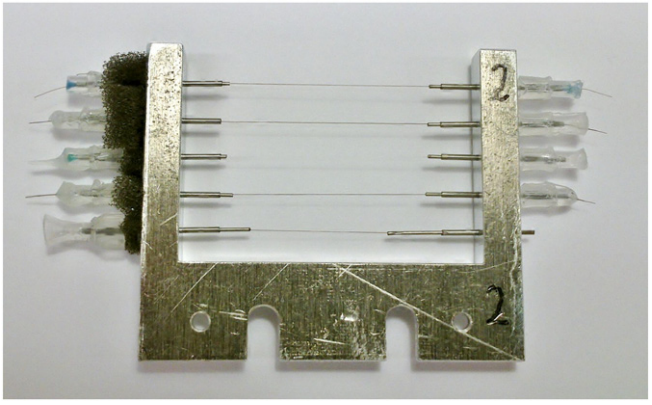

Fig. 1. Holder of hair shafts used during experiments.