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Distribution of uranium and selected trace metals in Balkan human scalp hair using inductively coupled plasma mass spectrometry

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ABSTRACT

Hair analysis is extensively used in forensic sciences, assessment of occupational or environmental exposure and in some cases for clinical and nutritional studies. The present study summarizes the analytical methodology and distribution of uranium and some selected trace metals e.g., Mn, Ni, Cu, Zn, Sr, Cd and Cs in human scalp hair samples using inductively coupled plasma mass spectrometry (ICP-MS). Uranium isotopic ratio ($^{235}U/^{238}U$) has been measured using thermal ionization mass spectrometry (TIMS). For quality control, five certified reference materials such as SRM 1571, NIES 13, IAEA 086, NCS ZC 81002 and BCR CRM 397 have been analyzed by the proposed methods and the measured uranium concentrations in some selected hair samples were compared with the results by radiochemical neutron activation analysis (RNAA). The methodology was applied for measurement of uranium and selected trace metals in human scalp hair collected from Balkans exposed to DU ammunitions. Uranium concentrations in human hair samples from Balkans show a wide variation ranging from 0.90 ± 0.05 ng/g to 449 ± 12 ng/g whereas other trace metal concentrations like Mn, Ni, Cu, Zn, Sr, Cd and Cs were found to be comparable with the reported values of healthy persons worldwide. Though hair samples were collected from a Balkan conflict zone, uranium isotopic measurement ($^{235}U/^{238}U$) indicated natural origin rather than depleted uranium.

1. Introduction

The proliferation of trace element analysis as a tool for biological investigation of nutrition, growth and development, and disease processes has led to consideration of (hair) trace element analysis as a means not only to present evaluation and estimation, but also as a technique for the reconstruction of past biological events [1]. Bioassay of hair is attractive over other types of clinical specimens like blood and urine as it is a natural bio-concentrator, samples can be easily collected, stored, and the concentration reflects an integrated value [2]. Hair has also been reported to be a valuable indicator of environmental pollution [3]. This tissue may prove a practical dosimeter for metallic environmental pollution [4]. This makes hair an excellent choice in certain situations and as a screening tool.

Major challenges to be addressed while measuring trace elements in hair include external contamination, lack of standardization and analytical accuracy [5]. Studies of trace elements in hair have led to many discussions and opinions about analytical difficulties [6]. Much controversy exists regarding the use of hair samples as an indicator for nutritional status and environmental exposure due to exogenous contaminants such as atmospheric pollutants, water, sweat and cosmetics [7]. As a result, trace elements in hair can be of both endogenous (internal) and exogenous (external) origin. To reduce the problem of surface contamination, different washing procedures have been proposed and used [8–10]. There are also difficulties in establishing normal or reference values for hair due to natural variance in hair composition [11].

In case of biological sample analysis, the spectral interferences and matrix effects may influence the accuracy of the results.

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However, these interferences can be overcome by using suitable analytical methods with different spectrometry techniques. Various analytical techniques like atomic absorption spectrometry [12], neutron activation analysis [13,14], X-ray fluorescence spectrometry [15–17], and inorganic mass spectrometry [18–24] have been employed so far in hair analysis for elemental quantification. Among them, inductively coupled plasma mass spectrometry (ICP-MS) is one of the most successful multi-elemental techniques with a large dynamic range from parts per trillion (ppt) to percent quantities (%) with good precision, short measurement time (1 min per sample), minimal sample preparation and requires less sample volume. Mostly, uranium has been determined in hair using ICP-MS [25–28].

A few authors accomplished the determination of depleted uranium (DU) by isotope ratio measurements. In fact, the presence of natural uranium (NU) in the environment makes this investigation extremely difficult [29]. NU comprises of 0.0055% of ^{234}U, 0.72% of ^{235}U and 99.27% of ^{238}U. On the other hand, DU, produced in the process of enrichment of NU, used in the production of munitions contains 0.001% of ^{234}U, 0.2% of ^{235}U and 99.8% of ^{238}U. Use of DU for military purposes in recent years is a major concern for its presence in environment and possible transfer to humans. There is a huge possibility of exposure to contaminative aerosol containing DU via inhalation by military personnel and the population in a war conflict zone, thereby, causing adverse effects to health. There are reports on the possible health consequences due to occurrence of DU in war conflicts by World Health Organization (WHO) [30] and United Nations Environment Programme (UNEP) [31] and also in the incidence of several cancers in Iraq after the gulf war [32]. Since DU has been used in the Balkan conflict during 1995 and 1999, exposure assessment of DU for the people and the environment of this region is expected to be significant. Selected individuals were interviewed regarding their life style and health. All subjects were screened to have a healthy life style with no previous medical conditions except one female subject. This investigation is focused on individuals especially those who were out or in the vicinity of targeted areas during bombing. Hair samples were taken from these selected subjects. Therefore, we have undertaken a study to measure not only the total uranium concentration but also uranium isotopic ratio to reveal the evidence of DU in the environment.

Alpha spectrometry has been used extensively for ^{234}U/^{238}U isotopic ratio measurement with great accuracy where as for ^{235}U/^{238}U its application is limited because of tedious sample preparation, long measurement time and large sample volume requirement [33]. TIMS equipped with energy filters is recognized as a precise technique for the determination of the isotopic composition of uranium and it is appreciated for its capability of analyzing very small aliquots [34,35]. Prior to measurement, pre-concentration of the element has been the determining factor in attaining precise isotope ratios. Recently, extraction chromatographic separation method [36,37] has been found more suitable over anion exchange chromatography or liquid–liquid extraction method for the pre-concentration of uranium from the sample to reduce large volume of matrix causing spectral interferences. In the present study, a combination of anion exchange and extraction chromatography has been applied for uranium separation.

Sample dissolution especially for biological material containing large amounts of organics should be carefully carried out for accurate determination of trace metals. In the present work, two different dissolution procedures, (i) microwave digestion (MD) and (ii) dry ashing (DA) followed by microwave digestion (DA and MD) have been tested to dissolve hair samples. Uranium and other trace metals were analyzed using ICP-MS. A systematic procedure has been performed on sample preparation and chemical separation for uranium. Quality control of the method has been achieved by analyzing certified reference materials. Measured uranium concentrations in few hair samples were also compared with radiochemical neutron activation analysis (RNAA) for analytical validation. Uranium isotopic ratios were measured using TIMS after pre-concentration of uranium using ion exchange resins.

Finally this method is applied for analyzing uranium, uranium isotopic ratios and some selected trace metals in hair samples collected from Balkan, expecting DU exposure since the evidence of DU in soil and drinking water in this area has been reported in our previous studies [38]. In clinical and forensic toxicology, Cd is one among other trace metals which play an important role in monitoring heavy metal exposures. The other trace metals e.g., Mn, Ni, Cu, Zn, Sr and Cs are of clinical or forensic interest. Thus, these elements have been selectively analyzed based on their abundance in hair samples, to check exposure levels as they are considered to be bioindicators.

2. Experimental

2.1. Reagents and standards

High purity water was obtained from a Millipore Milli-Q water purification system. High purity HCl, HNO_3, HF and $HClO_4$ were purchased from Tamapure chemical industries (Kawasaki, Japan). The strong anion exchange resin Dowex AG_1-X8 (200–400 mesh, Cl^- form) and extraction chromatographic resin, UTEVA, were purchased from Bio-Rad Labs (Richmond, CA, USA) and Eichrom Industries (Darien, IL, USA), respectively.

2.2. Instrumentation

The ICP-MS used was a Hewlett–Packard 4500 (Hewlett–Packard, Yokogawa Analytical Corporation, Japan). Uranium atom amount ratios for isotopic composition analysis were measured on a single focusing VG (Micromass) Sector 54-30 TIMS equipped with nine Faraday cup collectors and a Daly ion-counting system detector positioned behind axial Faraday and wide aperture retardation potential energy filter.

2.3. Sample description

Scalp hair samples were collected from nineteen volunteers from Balkan conflicted region, Bratoselce, Gornja Stubla and Han Pijesak, shown in Fig. 1. Han Pjesak and Bratoselce are both DU targeted areas in 1995 and 1999, respectively, whereas Gornja Stubla is identified as a natural high background radiation area with high radon and thoron concentration. Gornja Stubla is situated 26 km from DU targeted area Bratoselce. Gornja Stubla inhabitants reside in high radon area at 900 m above sea level. The combined estimated average annual effective dose from penetrating radiation and radon for this community, based on the measurements done there a year before DU attack, was 16.2 mSv/year [39]. The annual radiation effective dose is well above world averages where total gamma and cosmic penetrating is approximately 0.8 mSv/year and for terrestrial radiation 0.48 mSv/year. As approach to target area was restricted for two years after bombing, in 2002, United Nations Environment Programme (UNEP) published the first ever assessment of the environmental risks associated with the use of depleted uranium weapons in the real combat situation [31]. Subsequently, we collected hair samples in 2003 to compare uranium content in hair of subjects living in high natural background area with persons exposed during targets.