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**LA-ICP-MS for Trace Analysis of Long-lived Radionuclides in
Solid Non-conducting Radioactive Waste Samples**

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Introduction

The characterization of radioactive waste materials from nuclear reactors for recycling and final storage requires fast, sensitive and precise analytical methods, which are able to determine long-lived radionuclidic ultratraces in a short time. For the determination of long-lived α - and β -ray-emitting nuclides besides the classical radiochemical methods which are mostly include time-consuming radiochemical separation procedures, to an increasing extent inductively coupled plasma mass spectrometry (ICP-MS) has been used successfully as a powerful trace, ultratrace and isotopic analytical method for the determination of long-lived radionuclides in aqueous solutions [1-3]. Kim et al. [1] determined the detection limits for the long-lived radionuclides ^{99}Tc , ^{226}Ra , ^{232}Th , ^{237}Np , ^{238}U , ^{239}Pu and ^{240}Pu with half-lives of 10^3 - 10^{10} years in aqueous standard solutions using a double-focusing sector field ICP-MS ("PlasmaTrace", Fisons) coupled with an ultrasonic nebulizer (USN) and obtained detection limits ranging from 2 to 20 fg/ml. In our laboratory detection limits of ^{233}U , ^{236}U and ^{243}Am of 1-2 fg/ml were found in high purity water by double-focusing sector field ICP-MS ("ELEMENT", Finnigan MAT) with an USN [4]. In addition to the analysis of aqueous waste samples, a direct method for the determination of long-lived radionuclides in non-conducting solid samples without any sample preparation should be available for the characterization of solid nuclear waste. The mass spectrometric methods which allow the direct analysis of trace elements in non-conducting solids without sample digestion steps include laser ionization mass spectrometry (LIMS) [5], radiofrequency glow discharge mass spectrometry (rf GDMS) [6] and laser ablation ICP-MS (LA-ICP-MS). LA-ICP-MS is an established solid-state mass spectrometric method with increasing importance for the analysis of geological materials with detection limits in the 10 ng/g concentration range [7,8]. In a previous publication we described the first application of LA-ICP-MS as a promising and powerful analytical tool for sensitive multi-element determination of long-lived radionuclides in non-conducting materials [9]. The main problem in the quantification of analytical results is that no suitable standard reference materials are available. Therefore synthetic laboratory standards

(concrete matrix doped with some long-lived radionuclides) were investigated by a laser ablation system coupled both to a quadrupole ICP-MS and to a double-focusing sector field ICP-MS [9]. Comparing measurements with NAA (neutron activation analysis) on these standards showed that the relative sensitivity coefficients (RSCs) of the investigated elements differ for most elements by a factor of less than 3. That means a semiquantitative determination of the concentrations of long-lived radionuclides (and other trace impurities) in the concrete matrix is possible with LA-ICP-MS without using a standard reference material.

With double-focusing sector field LA-ICP-MS, the limits of detection are in general one order of magnitude lower and reach the sub ng/g range for ^{233}U and ^{237}Np [9]. The aim of this paper is the improvement of LA-ICP-MS in order to decrease the detection limits of selected long-lived radionuclides in non-conducting waste materials.

Experimental

In these experiments the laser ablation chamber is coupled to the very sensitive double-focusing sector field mass spectrometer (ELEMENT, Finnigan MAT) which allows a high mass resolution of up to $\approx 10\,000$. The experimental setup of LA-ICP-MS using the double-focusing sector field ICP-MS and a quadrupole based ICP-MS is shown in Ref. [9]. The UV wavelength of a Nd:YAG laser (4th harmonic, 266 nm) is used for laser ablation. The experimental parameters applied for laser ablation are: pulse duration - 5 ns; spot diameter - 0.2 mm; repetition frequency - 5 Hz; power density- 10^{10} W cm^{-2} ; energy per pulse - 15 mJ and raster width - 3 mm * 3 mm. The mass spectrometric measurements were carried out at low mass resolution ($m/\Delta m \approx 300$), at inductively coupled plasma power - 1400 W, and carrier gas flow rate (Ar-plasma gas) of 11 min^{-1} . All experimental parameters are optimized to maximum analyte ion intensities. The preparation of synthetic laboratory standards and the analytical method for determination of some long-lived radioactive nuclides (e.g. ^{99}Tc , ^{233}U , ^{234}U , ^{236}U and ^{237}Np) in non-conducting concrete matrix by LA-ICP-MS is described in [9]. In order to prepare a synthetic laboratory standard a concrete sample with Th and U (1.8 $\mu\text{g/g}$ Th and 0.7 $\mu\text{g/g}$ U) was doped with 4.3 $\mu\text{g/g}$ ^{232}Th , 1.04 $\mu\text{g/g}$ ^{233}U and 2.27 $\mu\text{g/g}$ ^{237}Np .

Results and Discussion

Part of the mass spectrum of the laboratory concrete standard using the double-focusing sector field LA-ICP-MS in the mass range of 230 u to 240 u is shown in Fig. 2. Besides the atomic ions of Th, U and Np, hydride ions of U are detected. A study of disturbing interferences is necessary for the determination of long-lived radionuclides at ultralow concentration. E.g. the formation of $^{232}\text{ThH}^+$ should be considered for the determination of ^{233}U in a Th-containing solution. The formation rate of $^{232}\text{ThH}^+$ relative to $^{232}\text{Th}^+$ was determined to be $8.7 \cdot 10^{-5}$ using LA-ICP-MS. The formation rate of $^{238}\text{UH}^+$ relative to $^{238}\text{U}^+$ is in the same order of magnitude ($^{238}\text{UH}^+ / ^{238}\text{U}^+ = 8.8 \cdot 10^{-5}$). The hydride formation rate of Th and U is comparable to that measured on aqueous solution by the application of a pneumatic nebulizer in ICP-MS. The intensity ratios of UO^+/U^+ and ThO^+/Th^+ were determined to be $0.9 \cdot 10^{-3}$ and $2.0 \cdot 10^{-3}$ in LA-ICP-MS compared to $3.4 \cdot 10^{-2}$ and $5.6 \cdot 10^{-2}$ in ICP-MS (using pneumatic nebulization) by the analysis of aqueous solution [3]. Whereas $^{232}\text{Th}^{16}\text{O}^+$ ions disturb the determination of ^{248}Cm by isobaric interference, no long-lived radionuclides were expected at mass 254 u where $^{238}\text{U}^{16}\text{O}^+$ occurs.

The limits of detection (LOD) of ^{99}Tc , ^{233}U , ^{234}U , ^{236}U and ^{237}Np were determined from the mass spectrum of the undoped concrete sample using the 3σ criterion (the limit of detection is given by $m_b + 3\sigma_b$, where m_b is the mean value of the blank measurements and σ_b the standard deviation of five independent measurements of the blank value). All mass spectra are averaged over 50 single measurements in order to minimize the influence of plasma instabilities, variations of the amount of ablated material and local inhomogeneities of the samples. Concentrations were evaluated from measured ion intensities of background in the undoped concrete sample using the known concentrations of the laboratory standard samples doped with well known concentrations of long-lived radionuclides.

The LOD using the double-focusing sector field LA-ICP-MS in concrete matrix are in the ng/g concentration range and lower. Whereas for ^{99}Tc and ^{237}Np the LOD was determined to be 1.5 ng/g and 110 pg/g respectively, for the uranium isotopes the LOD are 170 pg/g (^{233}U), 60 pg/g (^{234}U) and 20 pg/g (^{236}U).

The detection limits are more than one order of magnitude lower using double-focusing sector field ICP-MS in comparison to LA-ICP-QMS.

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