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Abstract

Tree ring proxies are employed in dendroanalysis as a valuable tool for evaluating past anthropogenic contamination. A wide variety of analytical methods are used to quantify tree ring content for a broad spectrum of chemical elements. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is often used to investigate element concentrations in the tree rings. However, several issues regarding the representativeness of laser ablation measurements for trace elements have to be addressed before definitive conclusions can be drawn. In this study, High Resolution (HR)-ICP-MS has been implemented to analyze the trace concentration of uranium (U) in annual growth rings of oak trees (*Quercus Petraea*) using both laser ablation (LA) and solution modes. The three tree samples taken for the present study were located upstream (with respect to the hydrologic system) of a former uranium mine site at Rophin (Puy de Dôme, France), where mining operations were performed between 1949 and 1958. According to the LA-HR-ICP-MS technique, two-dimensional quantitative (2D) mapping of uranium has developed to study the spatial distribution of uranium at the tree ring surface. A strong heterogeneity was observed, leading to an average uranium concentration with high uncertainty (50-66%). Pressed pellets of the standard reference material, NIST1570a spinach leaves and uranium doped cellulose powder were adopted as the uranium standards for quantification. No agreement was found between uranium concentrations measured after acid digestion and the values obtained by laser ablation. This comparison highlights the limitations of laser ablation technique; hence the solution mode should be preferred for quantifying uranium trace concentrations in tree rings. However, low uncertainty (< 9%) was found with the HR-ICP-MS solution, this result should be compared with the deviation observed both at the tree scale (≈ 40%) and across the ≈ 10 m sampling area (≈ 50%).

Keywords: HR-ICP-MS, laser ablation, tree rings, uranium mapping, mining activities.

1. Introduction

Dendrochemistry, i.e. the chronological quantification of chemical elements in tree rings, is based on the assumption that element concentrations in the tree-ring series reflect to some degree the chemical signal from the environment during the year of ring formation [1]. As a consequence, these annually resolved and precisely dated proxy records, available over large areas of the earth's land surface, have been widely used to track past and present pollution history. Applications include the biomonitoring of environmental pollution [2], detection and dating of volcanic eruptions [3,4], and

reconstruction of longer-term changes in environmental conditions [5–9]. A successful application of dendrochemistry implies that trees chronologically record changes provided the availability of certain elements in their environment. Yet the pathways of uptake and the incorporation and potential relocation of elements in the xylem remain poorly understood and vary widely among tree species [10,11]. More specifically, a careful selection of tree species that minimizes the radial translocation of elements, as well as the radial tendencies in element concentrations from pith to bark and physiological differences between heartwood and sapwood is a prerequisite for the proper use of radial distribution patterns in biomonitoring [12–14]. Moreover, this guarantees the adequacy of dendrochemistry in conducting historical environmental monitoring [15].

Dendrogeochemical studies specifically dedicated to uranium are scarce in the scientific literature. Edmands et al. [16] demonstrated the reliability of oak trees growing in a contaminated bog adjacent to a nuclear industrial facility in order to reconstruct shallow groundwater uranium contamination. In Northern Italy, Monticelli et al. [17] detected comparable uranium profiles in *Larix decidua* Miller (European larch) tree-ring series and in Lake Scais sediment cores sampled in the vicinity of the Val Vedello uranium orebody (Orobic Alps). Märten et al. [18] documented the contamination history of an area in Thuringia (Germany) influenced by 40 years of uranium mining and subsequent remediation actions by means of the dendroanalysis of oak trees (*Quercus* sp.). Based on the similar radial uranium distribution patterns of the three trees studied, they concluded the suitability of this technique for investigating past and recent uranium contamination in mining areas. Conversely, in Ohio (USA), Mitchell et al. [19] failed at quantitating the uranium contamination in cores from *Acer saccharum*, *Quercus coccinea* and *Populus deltoides* trees growing on the site of a former uranium metal processing facility.

Besides the potential interest of this method in reconstructing uranium pollution, as revealed by a majority of the aforementioned studies, another prerequisite herein is the precise and reliable quantification of element concentrations. A wide variety of analytical methods have been used in dendroanalysis to quantify tree-ring content for a broad spectrum of chemical elements, including: Instrumental Neutron Activation Analysis (INAA) [20], Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [21–23], Thermal Ionization Mass Spectrometry (TIMS) [16,24], X-ray fluorescence spectroscopy [25], Proton Induced X-ray Emission [26], and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) [17,27–29]. A common way to quantify uranium in tree rings is based on the LA-ICP-MS technique [17,18]. LA-ICP-MS does indeed yield a fast direct elemental analysis offering certain advantages, namely it is: (i) selective and nearly non-destructive, (ii) operational with minimal sample preparation required, and (iii) capable of providing high spatial resolution up to 10-100 µm. However, achieving of reliable quantitative measurements can prove to be difficult [30]. The main disadvantage inherent in this technique is its lack of certified reference materials for calibration [29,31–33]. Furthermore, the distribution of the analyte in the sample may also adversely affect the result. It is well known that tree rings are composed of both earlywood and latewood [34]. Also variable densities of the wood inside tree rings were identified, due to seasonality and climate variation [35]. Some researchers have pointed out that tree rings may be viewed as heterogeneous material at the tree ring scale when conducting LA-ICP-MS analyses (e.g. [36]). However, such studies are scarce, and the crucial question about the representativeness of data obtained by laser remains poorly documented.

The aim of the present work therefore is twofold: (i) to characterize uranium heterogeneities by developing quantitative two-dimensional (2D) image mapping; and (ii) to compare uranium concentrations obtained by LA-ICP-MS with those derived from solution. The precision of the measurements is discussed in light of the deviation observed both at the tree scale and across the ≈

10 m sampling area. The study will enable to determining the best method for a reliable quantification of uranium concentration in tree rings, thus providing clear information for further study on uranium pollution.

2. Materials and Methods

2.1 Site description and sampling

2.1.1 Study site

Rophin is one of 17 storage site for of uranium mining residues produced in France during the 20th century. Uranium is a metallic element that naturally occurs in Rophin area.

The initial mining activity intended for radium extraction dates back to 1924. Uranium was then extracted from 1948 to 1957 by the French Atomic Energy Commission (CEA). Several other ore bodies, discovered in the vicinity of the Rophin mine, were operated as well, *e.g.* Gagnol (1949-1953), Etang du Reliez (1951-1954), Reliez (1949-1952) and Bancherelle (1952-1954) (see Fig. 1).

Between 1948 and 1957, the mechanical leaching of some 44,625 tons of ore produced 33.9 tons of uranium. About 30,000 tons of mine waste are now stored at the site of former Rophin mine (Fig. 2) and covered by vegetation.

2.1.2 Sampling procedure

Oak samples (*Quercus petraea*) were collected from three trees (called T1, T6 and T7) located upstream of the storage residues (*i.e.* not affected by runoff water from mining activities). The trees are separated by a distance of about tens of meters at the same station and lie at an average altitude of 525 m (Fig. 2) and Table S1. (Appendix). However, trees were sampled upstream and downstream from the Rophin site in order to assess past transfer/transport that occurred during mining activities. As part of this methodological development work, we have chosen to work on trees that are not impacted. Only the analytical results of these trees are therefore presented.

Tree rings samples were collected on each tree using an increment borer (Pressler inner diameter: 5 mm). The selected trees were healthy, grew under similar surrounding natural conditions and belong to the same cohort (*i.e.* germination and growth at roughly the same time, circa1900). The tree ring samples (n = 5) were extracted from the trunk at about 1.5 m above ground in July 2015. For T6, sampling was performed at three locations about 120° from one another.

The sampling strategy allows assessing uranium heterogeneity at the ring level (≈ µm scale), the tree (≈ m scale) and the local spot where the trees were sampled (≈ 10 m scale). Since they are expected not to have been influenced by mining activities, the uranium concentrations should thus be constant and correspond to the geochemical background. Sampling was conducted with great care to avoid any contamination, *i.e.* the borer was washed with ethanol and Milli-Q water between each core extraction. After sampling, all the samples were immediately sealed in individual plastic tubes and transported to the laboratory for dendroanalysis.

The tree ring samples were dried at room temperature, and regular abrasive paper (grit 500) was used to polish them. To avoid any cross-ring contamination, the samples were then cleaned of dust by blowing with compressed air.

The samples were scanned (1,600 dpi) and the CooRecorder software [37] was run to identify the dating of each ring (to within 1 year). The time period covered by these tree growth rings is: 130 years for T1, 118 years for T6, and 152 years for T7. The rings formed in 1958 which correspond to

the last year of the on-site uranium mining activity, were arbitrary chosen for purposes of the present work; they were then cut into pieces approx. 2.4 cm in length so as to fit into the laser ablation cell.

2.2 Chemicals and reagents

Ultrapure water (18.2 MΩ·cm resistivity at 25° and < 5 µg L^{-1} TOC) obtained from a Milli-Q Advantage A10® system (Merck Millipore, France) was used for labware cleaning and preparation of solution analyses. Concentrated nitric acid (HNO_3, 70%, Fischer Scientific) was purified with the Savillex DST-1000 sub-boiling distillation system. Ultrapure NORMATOM® 30-32% hydrogen peroxide (H_2O_2) intended for wood acid digestion was purchased from VWR BDH® Chemicals. Cellulose powder (20 µm granulometry) and standard reference material NIST 1570a spinach leaves intended for direct analyses of uranium by laser ablation HR-ICP-MS were purchased from Sigma Aldrich and the National Institute of Standards and Technology (NIST, USA), respectively. The NIST 612 reference served to optimize the laser operating parameters. Uranium and thallium "PlasmaCAL" stock solutions at 1000 mg L^{-1}, purchased from SCP Science, were used for both calibration and the internal standard solution preparation prior to uranium analyses conducted by HR-ICP-MS in solution mode.

2.3 Instrumentation

The uranium in tree rings was directly analyzed by LA-HR-ICP-MS with a New Wave Research UP213 Nd-YAG laser ablation system (New Wave Research Inc., Huntingdon, Cambridgeshire, UK) coupled to a single-collector sector field ICP-MS instrument (ELEMENT XR, Thermo Scientific, Bremen, Germany).

This laser system is equipped with a standard ablation cell (volume 30 cm^3) mounted on a motorized xyz stage with sub-micron resolution for sample movement. The target visual inspection is performed by means of a built-in microscope/CCD camera system. The ablation cell was flushed with helium (carrier gas), which transported the laser-induced aerosol to the inductively coupled plasma mass spectrometer.

The LA-HR-ICP-MS system was optimized for sensitivity (e.g. gas flows, torch position) prior to sample analysis. The instrument was first tuned in solution mode, and the liquid sample introduction system was then replaced by the laser ablation device with the plasma still switched on.

The optimization step in laser mode was carried out using NIST 612 glass reference material with the following laser parameters: raster scan with raster spacing = 100 µm/scan, speed = 5 µm s^{-1}, repetition rate = 10 Hz, laser beam diameter = 80 µm, and laser energy output 60% (1.12 mJ). The helium carrier and argon sample gas flows were adjusted with respect to maximum sensitivity and stability for ^{43}Ca, ^{139}La, ^{232}Th and ^{238}U ion signals, as well as for a low $^{232}Th^{16}O/^{232}Th$ ratio (0.03%) and a $^{232}Th/^{238}U$ ratio close to one. The method's data acquisition set-up in laser mode, including mass offset and peak centering, was carried out with the ablation of NIST 612 at a lower energy output of 40% (0.33mJ). The detector cross-calibration was performed using ^{36}Ar.

The uranium concentrations of digested sample solutions were measured by HR-ICP-MS, featuring a liquid sample introduction system equipped with an ESI SC-E2 fast system, a Peltier cooler PC^3 containing a cyclonic spray chamber, a MP^2 peristaltic pump, and a GE micromist nebulizer. The optimized (LA)-HR-ICP-MS parameters are summarized in Table 1.

2.4 Applicable standard and sample preparation procedures

2.4.1 Laser ablation HR-ICP-MS

The quantification of element concentrations in LA-ICP-MS requires suitable external standards. For tree rings, quantification still presents a challenge because matrix matched standards for calibrations are not available. Consequently, homemade doped cellulose powder with a uranium standard solution was used [27,38,39]. The choice of cellulose powder as an external standard can be justified by the fact that this powder is the major component of wood and moreover its composition is similar to most types of wood. Standard reference material SRM NIST 1570a spinach leaves (U content = 0.155 ± 0.023 mg kg^{-1}) was introduced as the quality control and external standard.

Pellets of uranium-doped cellulose were prepared as follows: 2 g portions of powder were placed into PFA Savillex vials and doped with 10 mL of solution containing various uranium concentrations. The mixture was then shaken with a magnetic stirrer until obtaining a homogeneous solution. Next, it was dried at 80°C until constant weight using the closed evaporation system EvapoClean® (ANALAB) in order to prevent external contamination. The powders were ground in a mixer mill (Retsch MM 400, Germany) with 10 mL zirconium oxide (ZrO_2) grinding jars and two 9 mm ZrO_2 balls. The powders were homogenized for 3 min at a frequency of 25 Hz. The grinding parameters were carefully selected in order to obtain the smallest particle size and shortest preparation time. The dried powders were compacted into 13 mm diameter, 2 mm thick disc-shaped pellets at a pressure of 8 tons for 5 min in a Specac® 15T manual hydraulic press. The purchased standard NIST 1570a was transformed into pellets according to the same procedure.

The accuracy of the calibration step was verified by analyzing the pellets output. The uranium content was checked by means of HR-ICP-MS after microwave acid digestion using Anton Paar Multiwave 3000®. Results are displayed in Table 2; they are in close agreement (within measurement uncertainty (2σ)) with the gravimetric concentration values for both external standards.

In order to fit the samples into the ablation cell, tree core samples were cut into pieces approx. 2.4 cm long as indicated above (a mark was applied to identify the ring location). They were then fixed with Araldite® crystal adhesive onto an epoxy mount. The choice of ^{13}C as the internal standard for the external quantification method by LA-ICP-MS is common in dendroanalytical studies [14,27,28,40]. Indeed, carbon is widely used as internal standard when analyzing organic samples by LA-ICP-MS due to its uniformity across samples and its natural variation in wood can be neglected, since it is in the per-mille range [41]. Internal standardization allows correcting for various ablation efficiencies, matrix effects, differences in transport efficiency, and wood density properties [42]. Furthermore, the ^{13}C signal intensity in tree rings has the same order of magnitude as that those measured in cellulose and SRM NIST 1570a. However, ^{13}C must be applied with caution; indeed, Frick and Günther [43] have shown that carbon is not an optimal internal standard, as its transport into the ICP can partly occur in the form of carbon dioxide, which will lead to transport properties and efficiencies that can markedly differ from those elements that are transported as particulate matter only. Despite this criticism,^{13}C has been shown to be a suitable internal standard due to its considerable concentration and relatively homogeneous distribution. In addition, evidence of the previous study on trace element analyses in tree rings questioning the use of carbon as internal standard are not reported. Nonetheless, carbon concentrations in samples and standards should be determined with precision. The analyses were carried out with a Thermo Scientific Flash 2000 CHNS/O elemental analyzer, and the results are 39.9 ±0.9; 42.2 ±0.2; 46 ±1 % w w^{-1} (± 2σ) for NIST 1570a, Cellulose pellets and tree rings respectively. The average carbon content (n = 5) found in wood exceeds that for cellulose powder by about 10% and that for NIST 1570a by some 14%. This difference between wood and cellulose powder is greater than expected (by about 5%, value given in Hoffman et al. [27]).

2.4.2 HR-ICP-MS in solution mode

For the acid digestion of samples, individual rings were cut using a sterilized scalpel washed in ethanol and 5% (v/v) nitric acid and then rinsed with Milli-Q water between cuts. The obtained samples weights are respectively: 30, 31, 27, 24 and 12 mg for T1, T6-a, T6-b, T6-c and T7. The mineralization procedure was adapted from that described by Bukata and Kyser [44] which is suitable for these low mass samples. The wood sections were washed in 0.1 M nitric acid for roughly 1 h and then dried in an oven for 7 h at 70°C. Afterwards, the samples were weighed in a 5 mL Savillex container and 1 mL of concentrated HNO_3 was added. The containers were placed into an oven at 80 °C for one day and then 0.5 mL of ultra-pure 30% H_2O_2 was added and placed in the oven for an additional day. Once samples were digested, the solutions were cooled down and then diluted in 0.35 M HNO_3 using the working solution of internal standard prepared at a concentration of 50 ng L^{-1}. Suitability and accuracy of the method were tested through digested NIST 1570a with same procedure.

The external calibration solutions with uranium concentrations ranging from 10 to 50 ng L^{-1} were prepared by diluting uranium stock standard solution with 50 ng L^{-1} Tl solution in 0.35M HNO_3. The correlation coefficient (R^2) values of calibration curves were between 0.999 and 1.00 over the study duration.

2.5 2D mapping of uranium by LA-HR-ICP-MS

2.5.1 Identification of tree ring ablation area

Before analyses conducted by LA-ICP-MS, the tree rings were characterized by a Leica DCF290 HD Digital camera in order to locate the optimal ablation area. This step is important as it provides information on the surface structure of the tree ring before the ablation, size and dimension of the samples. All studied samples are shown in Figure 3.

The rings are composed of two parts, *i.e.* earlywood and latewood formed respectively during spring and summer/early autumn (until the beginning of the vegetative rest period). Earlywood is porous and characterized by white cells with large diameters, whereas latewood is composed of small cells and densely-layered, strong thick-walled cells. Not all rings are uniform; some are thinner, some thicker, some light and some dark. Among the samples, tree ring widths actually range from 0.7 to 4 mm depending on seasonal conditions, e.g. rainfall, temperature, and soil nutrients.

For the sake of optimization and representativeness, latewood was chosen in order to allow a maximum amount of material to be ablated; moreover 1 mm^2 surface (constant across all rings) was chosen with an ablation pattern containing 56 lines. Note that the digested part for uranium measurements by HR-ICP-MS solution also corresponds to latewood.

2.5.2 Laser data processing and automation of 2D quantitative uranium mapping at tree ring surface

The HR-ICP-MS was synchronized with the laser ablation device in external trigger mode. Then the optimum LA-HR-ICP-MS method developed for quantitative uranium mapping was used (see Table 1 for operational details). Prior to actual data acquisition, a pre-ablation was performed to remove any surface contamination. The tree rings were laser ablated though the use of single line patterns. The quantitative 2D uranium images were obtained from 56 lines (7 x 8) of ablation, and the total ablated surface was approx. 1 mm^2. The analysis allowed measuring of 55 scans in 1 min, with 20 s of sample acquisition during laser ablation once the laser was fired and 40 s of background collection with no ablation. Overall, the total analysis time by sample was about 2 h. Due to the slow aerosol washout time (50 s) already mentioned elsewhere [45], the spatial resolution was limited (100 µm(x)-80 µm(y)). The tree ring analyses were bracketed by standard measurements (five lines per standard).

^{238}U and ^{13}C time-resolved raw data were exported from the HR-ICP-MS in ASC or FIN format (Glitter software users) and processed offline using a series of in-house subroutines written in VBA language for Microsoft Excel 2010™. The average gas blank signal intensities for all elements recorded without laser ablation were calculated and then subtracted from the signal intensities measured during standard and sample ablation. The ^{238}U signal intensity at each time slice was normalized relative to the internal standard ^{13}C signal intensity, and both the average and standard error of the normalized ratio were calculated after an iterative procedure to remove outliers by means of the modified Thompson τ test [46,47]. A time drift correction was applied with a linear interpolation over time in using normalized ^{238}U signal intensities from the bracketing standard reference materials. The uranium concentration and associated error (k=1) of each analysis were calculated from the following equations below:

$$[\mathrm{U}]_{\mathrm{SMP}} = [\mathrm{U}]_{\mathrm{STD}} \times \frac{[\mathrm{C}]_{\mathrm{SMP}}}{[\mathrm{C}]_{\mathrm{STD}}} \times \frac{\bar{\mathrm{I}}_{\mathrm{U}}^{SMP}}{\bar{\mathrm{I}}_{\mathrm{C}}^{SMP}} \times \frac{(\mathrm{N}_2 - N_1)}{\left[\left[\left(\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{STD}}{\bar{\mathrm{I}}_{\mathrm{C}}^{STD}}\right)_1 \times (\mathrm{N}_2 - \mathrm{N}_i)\right] + \left[\left(\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{STD}}{\bar{\mathrm{I}}_{\mathrm{C}}^{STD}}\right)_2 \times (\mathrm{N}_i - \mathrm{N}_1)\right]\right]}$$

where $[\mathrm{U}]_{SMP,STD}$ and $[\mathrm{C}]_{SMP,STD}$ are the uranium and carbon contents in the sample (SMP) and standard reference material (STD); $\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{\mathrm{SMP}}}{\bar{\mathrm{I}}_{\mathrm{C}}^{\mathrm{SMP}}}$ the average normalized ^{238}U intensity signal in sample; $\left(\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{\mathrm{STD}}}{\bar{\mathrm{I}}_{\mathrm{C}}^{\mathrm{STD}}}\right)_{1,2}$ the average normalized ^{238}U intensity signals measured in bracketing standards 1 and 2; and N_1, N_2 and N_i are the analysis numbers in the sequence.

$$\mathrm{Err}_{[\mathrm{U}]_{\mathrm{SMP}}} = [\mathrm{U}]_{\mathrm{SMP}} \times \sqrt{\left(\frac{\mathrm{Err}_{[\mathrm{U}]_{\mathrm{STD}}}}{[\mathrm{U}]_{\mathrm{STD}}}\right)^2 + \left(\frac{\mathrm{Err}_{[\mathrm{C}]_{\mathrm{SMP}}}}{[\mathrm{C}]_{\mathrm{SMP}}}\right)^2 + \left(\frac{\mathrm{Err}_{[\mathrm{C}]_{\mathrm{STD}}}}{[\mathrm{C}]_{\mathrm{STD}}}\right)^2 + \left(\frac{\mathrm{Err}_{\left(\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{SMP}}{\bar{\mathrm{I}}_{\mathrm{C}}^{SMP}}\right)}}{\left(\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{SPM}}{\bar{\mathrm{I}}_{\mathrm{C}}^{SPM}}\right)}\right)^2 + \left(\frac{\mathrm{Err}_{\left(\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{STD}}{\bar{\mathrm{I}}_{\mathrm{C}}^{STD}}\right)}}{\left(\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{STD}}{\bar{\mathrm{I}}_{\mathrm{C}}^{STD}}\right)}\right)^2}$$

$$\text{with } \left(\frac{\mathrm{Err}_{\left(\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{STD}}{\bar{\mathrm{I}}_{\mathrm{C}}^{STD}}\right)}}{\left(\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{STD}}{\bar{\mathrm{I}}_{\mathrm{C}}^{STD}}\right)}\right)^2 = \frac{\left(\mathrm{Err}_{\left(\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{STD}}{\bar{\mathrm{I}}_{\mathrm{C}}^{STD}}\right)_1} \times (\mathrm{N}_2 - \mathrm{N}_i)\right)^2 + \left(\mathrm{Err}_{\left(\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{STD}}{\bar{\mathrm{I}}_{\mathrm{C}}^{STD}}\right)_2} \times (\mathrm{N}_i - \mathrm{N}_1)\right)^2}{\left[\left(\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{STD}}{\bar{\mathrm{I}}_{\mathrm{C}}^{STD}}\right)_1 \times (\mathrm{N}_2 - \mathrm{N}_i) + \left(\frac{\bar{\mathrm{I}}_{\mathrm{U}}^{STD}}{\bar{\mathrm{I}}_{\mathrm{C}}^{STD}}\right)_2 \times (\mathrm{N}_i - \mathrm{N}_1)\right]^2}$$

Where Err are the standard deviations (k=1) calculated from measured values (carbon concentrations in sample and standards, normalized ^{238}U signal intensities, gravimetric values (uranium concentrations in homemade standards) and reported by NIST (uranium concentration in the NIST1570a standard).

The quantitative two-dimensional mappings of the uranium distribution were obtained by plotting the signal intensity of each line based on the recalculated coordinate. 2D images were built by processing data with the Origin 8.6® software.

2.6 Limits of detection (LOD)

The limits of detection (LODs) of the LA-HR-ICP-MS for uranium were calculated based on 3 standard deviations (sd) of gas blank ^{238}U signal intensity measurements from five replicate analyses of NIST 1570a. In solution mode, the LODs were calculated over 3 standard deviations of the intercept parameter of the calibration line.

The LODs of uranium for both instrumental techniques were determined and listed in Table 3. The LODs for laser ablation range from 7 to 24 ng kg^{-1}, which is between approx. 20 and 100 times higher than those found in solution mode. This difference is primarily owed to the greater variability in signal intensities for LA compared with solution mode. In addition, the amount (mass) of sample transported into the plasma by LA is less than that in solution mode despite the dilution factor of the latter [48].

3. Results and discussion

3.1 Uranium distribution in tree rings

Uranium is present in plants despite the fact that it performs no known metabolic function [19]; in living systems, it even has a clearly toxic function. Since uranium does not constitute a main tree nutrient, it is found in low concentrations. To obtain the spatial distribution of uranium in the tree rings, the samples were pasted onto an epoxy support, scanned line by line with a focused laser beam and ultimately analyzed by HR-ICP-MS. The two-dimensional images (signal of ($^{238}U/^{13}C$)) and histograms of uranium concentration distribution are shown in Figure 4. The spatial resolution of 2D images depends on the integration time of the mass spectrometer instrument as well as on the washout time of the laser-generated aerosol through the transport system, including the ablation cell and transport tubing [49]. Furthermore, the signal obtained by LA-ICP-MS is not directly attributable to a specific location on the sample due to the involvement of sample transport and diffusion, unless considerable care is taken during the analysis [50]. The figures obtained show that the uranium distribution at the ring scale is indeed heterogeneous, leading to a mean concentration with a significant associated error (1σ) on the order of 50% to 66% (prior to the rejection of outliers). Moreover, the uranium distribution differs in each sample; it appears to be nearly homogenously distributed in tree ring T1, whereas in the other samples, the distribution seems quite heterogeneous. A recent study [51] evaluated the distribution of some elements in the tree rings of Tipuana tipu (*Fabaceae*). Results revealed a non-random distribution of these chemical elements within the rings, with a higher content in the cell walls of vessels and lower content in the fibers. In our case, uranium appears to be highly concentrated (> 200 µg kg^{-1}) in some parts of tree rings (hot spots), yet no correlation was observed between these "hot spots" and any specific tree ring location. The reasons for these localized maxima are unclear and the mechanism that controls uranium distribution is not yet known well enough to explain these observations. We can however hypothesize that this may be correlated with the tree ring anatomy. Tree rings can indeed be considered as heterogeneous or multi-phase samples (see Fig. 3), and trace elements taken up by a tree are fixed depending on their affinity to the different tree ring cells causing this heterogeneity. This assumption undoubtedly requires more substantiation. However, Narewski *et al.* [52] found that the elements present at higher concentrations (major elements) in bark samples are characterized by relative standard deviations (RSD) of the average concentration below 15%; for elements with much lower average concentrations, higher RSD values between 20% and 30% were obtained. Further studies are needed to gain more complete information. Nonetheless, an inhomogeneous elemental distribution leads to poor measurement precision and can result in a non-representative sampling by laser [53]. Data accuracy and interpretation (i.e. the quantitative analysis) can also be called into question. This aspect will be addressed in greater detail in the following section.

3.2 Quantification of analytical data in laser ablation mode

Elemental quantification in tree rings by means of LA-HR-ICP-MS is a challenging task because of the difficulty involved in finding a matrix that exactly matches the sample characteristics. In our study, calibration was carried out with two types of pressed pellets, and all count rates were normalized to ^{13}C. A slight difference in uranium content between the two methods of quantification (uranium-doped cellulose pellets and NIST 1570a) was observed (Figure 5). Cellulose pellet heterogeneity at the micron scale was indeed detected, which may explain this difference. The effects of sample grinding time and particle size are closely correlated with sample heterogeneity [31]. The longer the grinding time and the smaller the particle size, the higher the level of measurement precision. Nevertheless, when taking into account the uranium distribution and resulting high measurement uncertainty, this difference is not statistically significant. For the sake of precision, NIST 1570a was used as the external standard for elemental quantification in tree rings by LA-HR-ICP-MS.

3.3 Comparison of laser ablation and solution uranium data

A comparison between laser ablation and solution data of the tree ring analysis is presented in Figure 5. The uranium concentrations measured after acid digestion are significantly different from the average values (from 56 ablation lines) obtained by LA-HR-ICP-MS. This discrepancy can be explained by sample inhomogeneity, which was highlighted by the 2D mapping (see Fig. 4). For sample T1, whose uranium is nearly homogenously distributed, a consistency indeed exists between the result obtained by acid digestion and that recorded by laser ablation, whereas for the other samples, no agreement was found. The uranium concentration is systematically overestimated for LA-HR-ICP-MS, with the relative standard deviation ranging from 50% to 66% (1σ). This finding would indicate that the method adapted to 2D mapping is not adequate for absolute uranium quantification. Although the laser beam has ablated a wide area, the amount of ablated material may not be sufficient for good sample representativeness. The resulting ablated mass strongly depends on both the laser ablation process (scan modes, beam diameter, energy, number of lines or spots, etc.) and sample properties (density, thermal conductivity, etc.). Even though a large number of publications about trace element quantification in tree rings by LA-ICP-MS exists, the ablated mass and sample heterogeneity are seldom discussed. This point may have major consequences for the interpretation of results. Gough and Ridley [54] found, for certain trace elements, that duplicate analyses within a given tree ring indicated a tremendous difference in results. In this case, the possible differences between years (rings) cannot be assessed. In the present work, the ablated mass of material per tree ring equals approx. 1 mg, with this value being of the same order of magnitude as that mentioned by Prohaska *et al.* [55] (1-2 mg), but lower than that of Hoffman *et al.* [27] (≈ 5 mg). Due to the small ablated mass of material, the quantification by LA-ICP-MS for inhomogeneous samples might be limited without any matrix-matched calibration standards. Increasing the level of analytical precision and accuracy while overcoming heterogeneities would require either ablating a significant area in order to produce a sufficiently representative quantity of material or else grinding the wood to fine particles for pressing into laser ablation pellets. The latter approach is not only time-consuming but also a potential source of errors by contamination during sample preparation. Since quantification by laser ablation for heterogeneously-distributed tree ring elements appears to be a complicated issue, the literature contains only a very limited discussion on comparisons of elemental quantification in tree rings by ICP-MS laser ablation and ICP-MS solution. Nonetheless, Hoffman *et al.* [27] and Watmough *et al.* [36] did find good agreement between acid digestions values and values obtained by laser ablation for tree ring samples. Despite these findings, the Hoffman *et al.* work mentioned that the ablation process is complex and undermines both accuracy and calibration, while Watmough *et al.* indicated that elemental concentrations recorded by laser ablation are likely to differ slightly

from those recorded by acid digestion. Laser ablation can certainly become more representative when vaporizing a sufficiently large sample mass, but the most accurate method at the tree ring level is its digestion. The solution mode was thus chosen for the following section. If measurement accuracy at the ring level is important, then this aspect must be "balanced" against the elemental distribution heterogeneity in the ring at the level of the entire tree and the sampling area. This aspect will be discussed below.

3.4 Uranium concentration in rings at the level of the entire tree and sampling area

In growth ring T6, uranium was measured at three locations along the circular path of the tree ring (figure 5). For the same ring sampled at different trunk locations (at the same height), the uranium concentration only varies slightly. Here, the mean uranium concentration for all three T6 samples equals: 5.2 ± 2.2 (1σ) µg kg^{-1}. However, this variation is smaller than that obtained by Prohaska *et al.* [38] (up to 60%), which was explained by the changing proportion of compression wood on the various sides of the tree stem. In this study, the analyzed tree T6 is not affected by compression, mainly due to the wind, slope or proximity to another tree. The deviation (≈ 40%) is much higher than the post-digestion measurement precision (< 9%); a comparison should be drawn with the deviation at the sample location spot. The uranium concentrations recorded in the three trees are of the same order of magnitude, with a mean concentration of: 4.5 ± 2.2 (1σ) µg kg^{-1}. The deviation (roughly 50%) however is also much higher than that obtained for a single tree ring. Although it is important for trace element measurement uncertainty in the tree rings to be low, this condition must be placed in perspective if deviation at the sample location site is significant.

4. Conclusion

LA-HR-ICP-MS and HR-ICP-MS solution mode have been applied to measure uranium concentration in oak tree rings. No agreement between the results obtained with these two techniques was found, except for one sample (T1_1958). While LA-ICP-MS is often used in the literature to quantify elements in tree rings, these investigations have shown that before implementing laser ablation, it should first be clarified whether the sample is sufficiently homogeneous to produce representative results. Laser ablation only becomes worthwhile if certain conditions are met. In the present work, the uranium distribution in tree rings was found to be very heterogeneous, a finding highlighted by the 2D mapping that led to average values being associated with significant uncertainty (50% to 66%). Note that quantification is feasible with commercially available spinach leaves meeting the NIST 1570a Standard. The origin of this heterogeneous uranium distribution has yet to be well understood, but it may be related to the low concentration values. As regards quantification by laser ablation, the mean value is overestimated, in association with significant error. The ICP-MS solution is therefore preferable for the absolute quantification of trace elements in tree rings; even though sample preparation is labor intensive and can increase the likelihood of contamination, it is much more sensible and offers lower uncertainty (< 9%). This consideration however should be treated with caution. At the tree level, uranium concentration may vary as a function of location along the circular path of the tree ring, leading to a mean concentration with an RSD of approx. 40%. Compared to the deviation (≈ 50%) at the sample location level, it is preferable to use the same tree ring to analyze several samples taken from different trunk locations and then average the results. The ICP-MS solution measurement will provide an accurate quantitative value at the level of the ring whereas the measurement average will give a good concentration representativeness at the level of the tree.

In contrast, laser ablation is a powerful technique for developing quantitative 2D mapping; this technique may improve understanding of the trace element distribution mechanisms in tree rings.

Laser ablation remains preferable when the tree ring is narrow and impossible to be cut, in which case heterogeneity must be taken into account. It is recommended to make several ablation lines (or spots) in order to cover a large tree ring area.

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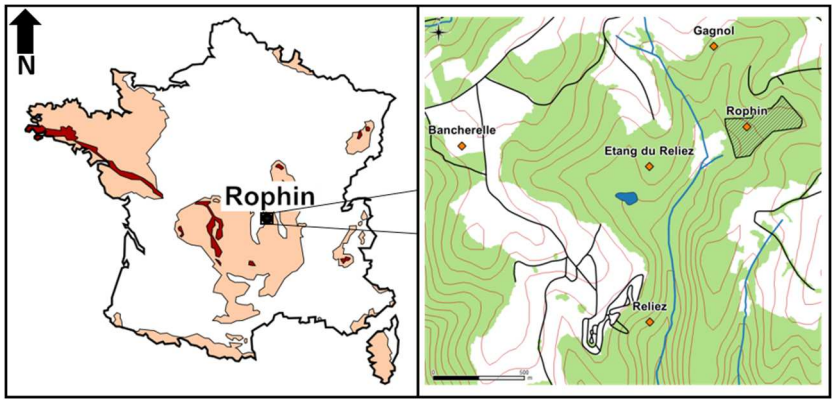


Figure 1: Location of the radioactive storage site at Rophin (France)

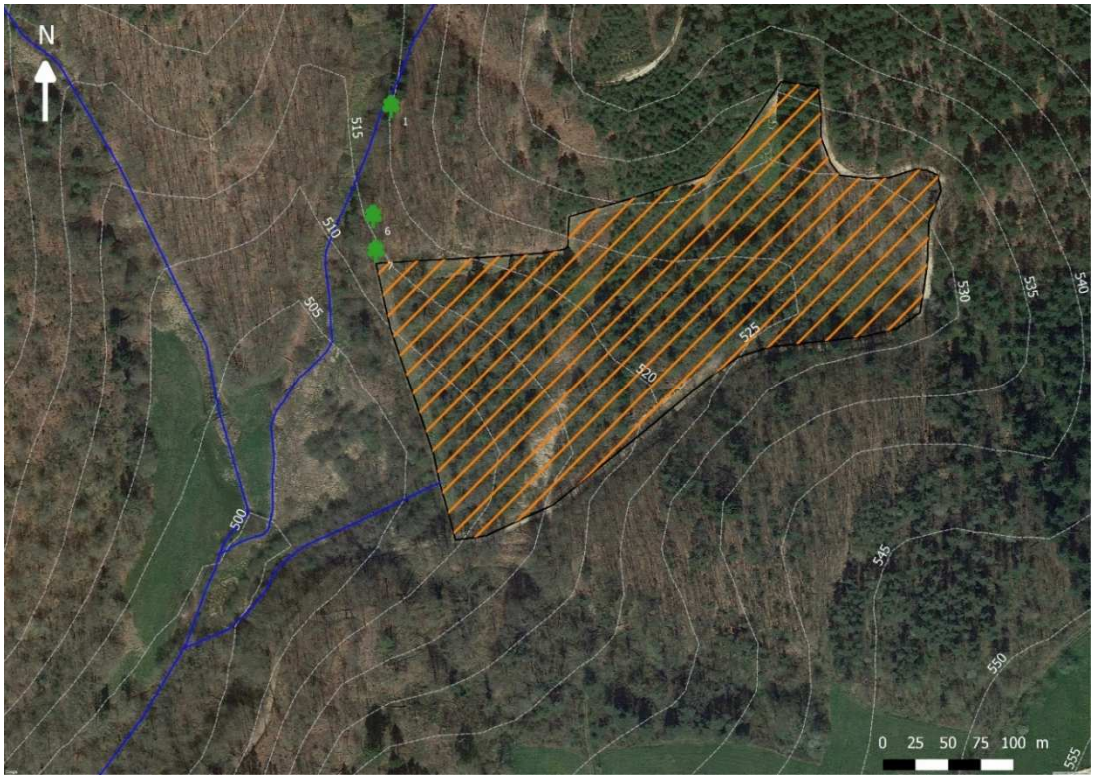


Figure 2: Location of the sampled trees (green spots, n=3) around the former Rophin mine (Puy de Dôme, France). The hatched area indicates mine waste storage.

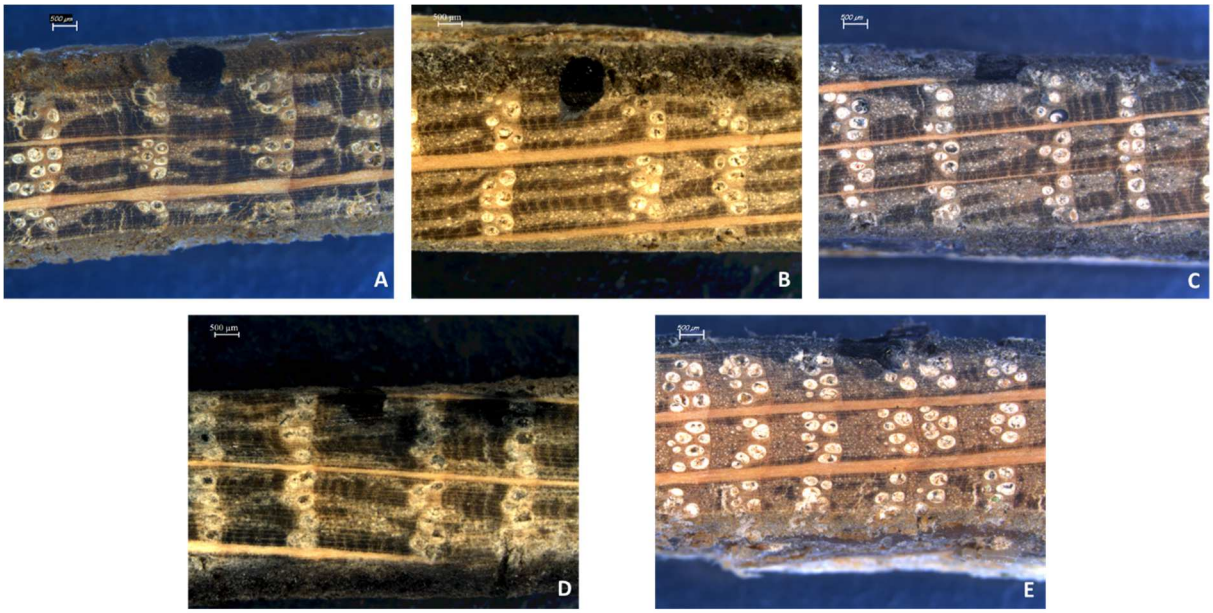
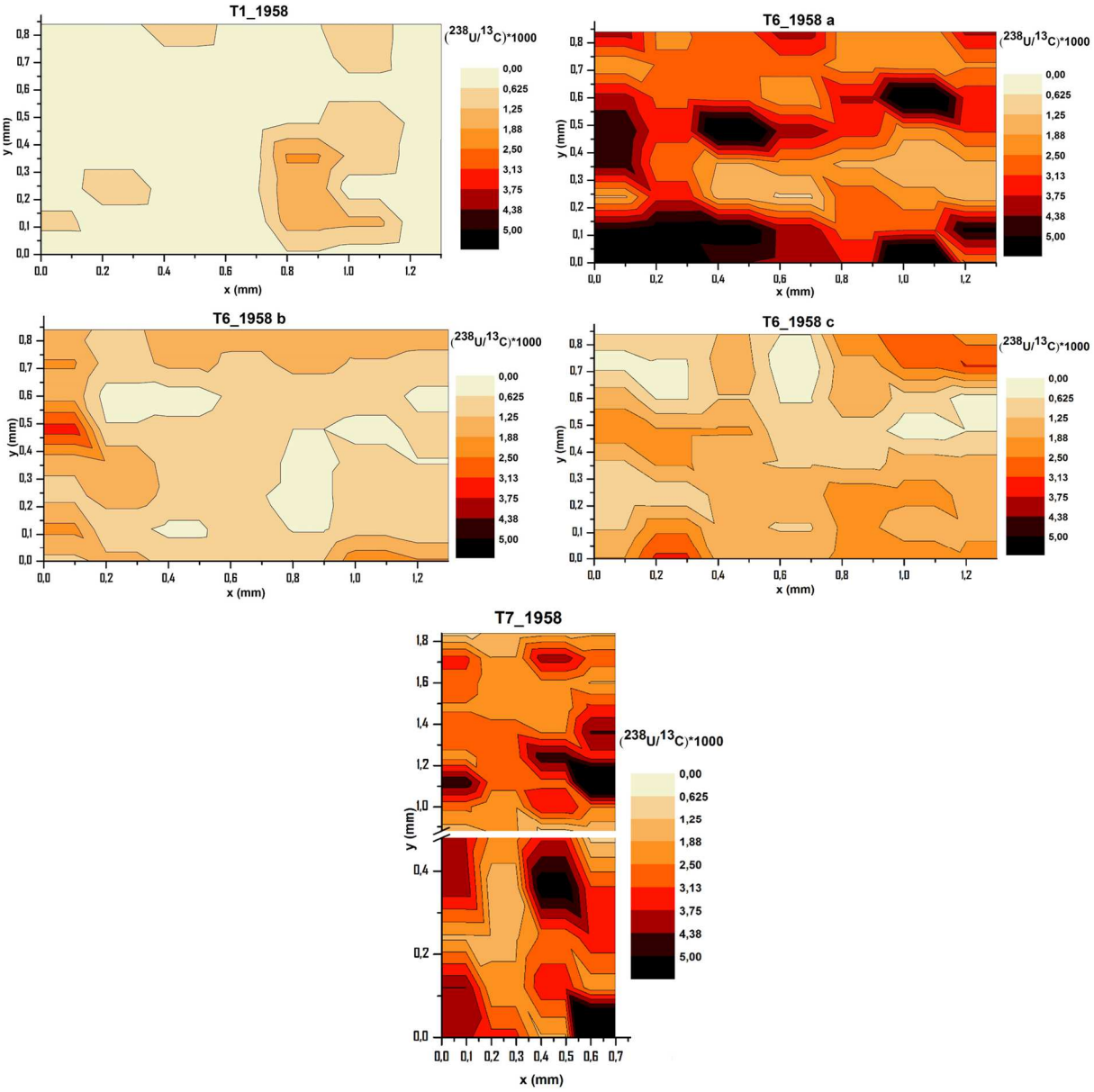


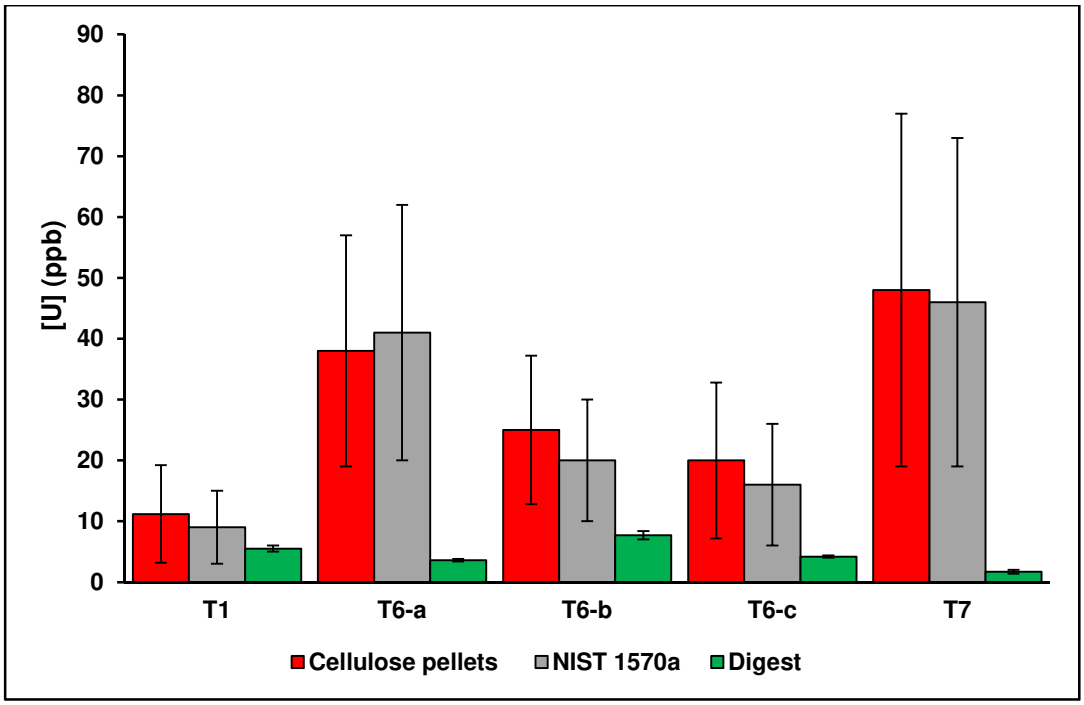
Figure 3: Tree ring samples characterized by a Leica DCF290 HD Digital camera (before ablation): (A) T1; (B) T6-a; (C) T6-b; (D) T6-c; (E) T7



621

622 **Figure 4:** 2D mappings of uranium distribution at the tree ring surface

623



624

625 **Figure 5:** Comparison of uranium contents in the tree ring samples using both techniques in LA-HR-
626 ICP-MS (red and gray) and HR-ICP-MS solution (green)

627 **Table 1:** Operating conditions for the (LA)-HR-ICP-MS technique

Laser ablation device	**NWR UP 213**
Wavelength	213 nm
Pulse energy	0.5 mJ (50%)
Fluence	10.8 J cm^{-2}
Repetition rate	10 Hz
Spot size diameter	80 µm
Scanning speed	(Pre)-ablation : (30 µm s^{-1}); 5 µm s^{-1}
Ablation mode	Line (100 µm)
Number of lines	56
Interline spacing	X = 200 µm ; Y = 120 µm
Washout time	50 s
Warmup time	10 s
Carrier gas flow rate (He)	0.87 L min^{-1}
Make-up gas flow rate (Ar)	0.92 L min^{-1}
HR ICP-MS	**Thermo Scientific Element XR**
RF power	1,200 W
Auxiliary gas flow rate (Ar)	0.84 L min^{-1} (LA mode); 0.8 L min^{-1} (solution mode)
Cool gas flow rate (Ar)	16 L min^{-1}
Internal standards	^{13}C (LA mode); ^{205}Tl (solution mode)
Sampler and skimmer cones	Ni
Acquisition time	60 s (LA mode); 75 s (solution mode)
Detector Mode	Triple
Mass resolution mode	300
Mass window	50%
Runs × passes	55 × 1 (LA mode); 5 × 5 (solution mode)

628

629 **Table 2:** Uranium concentrations in both external standards determined by HR-ICP-MS solution

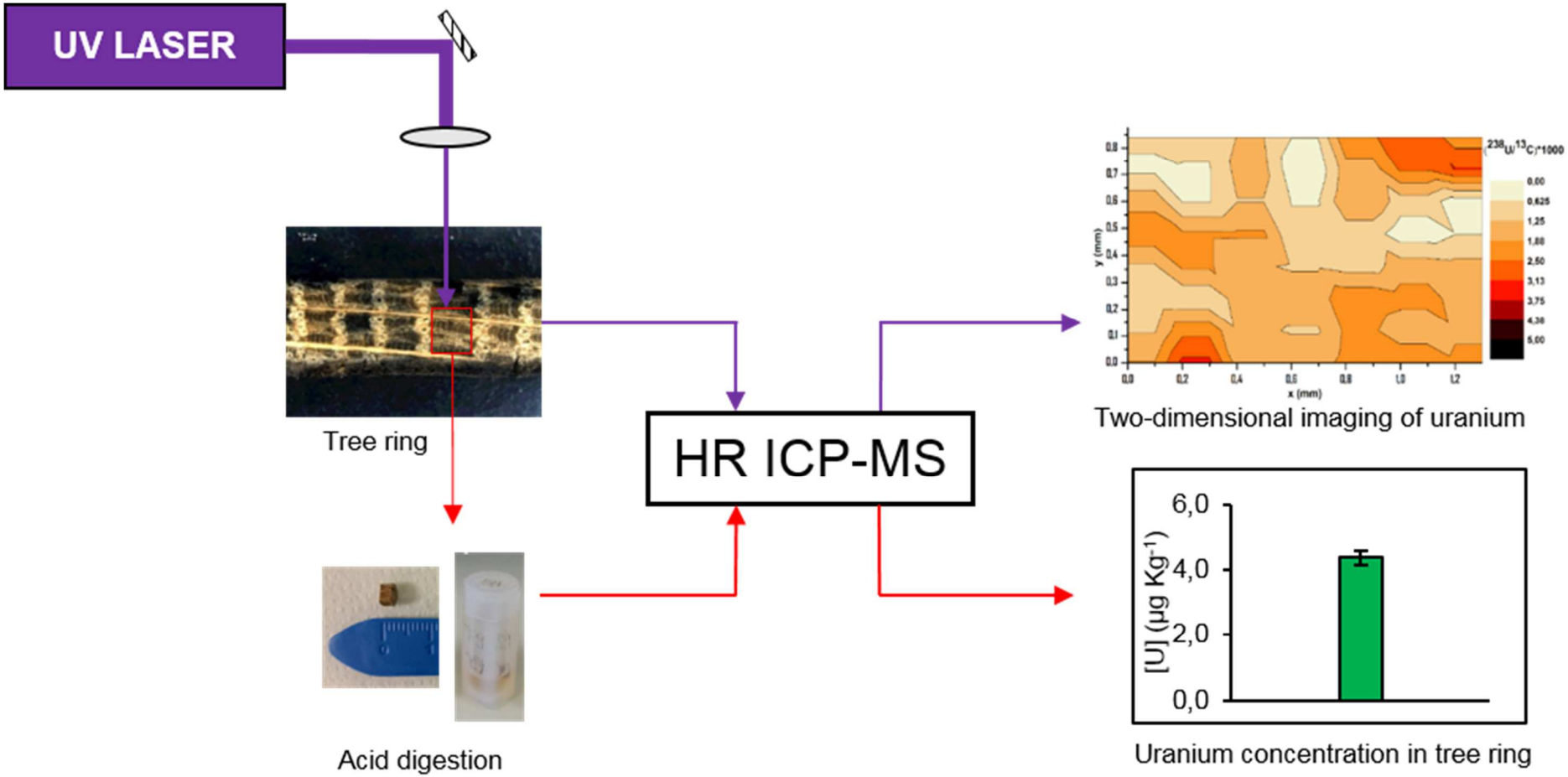
Sample	**[U] (µg kg^{-1}) (± 2σ)**	**[U] (µg kg^{-1}) (± 2σ)**
	Targeted values (gravimetric)	Measured values (HR-ICP-MS)
Point 1	48 ± 2	44 ± 3
Point 2	98 ± 3	102 ± 5
Point 3	203 ± 4	209 ± 13
Point 4	403 ± 7	413 ± 32
NIST 1570a	*155*± 23*	166 ± 11

630 **Certified value*

631 **Table 3:** Limits of detection (LODs) of uranium by with both methods (LA-ICP-MS and ICP-MS
632 solution)

Samples	LODs	
	LA-HR-ICP-MS (ng kg^{-1})	HR-ICP-MS Solution (ng kg^{-1})
T1	10	0.3
T6-a	24	0.3
T6-b	23	0.2
T6-c	7	0.2
T7	10	0.5

633


UV LASER
Tree ring
HR ICP-MS
Acid digestion
Two-dimensional imaging of uranium
Uranium concentration in tree ring
[U] (µg Kg-1)
6,0
4,0
2,0
0,0