

Supplementary material

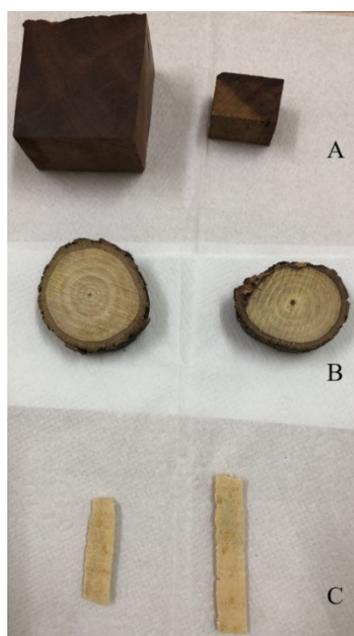


Figure SM1: Samples of *Hymenaea courbaril* (A), *Tipuana tipu* (B), *Cavanillesia arboraceae* donated by the xylotheque of the Institute of Biosciences – USP.

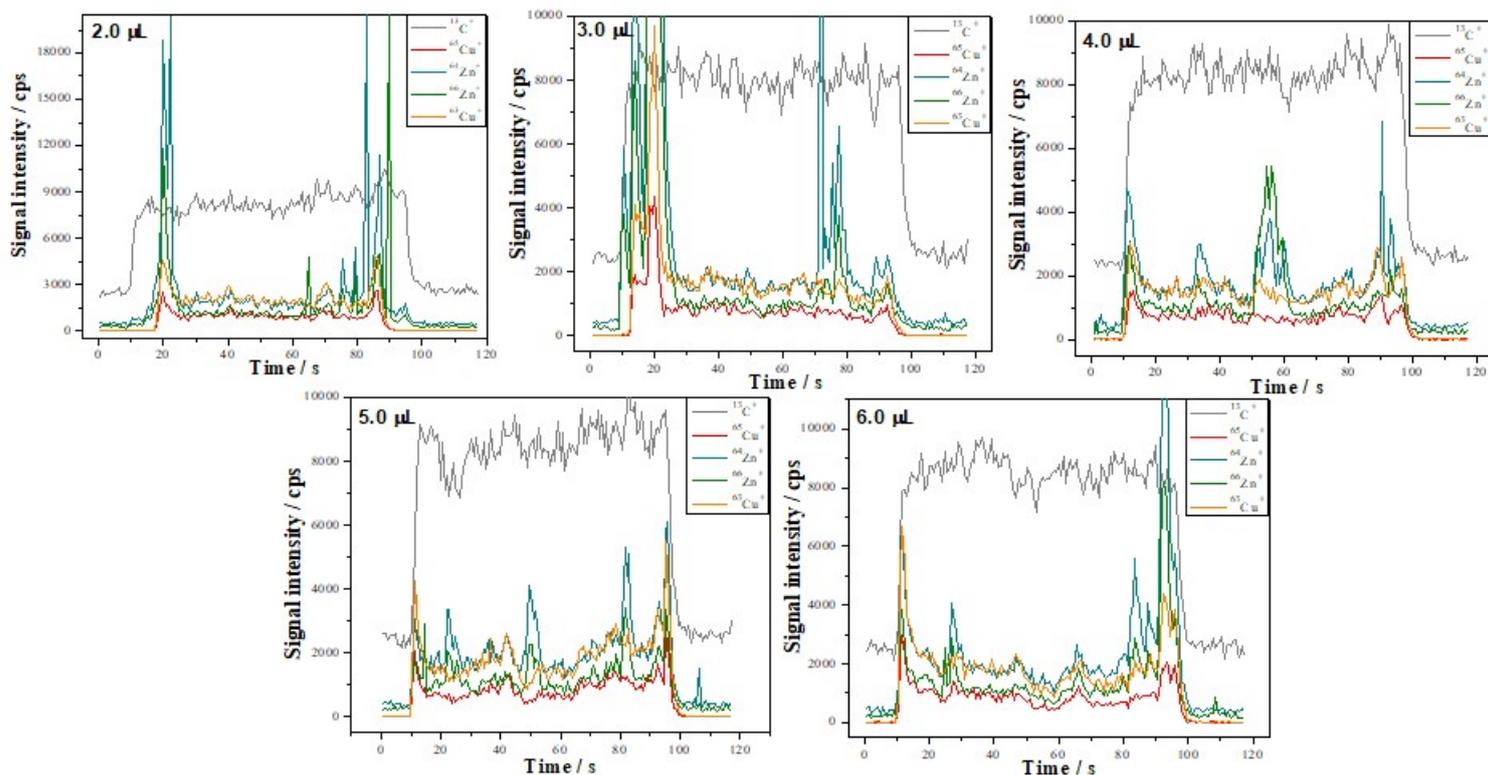


Figure SM2: Signal intensity (cps) of Cu, Zn and C ($^{13}\text{C}^+$; $^{65}\text{Cu}^+$; $^{64}\text{Zn}^+$; $^{66}\text{Zn}^+$; $^{63}\text{Cu}^+$) monitored isotopes along the whole diameter of the calibration support, for different volumes of standard solution addition over the 0.20 μm pore size diameter filter paper disk. Data acquired with LA-ICP-MS and final mass fraction of Cu and Zn in the filter paper disks was 10.0 $\mu\text{g g}^{-1}$.

Table SM1: Instrumental conditions established for LA-ICP-MS analysis of tree-rings.

Instrumental Parameters	Elan DRC-e
Radiofrequency Power (W)	1300
Carrier gas flow rate (L min ⁻¹)	1.2
Auxiliary gas flow rate (L min ⁻¹)	1.6
Data acquisition parameters	-
Analysis mode	Peak hopping
Detector mode	Pulsed
Sweeps	5
Dwell time (ms)	20
Integration time (ms)	100
Monitored ions	¹³ C ⁺ , ⁶³ Cu ⁺ , ⁶⁵ Cu ⁺ , ⁶⁴ Zn ⁺ , ⁶⁶ Zn ⁺
Laser conditions	New Wave UP-213
Laser wavelength (nm)	213
Laser intensity (J cm ⁻²)	0.60
Repetition rate (Hz)	20
Spot size diameter (μm)	110
Scan speed (μm s ⁻¹)	60

Table SM2: Instrumental conditions established for ICP-MS analysis decomposed tree samples and NIST 1575a.

Instrumental parameters	
Nebulizer chamber	Cyclonic
Nebulizer	Meinhard®
Radiofrequency power (W)	1400
Nebulizer gas flow rate (L min ⁻¹)	0.9041
Auxiliary gas flow rate (L min ⁻¹)	0.8
Spray Chamber Temperature (°C)	2.68
Acquisition parameters	
Scan mode	<i>Peak hopping</i>
Sweeps	10
Dwell time (ms)	100
Integration time (ms)	1000
Replicates	3
Monitored ions	⁶³ Cu ⁺ , ⁶⁵ Cu ⁺ , ⁶⁴ Zn ⁺ , ⁶⁶ Zn ⁺
⁶⁴ Zn ⁺ correction equation	-0,035297 x ⁶⁰ Ni ⁺

Table SM3: Mass fraction values for the monitored ions, determined in the CRM pellets using LA-ICP-MS, as well as the percentage of accuracy in comparison with the certified results, and the relative standard deviation for the measurements. Results obtained from external calibration using qualitative and 0.20 µm pore size diameter quantitative filter paper as calibration solid support. Results were obtained with data normalization using ¹³C as internal standard.

Monitored ion	Qualitative filter paper								Quantitative filter paper							
	NIST 1573a				NIST 1575a				NIST 1573a				NIST 1575a			
	Certified	Determined	Accuracy (%)	RSD (%)	Certified	Determined	Accuracy (%)	RSD (%)	Certified	Determined	Accuracy (%)	RSD (%)	Certified	Determined	Accuracy (%)	RSD (%)
⁶⁵ Cu ⁺ / ¹³ C ⁺	4.70 ± 0.14	3.4 ± 0.6	71	18	2.8 ± 0.2	1.4 ± 0.1	49	6	4.7 ± 0.1	3.9 ± 0.7	83	17	2.8 ± 0.2	1.7 ± 0.1	61	5
⁶³ Cu ⁺ / ¹³ C ⁺	4.70 ± 0.14	3.4 ± 0.5	72	15	2.8 ± 0.2	1.4 ± 0.1	51	6	4.7 ± 0.1	3.9 ± 0.6	84	14	2.8 ± 0.2	1.8 ± 0.1	63	5
⁶⁴ Zn ⁺ / ¹³ C ⁺	30.94 ± 0.55	17 ± 5	54	31	38 ± 2	26 ± 2	67	6	30.94 ± 0.55	20 ± 5	66	27	38 ± 2	28 ± 2	74	6
⁶⁶ Zn ⁺ / ¹³ C ⁺	30.94 ± 0.55	17 ± 8	53	47	38 ± 2	18 ± 2	46	11	30.94 ± 0.55	20 ± 8	65	40	38 ± 2	21 ± 2	55	10

Table SM4: Results of the accuracy and precision experiments for the solution based-ICP-MS measurements, with standard addition calibration method, for the quantification of Cu and Zn in the decomposed tree samples. Experiment performed with NIST 1575a SRM.

Monitored Ion	Certified	Determined	Accuracy (%)	RSD (%)
⁶⁵ Cu ⁺	2.8 ± 0.2	2.67 ± 0.02	95	1
⁶³ Cu ⁺	2.8 ± 0.2	2.66 ± 0.07	95	3
⁶⁴ Zn ⁺	38 ± 2	33 ± 1	87	3
⁶⁶ Zn ⁺	38 ± 2	32 ± 1	85	3