

Ultra Trace Determination of U, Pu, and Np by Resonance Ionization Mass Spectrometry

K. Wendt¹, Ch. Mattolat¹, S. Raeder¹, G. Passler¹,
R. Buda², Th. Wunderlich², J.V. Kratz², T. Reich², N. Trautmann²

¹*Institute for Physics, Johannes Gutenberg-University, D-55099 Mainz, Germany*

²*Institute for Nuclear Chemistry, Johannes Gutenberg-University, D-55099 Mainz, Germany*

In order to investigate the migration of uranium, plutonium and neptunium in the environment, highly sensitive and selective detection methods are required. Furthermore, the speciation of these elements is of high importance, as it determines solubility and mobility.

A few years ago Resonance Ionization Mass Spectrometry (RIMS) has been established as a suitable technique for ultra trace analysis, with particular emphasis on the determination of lowest contaminations of long-lived isotopes with unsurpassed sensitivity [1]. This method has several advantages:

- ◆ RIMS provides an excellent limit of detection (LOD) around 10^6 atoms per sample independent of the radioactive decay properties and lifetime of the isotope of interest.
- ◆ Through a multi-step resonant laser excitation and ionization process of the element of interest, e.g. using high power, high repetition rate tunable lasers, in combination with subsequent mass analysis, e.g. in a simple time-of-flight mass spectrometer (TOF-MS), high selectivity with respect to isobaric interferences is achieved. In this way the origin of a contamination can be determined from the mass spectrometric isotope pattern.
- ◆ By off-line and — for the near future planned — on-line coupling of chromatographic techniques, like Capillary Electrophoresis (CE), to RIMS, a species assignment is possible.

On-line coupling of CE to Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was developed to separate the oxidation states III, IV, V, and VI of plutonium, but the detection limit of this hyphenated technique of ~ 20 ppb (or $\sim 10^9$ atoms, respectively) for a given oxidation state of Pu is too high for studies under environmental conditions [2]. Thus, as a next step the coupling of CE to pulsed-laser-TOF-RIMS for a reduction of the LOD in speciation studies is presently tested and prepared for application [3].

Also the determination of the isotopic signature of uranium found in the environment can be of crucial importance for the detection of undeclared nuclear material. The major isotope of interest is ^{236}U , which is produced by neutron capture from ^{235}U . Due to the low neutron flux in the environment the natural abundance of ^{236}U compared to ^{238}U is well below 10^{-10} . However, in spent nuclear fuel the ^{236}U concentration can reach up to several percent due to the high neutron flux in nuclear reactors. So the uranium isotope ^{236}U is the most sensitive tracer for man-made uranium and its determination can provide information on the migration of anthropogenic nuclear contaminations in the environment.

High Resolution Ionization Mass Spectrometry (HR-RIMS) has been developed to precisely determine the isotopic composition of uranium samples [3]. For this, the sample is evaporated from a graphite furnace into vacuum to form a well collimated atomic beam. Neutral uranium atoms are resonantly and isotope-selectively excited by precisely tuned narrow-band width (continuous wave) laser light along a well chosen multi-step optical excitation process up to ionization. Afterwards, they are mass analyzed in a quadrupole mass filter for background reduction and further enhancement of the isotopic selectivity.

First tests of the HR-RIMS technique were carried out on synthetic samples of about 10^{17} uranium atoms. These were prepared on zirconium foil for an efficient reduction to the elemental state and heated up to $\sim 2500^\circ\text{C}$ in a graphite furnace. A LOD of $3 \cdot 10^8$ ^{236}U atoms for an isotopic ratio of $^{236}\text{U}/^{238}\text{U} \approx 10^{-8}$ was obtained so far. Measurements on synthetic samples within an isotopic range of $^{236}\text{U}/^{238}\text{U}$ ratios from 10^{-3} down to 10^{-8} confirmed the

linearity of the determination system and demonstrated the high dynamical range. The final characterization concerning accuracy and reproducibility is presently in progress using certified samples from IRMM (Institute of Reference Material and Measurements, Geel, Belgium). Apart from that the development of an on-line coupling interface to a chromatographic preselection stage is in preparation.

For the application of RIMS to ultra trace analysis of Np the identification and characterization of suitable optical excitation and ionization schemes is necessary. The necessary spectroscopic studies are presently performed, employing the Mainz University high power, high repetition rate titanium:sapphire laser system in combination with our standard TOF mass spectrometer.

References

- [1] N. Trautmann et al., *Anal. Bioanal. Chem.* 378, 348–355 (2004).
- [2] B. Kuczewski et al., *Anal. Chem.* 75, 6769-6774 (2003).
- [3] S. Buerger et al., *Radiochim. Acta* 95, 433–438 (2007).
- [4] B. Bushaw et al., *Spectrochim. Acta B* 62, 485–491 (2007).