

## SUPPLEMENTARY MATERIAL

### **Guanidinium ionic liquid-based surfactant as adequate solvent to separate and preconcentrate cadmium and copper in waters using *in-situ* dispersive liquid–liquid microextraction**

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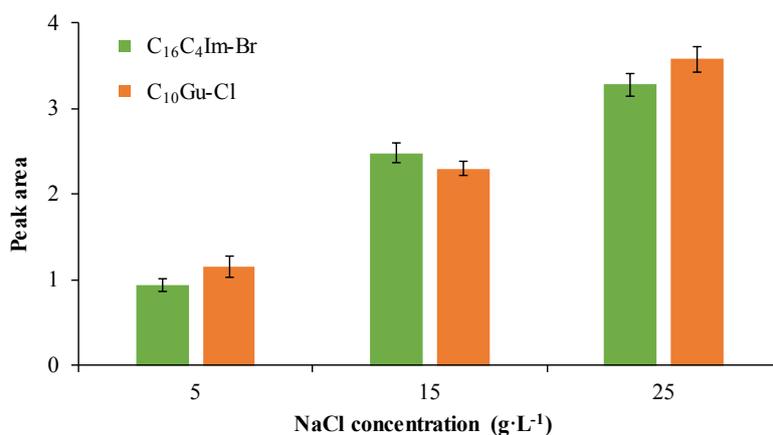
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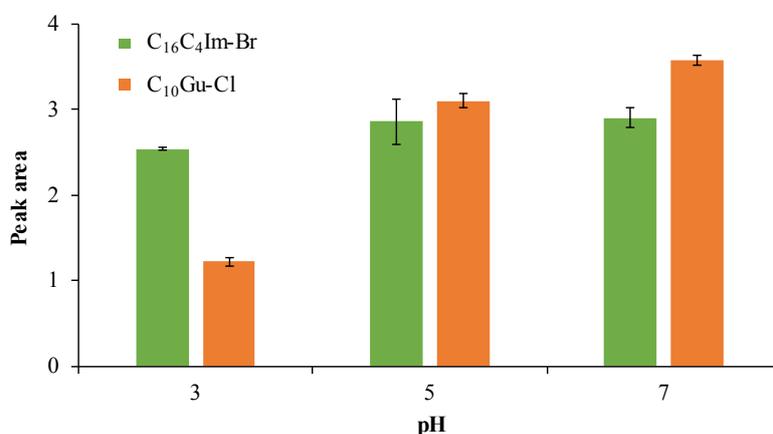
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### A) Effect of NaCl content



### B) Effect of pH



**Figure S1.** Influence of (A) the NaCl concentration and (B) the pH of the aqueous sample on the extraction efficiency of copper with the *in-situ* DLLME-FAAS method using either C<sub>16</sub>C<sub>4</sub>Im-Br or C<sub>10</sub>Gu-Cl IL-based surfactants as extraction solvent. Fixed experimental conditions: 10 mL of ultrapure water spiked with 0.5 μg·L<sup>-1</sup> of copper; 10 g·L<sup>-1</sup> of NaCl in the study of the effect of the pH; 500 μL of acetone containing 200 mg·L<sup>-1</sup> of BSTC, 10 mmol·L<sup>-1</sup> of C<sub>16</sub>C<sub>4</sub>Im-Br or 11 mmol·L<sup>-1</sup> of C<sub>10</sub>Gu-Cl; pH of 7 in the study of the effect of the NaCl content; 60 μL and 65 μL of Li-NTf<sub>2</sub> at 0.5 g·mL<sup>-1</sup> for C<sub>16</sub>C<sub>4</sub>Im-Br and C<sub>10</sub>Gu-Cl, respectively, 2 min of vortex, 2 min of centrifugation at 1921×g; and dilution of the microdroplet up to 120 μL with acetonitrile. All experiments were carried out in triplicate.

**Table S1.** Matrix of the Doehlert experimental design used for the optimization of the method with C<sub>10</sub>Gu-Cl IL-based surfactant, including the coded and operating values.<sup>45</sup>

Experiment	NaCl concentration (g·L <sup>-1</sup> )		pH	
	C <sub>1</sub>	X <sub>1</sub>	C <sub>2</sub>	X <sub>2</sub>
1	0	25.0	0	5.75
2	1.00	40.0	0	5.75
3	0.500	32.5	0.866	8.50
4	-1.00	10.0	0	5.75
5	-0.500	17.5	-0.866	3.00
6	0.500	32.5	-0.866	3.00
7	-0.500	17.5	0.866	8.50
8	-0.500	17.5	0	5.75
9	0.500	32.5	0	5.75

C<sub>1</sub> and C<sub>2</sub> are the coded values for the levels of NaCl concentration (g·L<sup>-1</sup>) and pH, respectively.

$$C_i = \left[ \frac{X_i - X_i^0}{\Delta X_i} \right] \alpha$$

The relationship between coded and real values is given by:

where C<sub>i</sub> is the coded value for the level of factor i, X<sub>i</sub> is its real value in an experiment, X<sub>i</sub><sup>0</sup> is the real value at the center of the experimental domain, ΔX<sub>i</sub> is the step of variation of the real value, and α is the coded value limit for each factor.

The number of experiments required (N) is given by N = k<sup>2</sup> + k + C<sub>0</sub>, where k is the number of variables and C<sub>0</sub> is the number of center points.

**Table S2.** Matrix of the Doehlert experimental design used for the optimization of the method with C<sub>16</sub>C<sub>4</sub>Im-Br IL-based surfactant, including the coded and operating values.<sup>45</sup>

Experiment	NaCl concentration (g·L <sup>-1</sup> )		Vortex time (min)	
	C <sub>1</sub>	X <sub>1</sub>	C <sub>1</sub>	X <sub>1</sub>
1	0	25	0	2.25
2	1	40	0	2.25
3	0.5	32.5	0.866	4
4	-1	10	0	2.25
5	-0.5	17.5	-0.866	0.5
6	0.5	32.5	-0.866	0.5
7	-0.5	17.5	0.866	4
8	-0.5	17.5	0	2.25
9	0.5	32.5	0	2.25

C<sub>1</sub> and C<sub>2</sub> are the coded values for the levels of NaCl concentration (g·L<sup>-1</sup>) and vortex time (min), respectively.

$$C_i = \left[ \frac{X_i - X_i^0}{\Delta X_i} \right] \alpha$$

The relationship between coded and real values is given by:

where C<sub>i</sub> is the coded value for the level of factor i, X<sub>i</sub> is its real value in an experiment, X<sub>i</sub><sup>0</sup> is the real value at the center of the experimental domain, ΔX<sub>i</sub> is the step of variation of the real value, and α is the coded value limit for each factor.

The number of experiments required (N) is given by N = k<sup>2</sup> + k + C<sub>0</sub>, where k is the number of variables and C<sub>0</sub> is the number of center points.

**Table S3.** Reproducibility of the entire *in-situ* DLLME-FAAS method evaluated as the ratio between the slopes corresponding to calibration curves obtained in different non-consecutive days.

<b>Calibration curve</b>	<b>Slope <math>\pm t_{n-2} \cdot SD^*</math></b>	<b>Dataset</b>	<b>Slopes ratio</b>
<b>Cu<sup>2+</sup> determination using C<sub>10</sub>Gu-Cl</b>			
day 1	4.2 $\pm$ 0.3	test 1 – 2	0.89
day 2	4.7 $\pm$ 0.2	test 1 – 3	1.04
day 3	4.0 $\pm$ 0.2	test 2 - 3	1.16
<b>Cu<sup>2+</sup> determination using C<sub>16</sub>C<sub>4</sub>Im-Br</b>			
day 1	7.00 $\pm$ 0.05	test 1 – 2	1.09
day 2	6.4 $\pm$ 0.2	test 1 – 3	1.06
day 3	6.6 $\pm$ 0.2	test 2 - 3	0.97
<b>Cd<sup>2+</sup> determination using C<sub>10</sub>Gu-Cl</b>			
day 1	9.8 $\pm$ 0.4	test 1 – 2	1.04
day 2	9.4 $\pm$ 0.5	test 1 – 3	0.96
day 3	10.2 $\pm$ 0.4	test 2 - 3	0.92

\* Confidence interval of the slope for n = 7 calibration levels

**Table S4.** Comparison of several parameters of the analytical performance of the developed *in-situ* DLLME method and other *in-situ* DLLME methods reported in the literature for the determination of Cu<sup>2+</sup> or Cd<sup>2+</sup> in water samples.

<b>Metal</b>	<b>Sample (mL)</b>	<b>Complexing agent</b>	<b>IL (concentration)</b>	<b>Anion-exchange reagent</b>	<b>μL of the final extract (diluted or not) / μL subjected to AAS</b>	<b>Detection</b>	<b>LOD<sup>a</sup> (μg·L<sup>-1</sup>)</b>	<b>E<sub>F</sub><sup>b</sup></b>	<b>Ref.</b>
Cu <sup>2+</sup>	tap water (10 mL)	BSTC <sup>c</sup>	C <sub>10</sub> Gu-Cl (11 mmol·L <sup>-1</sup> )	Li-NTf <sub>2</sub>	120 / 50	FAAS <sup>d</sup>	0.3	77	this work
Cu <sup>2+</sup>	tap water and wastewater (10 mL)	DDTC <sup>e</sup>	C <sub>16</sub> C <sub>4</sub> Im-Br (25.2 mmol·L <sup>-1</sup> )	Li-NTf <sub>2</sub>	270 / 50	FAAS <sup>d</sup>	5.1	36	[25]
Cu <sup>2+</sup>	aqueous extract from soil and sediments (10 mL)	DDTC <sup>e</sup>	C <sub>6</sub> MIm-Cl (~10 mmol·L <sup>-1</sup> )	Li-NTf <sub>2</sub>	48 / 10	ETAAS <sup>f</sup>	0.004	200	[26]
Cd <sup>2+</sup>	tap water (10 mL)	BSTC <sup>c</sup>	C <sub>10</sub> Gu-Cl (11 mmol·L <sup>-1</sup> )	Li-NTf <sub>2</sub>	120 / 50	FAAS <sup>d</sup>	0.5	70	this work
Cd <sup>2+</sup>	seawater, spring and river water (5 mL)	DDTP <sup>g</sup>	C <sub>6</sub> MIm-BF <sub>4</sub> (~24 mmol·L <sup>-1</sup> )	Na-PF <sub>6</sub>	58 / 58	FAAS <sup>d</sup>	0.07	78	[27]
Cd <sup>2+</sup>	tap water, bottled water and seawater (10 mL)	APDC <sup>h</sup>	C <sub>8</sub> MIm-Cl (10 mmol·L <sup>-1</sup> )	Li-NTf <sub>2</sub>	30 / 30	ETAAS <sup>f</sup>	0.0002	280	[28]

<sup>a</sup> limit of detection

<sup>b</sup> enrichment factor

<sup>c</sup> N,N'-bis(salicylidene)thiocarbohydrazide

<sup>d</sup> flame atomic absorption spectroscopy

<sup>e</sup> diethyl dithiocarbamate

<sup>f</sup> electrothermal atomic absorption spectroscopy

<sup>g</sup> O,O-diethyldithiophosphate

<sup>h</sup> ammonium pyrrolidine dithiocarbamate