

SUPPORTING INFORMATION

Melted Paraffin Wax as an Innovative Liquid and Solid Extractant for Elemental Analysis by Laser-Induced Breakdown Spectroscopy

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Figure S3. Influence of (a) pH ; (b) DDTC:Cu(II) ratio; (c) Triton X-100 concentration. (d) vortex agitation time; (e) time complexation and (f) different types of paraffin wax on the analytical signal and the standard deviation obtained by LIBS. Experiments in triplicate ($n = 3$). Fixed $[\text{Cu}^{2+}] = 1.57 \times 10^{-4}$ mol L^{-1} , 25 laser pulses of 50 J cm^{-2} (230 mJ per pulse; 750 μm laser spot size) at 2.0 μs delay and 5.0 μs integration time.

Figure S4. Linear regression forcing zero in intercept of the amount of copper extracted in the function of the initial amount in aqueous solution. Linear regression equation ($y = 0.941 (\pm 0.002) x$, $R^2 = 0.9997$, $n = 7$). Vertical error bars refer to ± 1 standard deviation of triplicate ($n = 3$).

Figure S5. AFM images relating to paraffin waxes extracts containing different concentrations of $[\text{Cu}(\text{DDTC})_2]$. (A) paraffin wax without $[\text{Cu}(\text{DDTC})_2]$ – method blank (B) extract to the solution of 0.75 mg L^{-1} of copper (C) extract to the solution 2.50 mg L^{-1} of copper, (D) extract to the solution 5.00 mg L^{-1} of copper and (E) extract to the solution 7.50 mg L^{-1} of copper. Each image covered an area of 45 $\mu\text{m} \times 45 \mu\text{m}$ and is representative of three different regions of each sample.

Supplementary experimental section

Table S1. GF AAS heating program for copper determination in aqueous samples.

Type	Temperature (°C)	Ramp (°C/s)	Hold (s)	Argon Gas Flow
Drying	130	10	10	1.0 L min ⁻¹
Pyrolysis	1200	100	20	1.0 L min ⁻¹
Atomize	2300	1300	6	Stop
Cleanout	2600	1100	6	1.0 L min ⁻¹

Table S2. Order of addition and quantities used in the extraction procedure after optimization

Order of addition	Method Blank	Calibration	Application in Samples and CRM	Addition and Recovery in Samples
Sample	-----	----	10 mL	10 mL
Copper Reference Solution (0.50 – 10.0 mg L ⁻¹)	-----	10 mL	-----	-----
Citric Acid Buffer Solution (pH = 5.0, 1.5 mol L ⁻¹)	1 mL	1 mL	1 mL	1 mL
Triton X-100 Solution (13.0 g L ⁻¹)	250 µL	250 µL	250 µL	250 µL
DDTC Solution (0.210 mol L ⁻¹)	750 µL	750 µL	750 µL	750 µL
Deionized Water	11 mL	1 mL	1 mL	-----
Copper Reference Solution (5.0 – 100 mg L ⁻¹)	-----	-----	-----	1 mL
Final Volume (Aqueous Phase)	13 mL	13 mL	13 mL	13 mL
Molten Paraffin Wax added	700 µL	700 µL	700 µL	700 µL
Extract Collected	600 µL	600 µL	600 µL	600 µL

* The solutions addition were performed from top to bottom.

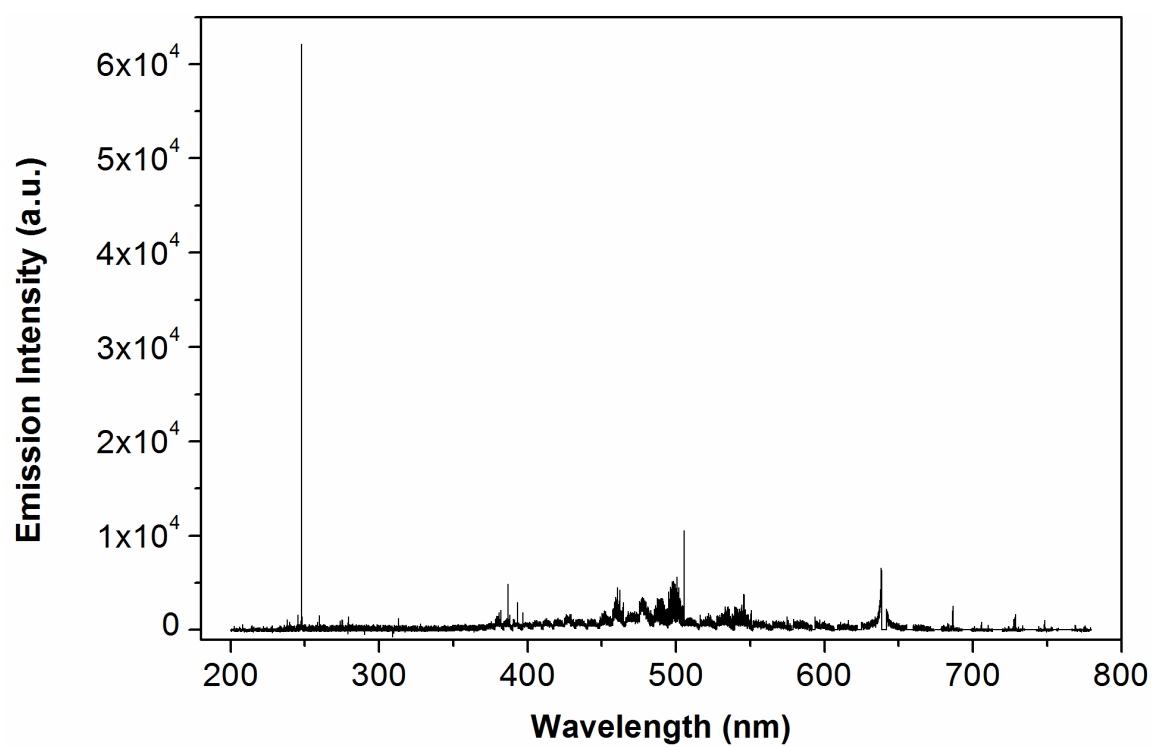


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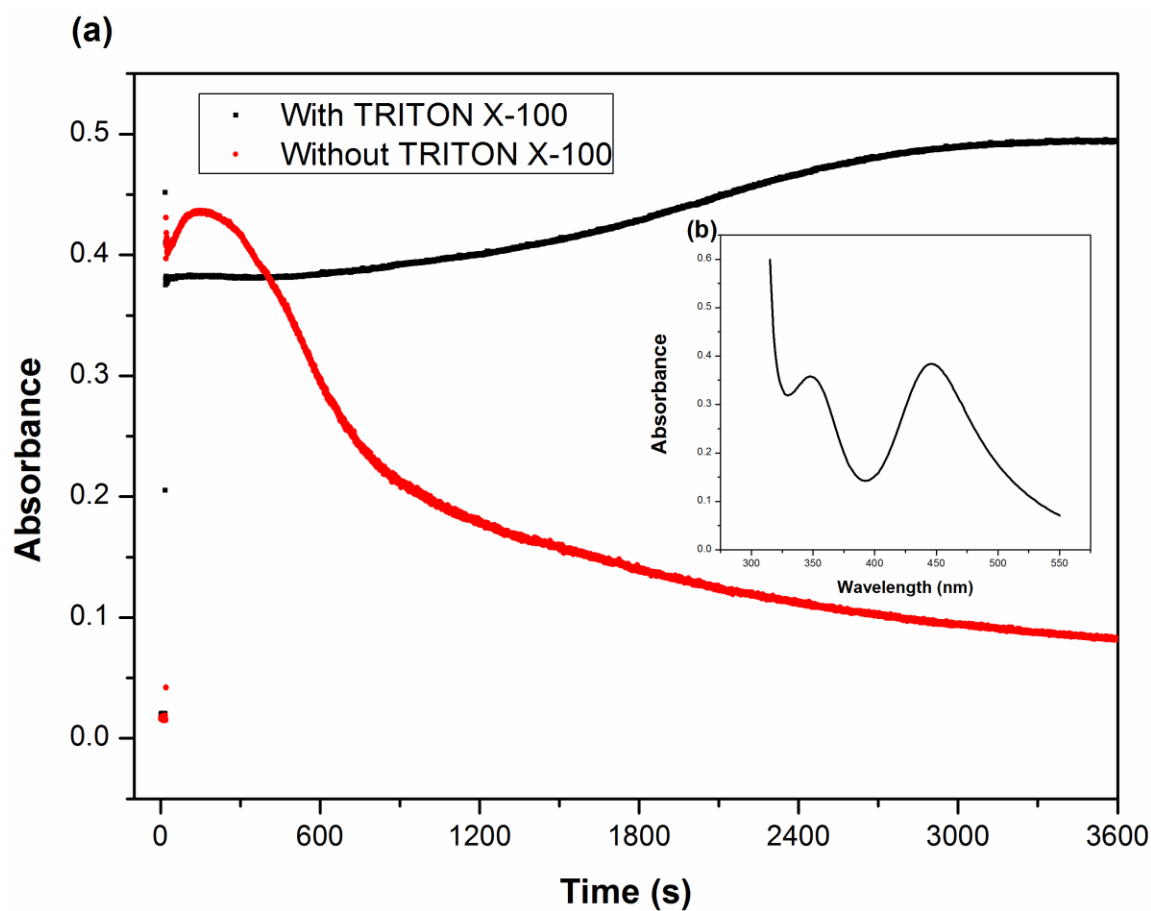


Figure S2. Efficiency of Triton X-100 as a protective colloid. (a) Absorbance (446 nm) versus time. Complex solution prepared by the addition of 750 μL of copper reference solution 0.010 g L^{-1} in a mixture containing 750 μL of diethyldithiocarbamate solution 0.021 mol L^{-1} , 1200 μL of acid citric solution ($\text{pH} = 5.0$; 1.5 mol L^{-1}), 300 μL of Triton X-100 solution 2.5 g L^{-1} (in the presence of surfactant) and 300 μL of deionized water (in the absence of surfactant). (b) The inset represent the $[\text{Cu}(\text{DDTC})_2]$ spectrum in the presence of Triton X-100 and $\text{pH} = 5.0$.

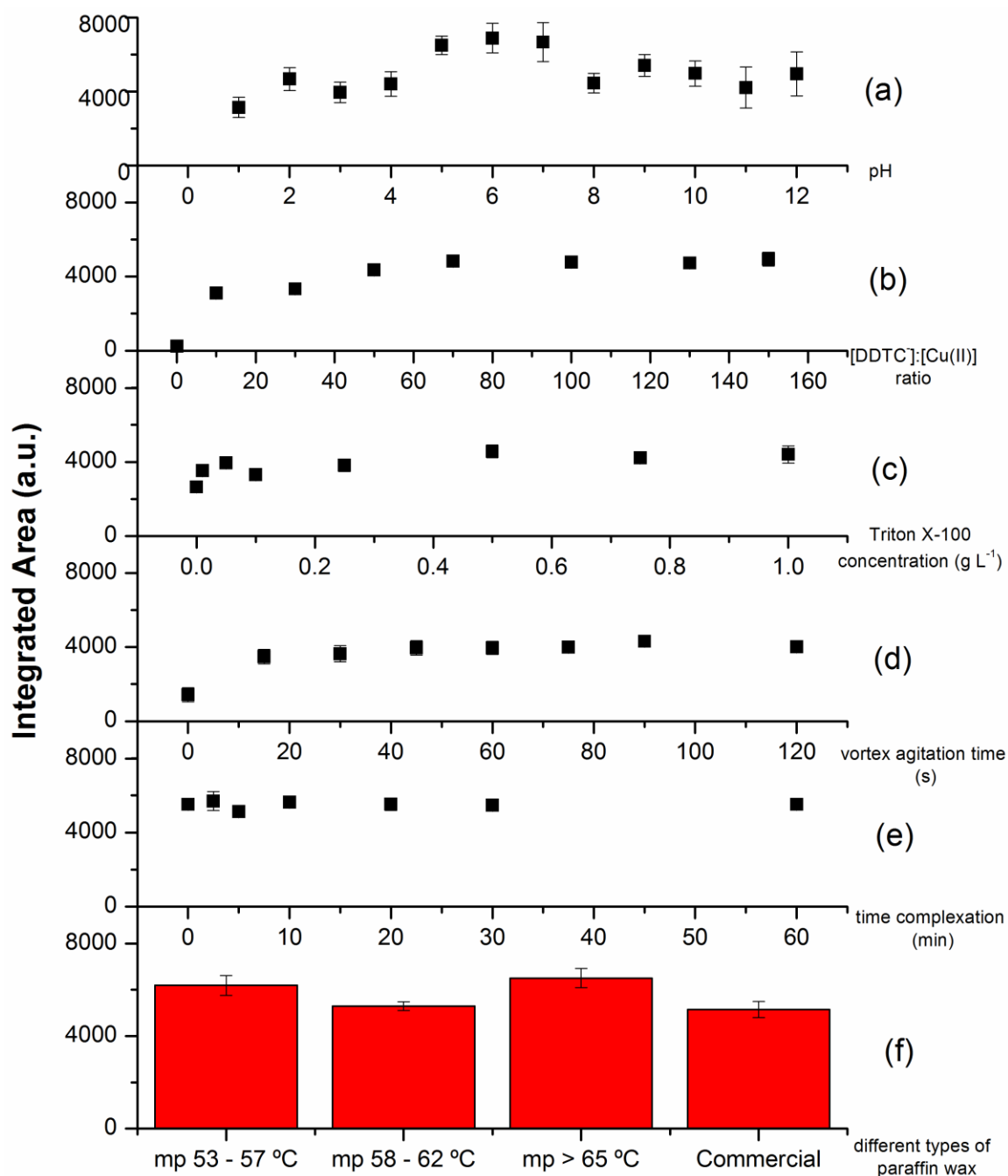


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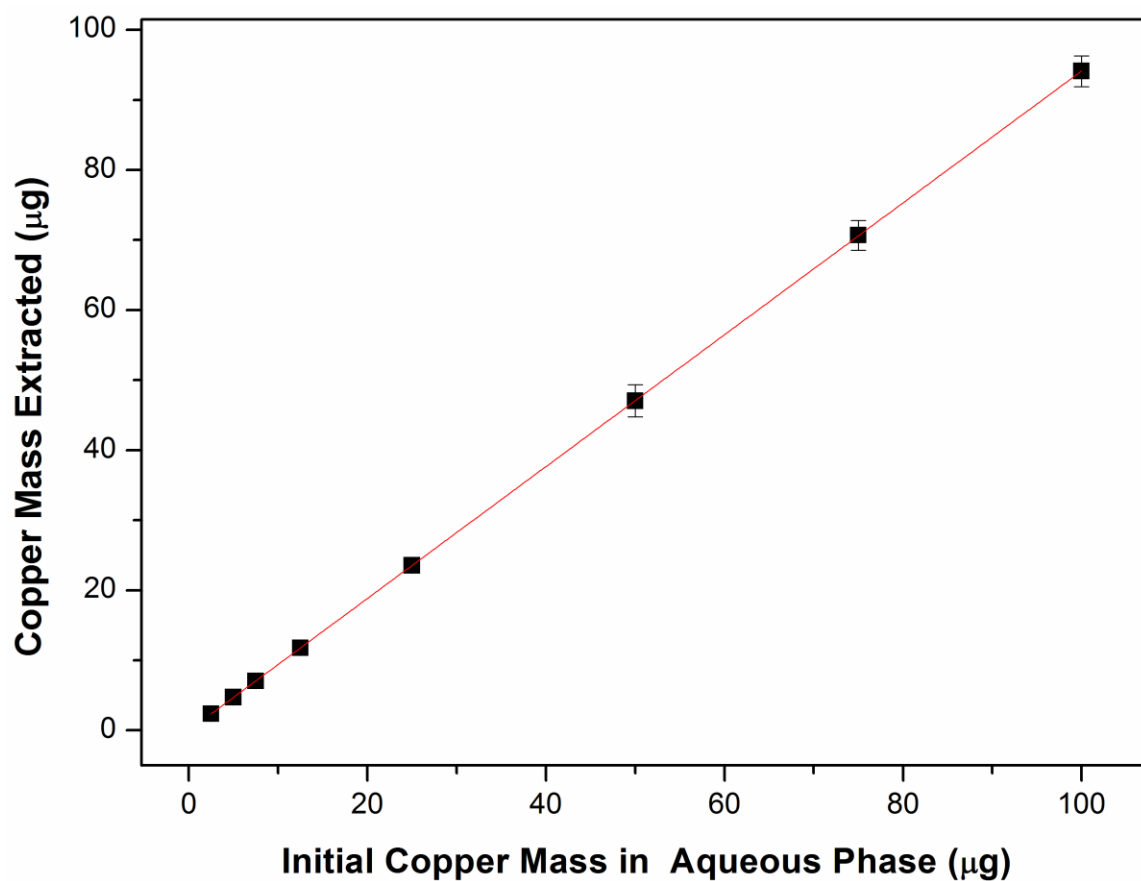


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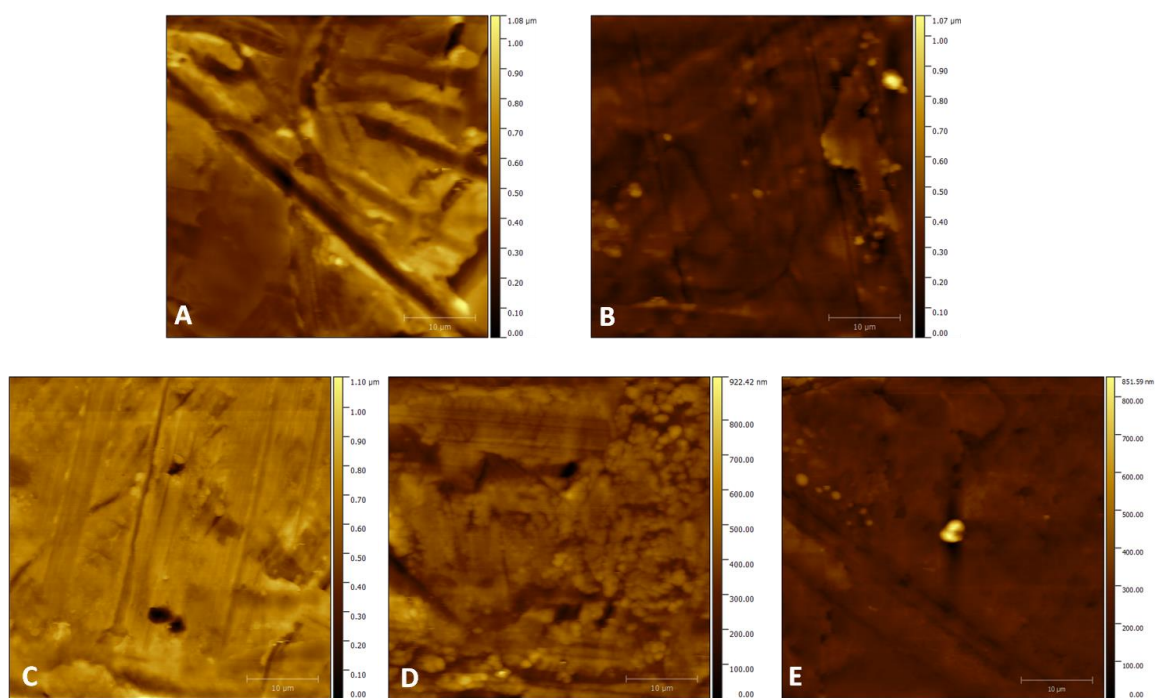


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Supplementary experimental section

Buffer solutions utilized to evaluated pH influence

For the pH adjustment, buffer solutions were prepared in the range from 1 to 12, comprising 0.50 mol L⁻¹ H₂C₂O₄ (Synth) and 0.18 mol L⁻¹ NaOH (Sigma-Aldrich) to pH 1, 0.50 mol L⁻¹ KH₂PO₄ (Sigma-Aldrich) and 0.27 mol L⁻¹ HNO₃ (Merck) to pH 2, 0.50 mol L⁻¹ citric acid - C₆H₈O₇ (JT Baker) and 0.25 mol L⁻¹ NaOH to pH 3, 0.50 mol L⁻¹ C₆H₈O₇ and 0.62 mol L⁻¹ NaOH to pH 4, 0.50 mol L⁻¹ C₆H₈O₇ and 0.95 mol L⁻¹ NaOH to pH 5, 0.50 mol L⁻¹ C₆H₈O₇ and 1.21 mol L⁻¹ NaOH to pH 6, 0.31 mol L⁻¹ KH₂PO₄ (Sigma-Aldrich) and 0.19 mol L⁻¹ Na₂HPO₄ (Sigma-Aldrich) to pH 7, 0.50 mol L⁻¹ Tris(hydroxymethyl) aminomethane (Sigma-Aldrich) and 0.30 mol L⁻¹ HNO₃ to pH 8, 0.50 mol L⁻¹ H₃BO₃ (Vetec) and 0.22 mol L⁻¹ NaOH to pH 9, 0.32 mol L⁻¹ NaHCO₃ (Sigma-Aldrich) and 0.18 mol L⁻¹ Na₂CO₃ (Sigma-Aldrich) to pH 10, 0.42 mol L⁻¹ NaHCO₃ and 0.08 mol L⁻¹ Na₂CO₃ to pH 11, 0.50 mol L⁻¹ Na₂HPO₄ and 0.23 mol L⁻¹ NaOH to pH 12.