8.5 AMS

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In co-operation with:

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Introduction

The analytical capability of determining actinides (An) and long lived fission products, like ^{99}Tc, in natural samples at ultra-trace levels (fg/g and ag/g) is of great relevance both for environmental studies and for *in situ* tracer tests and diffusion experiments aiming to evaluate the safety of the geological disposal of nuclear waste. With the multi-actinides analysis and accelerator mass spectrometry (AMS) at the VERA Laboratory (University of Vienna) we have investigated the long-term migration behavior of actinides at the fg/g and ag/g levels in a water conducting granodiorite fracture in the frame of the CFM Project run 12-02 [1] and 13-05 [2].

Similarly, at the AMS facility of the Technical University of Munich (TUM) in Garching, with the Gas-Filled Analyzing Magnet System (GAMS) [3], the concentration of ^{99}Tc in samples belonging to the **L**ong-Term **I**n situ **T**est (LIT) has been determined at the fg/g levels. In order to investigate both the actinides and ^{99}Tc at ultra-trace levels given a limited groundwater sample volume of ca. 3 ml, we are testing an analytical procedure allowing for the separation of the group of An and Ru from Tc. In the actual report, we present the recent outcomes achieved with AMS in the frame of the CFM run 13-05 and the first results on the determination of ^{99}Tc with AMS and its chemical separation from the actinides.

In the frame of a joint GENTLE project with HZDR, we adapted the multi-actinides analysis approach with AMS to more complex sample matrices than groundwater, e.g., soil, sediments or clay deposits. For that purpose, a chemical procedure consisting in the group separation of the actinides with the DIPEX® extractant (Eichrom) was successfully tested.

Investigation on ^{241}Am and ^{244}Pu in samples of CFM run 13-05

The injected tracers ^{233}U, ^{237}Np, ^{242}Pu and ^{243}Am were determined with AMS over six orders of magnitude: from the maximum value of the ^{242}Pu concentration equal to (3.71 ± 0.04) × 10^{10} atoms/g (ca. 15 pg/g) to the minimum value of the ^{243}Am concentration of (6.2 ± 0.6) × 10^4 atoms/g (ca. 0.025 fg/g) as shown in Figure 1. The first four samples collected between 0.01 d (14 min) and 0.4 d (9 hours) represent the levels of the investigated actinide nuclides in the groundwater before the arrival of the migration front.

In order to explain the origin of this unexpected signal, we have considered the hypothesis of a background from the previous *in situ* tracer experiments. In fact, ^{237}Np, ^{242}Pu and ^{243}Am were injected as tracers in the granodiorite fracture in the frame of both the CFM run 12-02 and the CRR run 1, while ^{237}Np, ^{233}U, ^{241}Am and ^{244}Pu were employed in the CRR run 2 [4]. The only two An nuclides exclusive of such previous experiments and not employed in CFM run 13-05, were ^{241}Am and ^{244}Pu. Therefore, we have performed a further determination with AMS of the concentration of masses 241 u and 244 u in a group of chosen samples of run 13-05. Such masses are present also as minor nuclides in the ^{242}Pu and ^{243}Am solutions used for the composition of the injection cocktail. The atomic ratios of mass 241/^{243}Am and mass 244/^{242}Pu in the injection cocktail determined with SF-ICPMS, are equal to (2.6 ± 0.6) × 10^{-3} and (3 ± 4) × 10^{-5}, respectively. As it can be seen in Figure 2, the corresponding atomic ratios measured in the samples of run 13-05 are significantly higher than those of the injection cocktail both before and after the peak of the breakthrough curve, while they are consistent with the values of the injection cocktail in correspondence to the peak (Figure 1 and Figure 2). Considering such results, we can conclude that there are two sources of masses 241 u and 244 u in the samples: one is likely to be the injection cocktail itself, which becomes dominant with the arrival of the peak of the breakthrough curve; the second source could be identified as a signal superimposed by the isotopic signature of previous *in situ* tracers tests.

The amount of An left in the fracture after the CRR tests [4] can be roughly estimated as follows: 5.2 × 10^{14} (^{233}U), 1.2 × 10^{16} (^{237}Np), 1.2 × 10^{13} (^{241}Am), 4.2 × 10^{14} (^{242}Pu), 2.0 × 10^{14} (^{243}Am) and 5.7 × 10^{13} (^{244}Pu) atoms. Considering the series of *in situ* tests performed at the GTS in the period between the CRR tests and the CFM run 13-05, we estimate a total volume of groundwater passing through the fracture equal to ca. 1.1 × 10^5 L. In a simple hypothesis in which the total number of An atoms left in the fracture before the starting of CFM run 13-05 is entirely released into the aforementioned volume of groundwater, concentrations equal to ca. 5 × 10^6 (^{233}U), 1 × 10^8 (^{237}Np), 1 × 10^5 (^{241}Am), 4 × 10^6 (^{242}Pu), 2 × 10^6 (^{243}Am) and 5 × 10^5 (^{244}Pu) atoms/ml are estimated. Clearly, such scenario does not reflect the complexity of the sorption/desorption dynamics of the various An in the

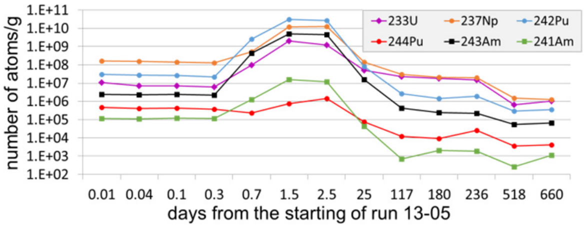

Fig. 1: *Concentrations expressed in atoms/g of ^{233}U (violet rhombuses), ^{237}Np (orange circles), ^{242}Pu (blue circles), ^{244}Pu (red circles), ^{243}Am (black squares) and ^{241}Am (green squares) determined with AMS in chosen samples of CFM run 13-05.*

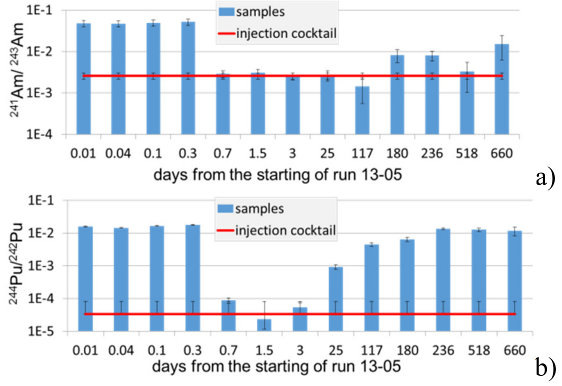

Fig. 2: *Atomic ratio between mass 241 u and ^{243}Am (a), mass 244 u and ^{242}Pu (b) determined with AMS in eleven chosen samples of run 13-05 and in two samples collected after 518 and 660 d from the starting of the experiment; the corresponding atomic ratios in the injection cocktail are depicted as red line.*

system of groundwater - bentonite colloids - fault gouge minerals at the GTS. However, with the sensitivity of AMS we can determine the aforementioned estimated levels which may give us the opportunity to extend the present and upcoming *in situ* studies of the An long-term behavior to longer time spans, e.g. a decade or more [2].

Determination of ^{99}Tc and the actinides at ultra-trace levels in environmental samples

At the 14 MV Tandem AMS facility of TUM, the GAMS is used in order to suppress atomic isobaric interferences [3], which in the case of ^{99}Tc are represented mainly by ^{99}Ru. With this setup, concentration of ^{99}Tc in four investigated LIT samples have been determined in the range of 7 and 250 fg/g.

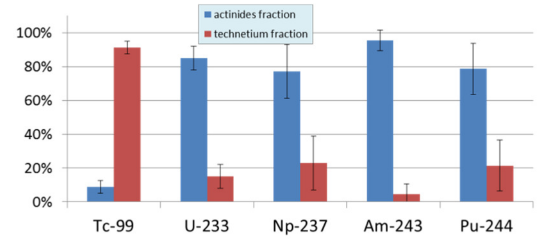

Fig. 3: *Recovery of ^{99}Tc, ^{233}U, ^{237}Np, ^{243}Am and ^{244}Pu in the Tc (red bars) and An fraction (blue bars), determined with ICPMS.*

In order to determine both the actinides and ^{99}Tc in the LIT samples with small volumes we are testing an analytical procedure allowing for the ultra-trace determination of the actinides and ^{99}Tc in the same sample employing TEVA® Resin. Six samples containing ca. 60 ppt each of ^{99}Tc and ca. 2 ppt each of ^{233}U, ^{237}Np, ^{244}Pu and ^{243}Am were prepared and adjusted to 0.2 M HCl. With such loading solution, the An pass through the chromatographic column and are separated as a group from Tc. After a further washing with 0.2 M HCl, Tc is eluted with a 8 M HNO_3 solution. In this way, two fractions are obtained: the first one containing the An as a group as well as the matrix elements and the second one containing the Tc fraction. Figure 3 depicts the recovery of ^{99}Tc, ^{233}U, ^{237}Np, ^{244}Pu and ^{243}Am in the An and Tc fraction, respectively, obtained with ICPMS.

The separation of the group of An from Tc is successful with ca. 91% of ^{99}Tc recovered in the Tc fraction and ca. 85%, 77%, 79% and 96% of ^{233}U, ^{237}Np, ^{244}Pu and ^{243}Am, respectively, recovered in the An fraction.

For the investigation of the LIT specimens as well as of natural waters, the samples will be appropriately spiked with tracers before the chemical separation with TEVA® Resin, after which the An and Tc fractions will be further processed for AMS analysis.

References

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