## **Electronic supplementary information**

## Table S1

Emission wavelengths employed in this work

	Element	Tuno	Wavelength	Element	Type	Wavelength
	Liement	Type	(nm)	Liement	Type	(nm)
Analytes	Ag	I	328.068	Mn	I	403.076
	Al	Ι	396.152	Мо	Ι	379.825
	В	Ι	249.772	Na	Ι	588.995
	Cd	Ι	228.802	Ni	Ι	352.454
	Со	Ι	340.512	Pb	Ι	405.781
	Cr	Ι	425.433	Sn	Ι	317.505
	Cu	Ι	324.754	Sr	П	407.721
	Fe	Ι	371.993	Ti	П	334.941
	К	Ι	766.491	TI	Ι	535.046
	Li	Ι	670.784	V	Ι	309.311
	Mg	П	280.270	Y	П	371.029
	Mg	Ι	285.213	Zn	Ι	213.857
Molecular ba	and					
	CN	-	388.340 (Cr I 388.327)	СН	-	431.420 (Sc II 431.408)
	C <sub>2</sub>	-	473.700 (Fe I 473.677)	ОН	-	308.970 (Tb II 308.958)
	$N_2^+$	-	391.439 (Nb I 391.470)			

Variables		Levels			
	++	+	0	-	
NaCl concentration (w v <sup>-1</sup> %)	8	6	4	2	0
DDTP concentration (w w <sup>-1</sup> %)	3.3	2.5	2	0.9	0.1
Mass of disperser solvent (mg)	600	500	400	300	200
Mass of extraction solvent (mg)	475	400	325	250	175

**Table S2.** Central composite design for Cd extraction with DLLME operatingchloroform as extractant.

NaCl	DDTP	Ethanol	Chloroform	Integrated signal
(% w w-1)	(% w w <sup>-1</sup> )	(mL)	(mL)	(counts) ·10 <sup>3</sup>
2	2.5	500	400	1440±30
2	2.5	300	250	1200±130
2	2.5	300	400	630±60
8	1.7	400	325	2600±140
6	0.9	300	250	1800±120
4	1.7	400	325	1380±8
6	2.5	300	400	1050±60
4	1.7	200	325	900±40
4	1.7	600	325	2300±190
6	2.5	500	400	1430±20
4	1.7	400	475	1000±50
6	0.9	500	400	1640±30
6	2.5	500	250	2600±170
2	0.9	300	400	900±70
4	1.7	400	175	1340±20
2	0.9	300	250	2025±7
2	2.5	500	250	2900±200
4	3.3	400	325	1600±170
6	0.9	300	400	950±70
4	1.7	400	325	1300±170
2	0.9	500	250	3000±400
4	0.1	400	325	1230±91
0	1.7	400	325	1900±100
2	0.9	500	400	1370±80
6	2.5	300	250	2400±140
6	0.9	500	250	2100±180

**Table S3.** Cadmium signal response for a CCD design operating DLLME with chloroform.  $Q_g$ : 0.3 L min<sup>-1</sup>; analyte concentration: 0.5 mg L<sup>-1</sup>.

**Table S4.** Central composite design for Cd extraction with DLLME operating thesupramolecular solvent as extractant.

Variables			Levels		
	++	+	0	-	
NaCl concentration (w v <sup>-1</sup> %)	4	3	2	1	0
DDTP concentration (w w <sup>-1</sup> %)	3.3	2.5	1.7	0.9	0.1
Mass of THF (mg)	750	600	450	300	150
Mass of 1-decanol (mg)	240	200	160	120	80

NaCl	DDTP	THF	1-decanol	Integrated signal
(% w w-1)	(% w w <sup>-1</sup> )	(mL)	(mL)	(counts) ·10 <sup>3</sup>
1	0.9	600	200	375±2
2	1.7	150	160	482±7
3	0.9	300	120	570±15
2	1.7	450	240	365.7±0.5
1	0.9	300	200	406±1.4
3	2.5	600	200	400±19
3	2.5	300	200	100±2
3	2.5	300	120	500±100
2	3.3	450	160	141±1.5
1	2.5	300	120	530±40
2	1.7	450	80	720±10
4	1.7	450	160	296±9
3	0.9	300	200	360±30
3	0.9	600	200	125±4
2	1.7	750	160	440±20
3	0.9	600	120	360±60
2	0.1	450	160	170±12
1	0.9	300	120	327±6
3	2.5	600	120	250±11
1	0.9	600	120	300±40
1	2.5	600	120	470±50
1	2.5	300	200	380±13
2	1.7	450	160	244±7
0	1.7	450	160	190±30
2	1.7	450	160	240±20
1	2.5	600	200	450±13
I	2.0	000	200	400±10

**Table S5.** Cadmium signal response for a CCD design operating DLLME with the supramolecular solvent.  $Q_g$ : 0.3 L min<sup>-1</sup>; analyte concentration: 0.5 mg L<sup>-1</sup>.

**Fig. S1.** Emission spectra for N<sub>2</sub><sup>+</sup> molecular band (391.439 nm) operating ( $\bullet$ ) 1.0 w w<sup>-1</sup> nitric acid, ( $\Box$ ) the supramolecular solvent and ( $\circ$ ) chloroform. Q<sub>g</sub> 0.3 L min<sup>-1</sup>.



**Fig. S2.** Pareto charts obtained in the optimization study of the main variables affecting Cd extraction with DLLME for (A) chloroform and (B) the supramolecular solvent. (□) positive effect; (■) negative effect.

