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Determination of uranium isotopic ratios in biological samples using laser ablation inductively coupled plasma double focusing sector field mass spectrometry with cooled ablation chamber

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Abstract

An analytical procedure has been proposed for the determination of precise uranium isotope ratios in a thin uranium layer on a biological surface by laser ablation inductively coupled plasma sector field mass spectrometry (LA-ICP-MS). A cooled laser ablation chamber using a Peltier element was developed in order to analyze element distribution in thin cross-sections of frozen tissues with a lateral resolution in the μm range. In order to study the figures of merit of LA-ICP-MS with the cooled laser ablation chamber, one drop (20 μL, U concentration 200 ng mL^{-1}), each of the certified isotope reference materials NIST U350 and NIST U930, the uranium isotopic standard CCLU-500 and also a drop of uranium with a natural isotopic pattern was deposited and analyzed on the biological surface (flower leaf). The precision and accuracy of isotope ratio measurements are significantly improved using cooled laser ablation chamber in comparison to non-cooled chamber. The precision of the measurements of isotope ratios in the range of 2.0–1.6% for $^{234}U/^{238}U$, 1.3–0.4% for $^{235}U/^{238}U$ and 2.1–1.0% for $^{236}U/^{238}U$ in selected uranium isotopic standards reference material were determined by microlocal analysis (diameter of laser ablation crater: 15, 25 and 50 μm) using LA-ICP-MS with a cooled laser ablation chamber. The accuracy of $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratio measurements varied in the range of 4.2–1.1%, 2.4–0.5% and 4.8–1.1%, respectively, and were dependent on the diameter of the laser beam used.

Keywords: LA-ICP-MS; Isotope ratio measurements; Uranium; Biological samples

1. Introduction

Accurate and precise isotope ratio measurements of long-lived radionuclides, such as uranium or plutonium isotopes, are required in environmental monitoring for evidence of nuclear contamination in nuclear safeguards and nuclear forensic studies [1–4]. Uranium in natural samples with changed isotopic ratios for $^{235}U/^{238}U$, $^{234}U/^{238}U$ in comparison to the IUPAC table values (e.g., $^{235}U/^{238}U = 0.00725$) [5,6] and/or the evidence of ^{236}U at an abundance which is higher than observed in nature $>10^{-10}$ demonstrate an enrichment/depletion of uranium in the investigated samples. Small variation of uranium isotope ratios were also found in nature [7]. Therefore, isotope ratio measurements are of special importance because they can give information on the origin of the uranium contamination or natural isotope variations. Due to different applications of uranium (e.g., in nuclear reactor technology or as depleted uranium in ammunition), careful monitoring of the environment is required in order to detect possible contaminations with radionuclides. Rapid analysis for isotope ratio measurements of surface contamination in biological tissue or medical samples is of increasing interest. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a powerful analytical technique for the determination of element concentrations at the trace and ultratrace level and isotope ratio measurements of long-lived radionuclides in solid samples [8], but it can also be applied as a surface analytical technique. Recently, we used LA-ICP-MS for uranium isotope ratio measurements and

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determination of U and Th concentration in urine. LA-ICP-MS was applied after evaporation of urine samples to dryness and careful homogenization in order to reduce the danger of contamination during sample preparation [1,9]. Furthermore, we applied LA-ICP-MS to determine plutonium isotope ratios in moss samples after digestion, chemical separation of long-lived radionuclides and electrolytic deposition on a target (used for comparing α spectrometric measurements) [10]. The application of LA-ICP-MS as a microlocal analytical technique has been described by several working groups, especially in geological [11,12] and biological research [13,14]. However, the precision and accuracy of these measurements are usually worse in comparison to the convenient ICP-MS [15]. Fractionation effects, molecular ion formation [16–19], as well as evaporation of the water from the vicinity of the laser shot (e.g., when the biological sample is analyzed [14]), which takes place during the ablation process cause an addition source of error in LA-ICP-MS and therefore, leads to decreasing precision and accuracy of the measurements.

The aim of the present work was to study a method utilizing LA-ICP-MS with cooled laser ablation cell in order to improve precision and accuracy of direct microlocal uranium isotope ratio measurement at the ultratrace level on the surface of biological samples.

2. Experimental

2.1. Instrumentation

A double focusing sector field ICP-MS (Element, Thermo Electron, Bremen) coupled with a laser ablation system from Bioptic (Ablascop, Bioptic laser system, Berlin) was used for the determination of uranium isotope ratios on biological samples. The UV wavelength of a Nd-YAG laser (5th harmonic, 213 nm at pulse duration of 5 ns, repetition frequency of 20 Hz, laser power density of 10^9 W/cm^2) was applied for laser ablation. With this arrangement, it is possible to obtain a diameter of the laser crater in the range of 5–50 μm. In order to analyze biological surfaces, a cooled PFA laser ablation chamber was developed. The cooling system of the ablation chamber is arranged using two Peltier elements in serial connection under the target holder made of aluminum. Using this setup at the current and voltage of 0.6 A and 16 V, respectively, applied to the Peltier elements, a temperature of the target holder of about −15 °C was observed. The schematic of such an experimental arrangement of LA-ICP-MS is shown in Fig. 1

2.2. Sample preparation and isotope standard reference materials

A small volume (20 μL of uranium concentration 100 ng mL^{-1}) of the isotope standard reference materials NIST U350, NIST U930 and CCLU-500 [20,21] as well as uranium with natural isotopic composition (uranium concentration 100 ng mL^{-1}) were dropped onto the surface of the biological sample (flower leaf). For mass bias correction on the surface of the flower leaf, one droplet of isotopic standard reference material NIST U020 (20 μL, uranium concentration 100 ng mL^{-1}) was added. After the drying in the heating oven (T = 75 °C, 2 h), the sample was analyzed by LA-ICP-MS using the cooled laser ablation chamber developed in this work.

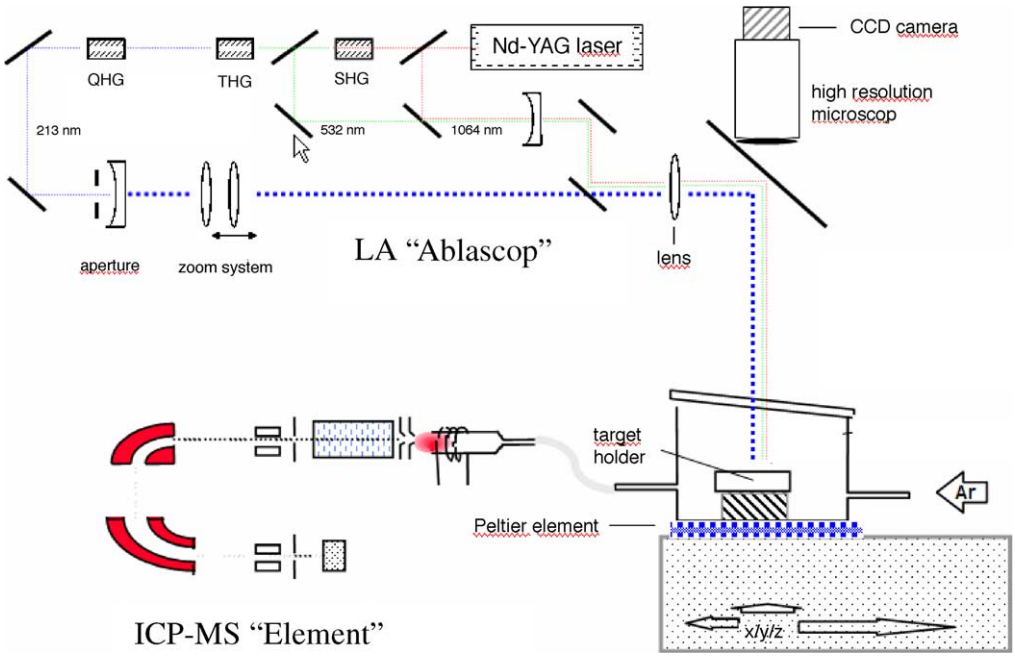

Fig. 1. Schematic for experimental arrangement of LA-ICP-MS with cooled laser ablation chamber.

Table 1
Optimized operating conditions of LA-ICP-MS with cooled laser ablation chamber for uranium isotope ratio measurements on the surface of biological samples

	LA-ICP-MS
Laser ablation system	Ablascope (Bioptic^{TM})
Wavelength of Nd-YAG laser (nm)	213
Laser power density (W cm^{-2})	3.5×10^9
Laser pulse duration (ns)	5
Number of laser shots	100
Repetition frequency (Hz)	20
Temperature of laser ablation chamber (°C)	Approximately −15
Inductively coupled plasma mass spectrometer	Element (Thermo Electron)
RF power (W)	1199
Cooling gas flow rate (L min^{-1})	18
Auxiliary gas flow rate (L min^{-1})	1.25
Nebulizer gas flow rate (L min^{-1})	1.20
Extraction lens potential (V)	2000
Sampler cone	Nickel, 1.1 mm orifice diameter
Skimmer cone	Nickel, 0.9 mm orifice diameter
Mass resolution, $m/\Delta m$	300
Mass window (%)	10
Runs	400
Passes	1
Scanning mode	Peak hopping
Analysis time (min)	5

2.3. Optimization of experimental parameters of LA-ICP-MS and uranium isotope ratio measurements

Optimization of the experimental parameters of LA-ICP-MS was performed with respect to maximum $^{238}U^+$ ion intensity and minimum uranium hydride formation rate $^{238}UH^+/^{238}U^+$ using uranium with natural isotopic composition. Optimized experimental conditions are summarized in Table 1. Further details about the measurement procedure used are described elsewhere [22,23]. The measured uranium isotopic ratio was corrected to account for UH^+ formation, mass bias, and detector dead time. The mass bias factor (assuming an exponential correction [24]) was determined using NIST U020 standard solution added to flower leaf. The dead time of the ion detector of the ICP-MS was determined using a method described by Ketterer et al. [25] and was found to be 45 ns using 0.1 ng mL^{-1} of NIST U020 isotopic standard reference material.

3. Results and discussion

3.1. Isotope ratio measurements of uranium by LA-ICP-MS varying laser spot size in the 15–50 μm range

A relatively high laser power density (3.5×10^9 W cm^{-2}) — in order to avoid fractionation effects — in connection with the small laser crater diameter (down to 5 μm) can be obtained with the "Ablascope" laser ablation system. In Fig. 2a and b, the dried droplet of CCLU-500 and the laser craters generated on it under optimized ablation conditions are shown. The laser produces well-defined craters with a diameter of 10, 15, 25 and 50 μm if the laser beam is focused on the sample surface. Variation of the laser beam diameter has a direct influence on the amount of ablated material if the sample surface was scanned. Since the energy density of the laser remains constant it can be expected that the laser crater size is directly related to the intensity. Fig. 3a shows the dependence of the $^{238}U^+$ ion intensity signal on the different size of the focused laser beam, measured on the dried droplet of natural uranium solution on flower leaf surface. A good correlation between the measured ion intensity of $^{238}U^+$ and the diameter of the laser crater (i.e., the amount of ablated material) of the analyzed sample was found with a correlation coefficient (R) of 0.9988 (Fig. 3b).

If a substantial amount of material is transported into the plasma, it may cause a change in the plasma conditions and would result in a reduction of the ionization efficiency. In our experiment, the dependence of laser crater diameters does correlate linearly to the intensity of the peaks ($R^2 = 0.9988$), and therefore, will not affect the

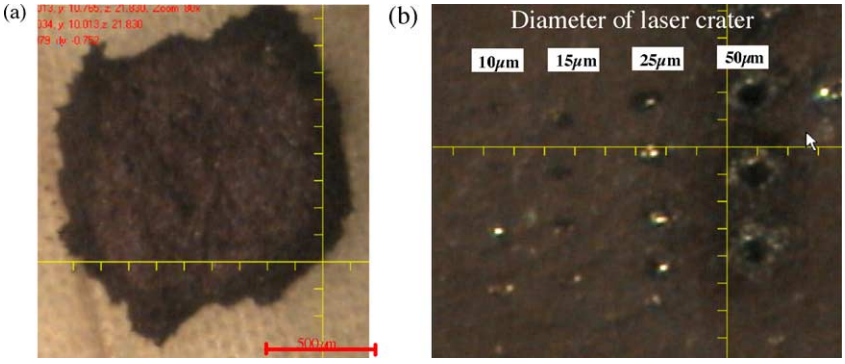

Fig. 2. Dried droplet of CCLU-500 isotopic standard reference material deposited onto flower leaf and craters of different diameters produced on the leaf under optimized conditions of LA-ICP-MS.

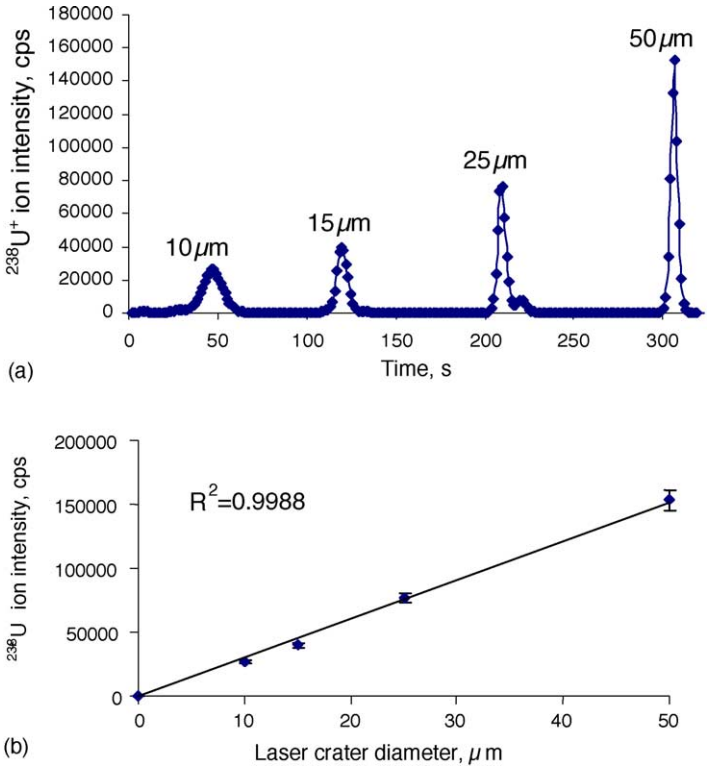

Fig. 3. (a) Dependence of $^{238}U^+$ ion intensity signal on the spot size (100 laser shots, repetition frequency 20 Hz) measured by LA-ICP-MS with cooled laser ablation chamber on the dried droplet of natural uranium standard solution (20 μL, U concentration 100 ng mL^{-1}) deposited onto the flower leaf. (b) Correlation curve of uranium ion intensity as a function of laser crater diameter measured by LA-ICP-MS with cooled laser ablation chamber.

Table 2
Precision and accuracy of uranium isotope ratio, measured in dried droplet of NIST U350, NIST U930 and CCLU-500 uranium isotope reference materials using cooled and non-cooled ablation chamber

Standard reference material	Isotope ratio	Measured isotope ratio			RSD%			Accuracy%			Certified isotope ratio
		15[a]	25[a]	50[a]	15[a]	25[a]	50[a]	15[a]	25[a]	50[a]	
Non-cooled laser ablation chamber											
NIST U350	$^{234}U/^{238}U$	0.00325	0.00340	0.00350	9.4	8.2	8.1	16.1	12.3	10.0	0.00387
	$^{235}U/^{238}U$	0.50714	0.50768	0.57982	6.3	6.1	5.9	7.2	7.1	−6.1	0.54648
	$^{236}U/^{238}U$	0.00286	0.00284	0.00281	7.9	7.3	6.9	−10.2	−9.4	−8.0	0.00259
NIST U930	$^{234}U/^{238}U$	0.17886	0.17906	0.18207	10.7	9.2	9.0	11.0	10.9	9.4	0.20097
	$^{235}U/^{238}U$	15.63	15.92	15.92	5.1	4.9	4.5	9.9	8.2	8.2	17.34
	$^{236}U/^{238}U$	0.04103	0.04091	0.04069	9.9	9.8	9.0	−8.9	−8.6	−8.0	0.01112
CCLU-500	$^{234}U/^{238}U$	0.00946	0.00966	0.00971	12.7	9.7	8.3	14.9	13.1	12.7	0.01112[b]
	$^{235}U/^{238}U$	0.89792	0.90091	0.90191	5.7	5.5	4.0	10.2	9.9	9.8	0.99991[b]
	$^{236}U/^{238}U$	0.00313	0.00268	0.00302	5.5	5.2	5.0	−12.1	3.9	−8.2	0.00278[b]
Cooled laser ablation chamber											
NIST U350	$^{234}U/^{238}U$	0.00372	0.00369	0.00276	2.0	1.6	1.4	4.2	4.7	3.2	0.00387
	$^{235}U/^{238}U$	0.5344	0.5366	0.5524	1.3	1.2	0.9	2.2	1.8	−1.1	0.54649
	$^{236}U/^{238}U$	0.00272	0.00265	0.00252	2.1	2.0	1.9	−4.8	−2.1	3.2	0.00259
NIST U930	$^{234}U/^{238}U$	0.19453	0.19494	0.19594	1.8	1.6	1.1	3.2	3.0	2.5	0.20097
	$^{235}U/^{238}U$	17.07	17.19	17.21	1.0	0.8	0.4	1.6	0.9	0.8	17.34
	$^{236}U/^{238}U$	0.19453	0.03715	0.03809	1.5	1.3	1.0	−2.2	1.4	−1.1	0.01112
CCLU-500	$^{234}U/^{238}U$	0.01083	0.01137	0.01124	1.5	2.0	1.6	2.6	−2.2	−1.1	0.01112[b]
	$^{235}U/^{238}U$	0.9889	0.9909	1.0049	1.3	1.2	0.9	1.1	0.9	−0.5	0.99991[b]
	$^{236}U/^{238}U$	0.00285	0.00284	0.00276	1.4	2.0	1.6	−2.4	−2.1	1.2	0.00278[b]

[a] Laser crater diameter in μm.
[b] Recommended value.

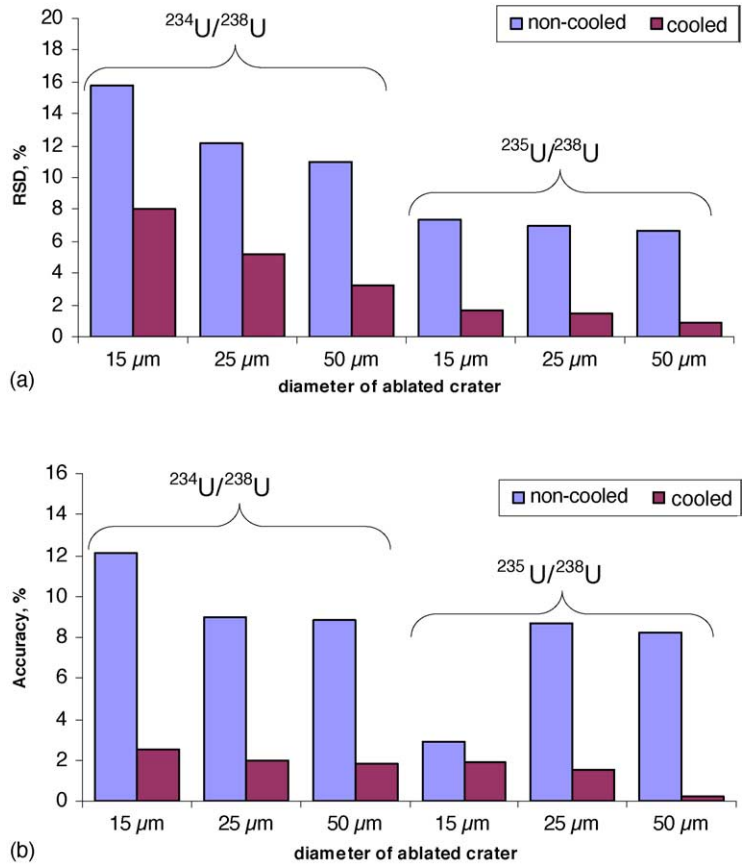

Fig. 4. (a) Precision of $^{234}U/^{238}U$ and $^{235}U/^{238}U$ isotope ratios, measured by LA-ICP-MS in dried droplet of uranium with natural isotopic composition using cooled and non-cooled laser ablation chamber. (b) Accuracy of $^{234}U/^{238}U$ and $^{235}U/^{238}U$ isotope ratios, measured in dried droplet of uranium with natural isotopic composition by LA-ICP-MS using cooled and non-cooled ablation chamber.

accuracy of the measurements with varying laser beam diameter.

3.2. Accuracy and precision of uranium isotope ratio measurements with non-cooled laser ablation chamber

The accuracy and precision of this LA-ICP-MS procedure for uranium isotope ratio measurements were studied using NIST U350, NIST U930 and CCLU-500 uranium isotope reference materials as well as uranium with natural isotopic composition. The results of these measurements are presented in Table 2 and Fig. 4a and b.

For the experiments with the non-cooled laser ablation chamber, the precision (relative standard deviation, $n = 6$) and accuracy were in the range of 4.0–12.7% and 6.1–16.1% for the uranium isotopic standards reference material, and 6.7–15.8% and 8.2–12.1% for natural uranium. All the measured accuracies and relative standard deviations (RSDs) were strongly dependent on the measured isotopic ratios as well as on laser crater diameter. Accuracy and precision were better with the higher uranium isotopic ratio in samples and larger laser beam focus. All data for precision and accuracy presented are comparable with previous measurements [17,26,27].

3.3. Accuracy and precision of uranium isotope ratio measurements with cooled LA chamber

An improvement of analytical results was observed when the ablation chamber of the laser ablation system was cooled to about −15 °C (see Table 2). The accuracy and precision in all measured samples were up to one order of magnitude better than in the case of the non-cooled LA chamber. For the measured uranium isotopic standards, for instance, precision for $^{235}U/^{238}U$ isotopic ratio with 50 μm spot size ranged from 0.4 to 0.9% RSD, whereas accuracies were in the range of 0.5–1.1%. For the uranium with natural isotopic composition (see Fig. 4a and b) the best precision and accuracy were also achieved for $^{235}U/^{238}U$ isotopic ratio with 50 μm laser crater diameter and found to be 0.9 and −0.2%, respectively. The same behavior for precision and accuracy was observed in $^{234}U/^{238}U$ isotopic ratios, which for cooled LA chamber (50 μm laser crater) were 3.2 and 1.8% in comparison to the non-cooled LA chamber with 11.0 and 8.8%, respectively.

The most probable reason for this improvement in precision and accuracy is that in the case of non-cooled analyzed sample (in comparison to the cooled one) the water vapor produced during the laser ablation of biological sample (flower leaf) is very difficult to control and will lead to changes in the plasma condition and ionization efficiency. However, when the ablated sample is cooled, these vapors have less effect on the plasma and therefore, result in increased precision and accuracy. In addition, the adsorption properties of the laser energy in ice are significantly better than in water matrix [28,29], which would also leads to improvements in the precision and accuracy of the measurements.

4. Conclusions

The goal of this work was pre-investigations of LA-ICP-MS with cooled laser ablation chamber for its application for element mapping (element distribution) in thin section of brain samples. We demonstrated that LA-ICP-MS is a very powerful element and isotope analytical technique for isotope ratio measurements on surfaces of biological samples. Using the cooled laser ablation chamber developed in this study, significant improvements (up to one order of magnitude) in the precision and accuracy of uranium isotopic ratios in comparison to the non-cooled laser ablation chamber can be achieved.

In addition, the application of LA-ICP-MS with cooled laser ablation chamber would be of great interest for precise determination of the ratios of different elements, that is widely used in geochronology for age dating (e.g., Rb–Sr, or U–Pb) and where the precision of the measurements are very crucial. In such case, beside the water vapors, significant elimination of fractionation effects may be possible due to more homogeneous spread of the laser energy in the cooled ablated sample and elimination of spontaneous evaporation from the sample elements with the low melting point.

Furthermore, coupling of multiple collector ICP mass spectrometer and laser ablation system with cooled chamber for determination of element isotopic ratios would results in addition improvement of the precision and accuracy of isotopic ratio measurements.

In future work, the application of LA-ICP-MS with cooled laser ablation chamber would be of great interest for microlocal analysis of element distribution in thin section of tissue samples (e.g., brain, liver, etc.).

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